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(Metallurgy)
METALLOGRAPHIC ASPECTS OF FATIGUE DEFORMATION IN SOME ORDERING SOLID SOLUTIONS

A Thesis submitted in requirement of the Degree of Doctor of Philosophy to the University of London

by

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The deformation and fracture of some alloys possessing the B2 structure when ordered was investigated under conditions of bending fatigue at 293° and 77°K by optical and replica electron microscopy. Alloys included β'-copper-zinc (42.5 to 48.25 at.% zinc), β'-gold-zinc, ordered and disordered equiatomic iron-cobalt (containing 2% vanadium) and ordered and disordered iron-23.5 at.% aluminium.

Cross slip was found to be more frequent with increasing zinc content in binary β'-copper-zinc alloys, and on addition of gold, but to be reduced by the addition of manganese or by reducing the test temperature. A cross slip mechanism not previously considered for alloys of the B2 structure is proposed. The localisation of fatigue damage near grain boundaries in β'-copper-zinc is attributed to the stress concentration resulting from the deformation of a polycrystal of strongly elastically anisotropic grains, for which a simple model is presented. The nature of fatigue crack initiation and propagation is rationalised in terms of the changing ease of cross slip with zinc content or temperature.

The formation of intense fatigue slip bands in β'-gold-zinc was found to be consistent with a cross slip process on intersecting {110} planes. The distribution of damage is considered in terms of the plastic and elastic anisotropy of the alloy.
The nature and distribution of fatigue damage in ordered and disordered iron-cobalt alloys emphasises the importance of cross slip in fatigue processes.

The cleavage fracture plane of β'-copper-zinc was determined as \{110\}, that of ordered and disordered iron-cobalt and iron-23.5 at.% aluminium as \{100\} and that of iron-49 at.% aluminium as \{111\}. These results are considered in terms of broken bond energy densities and anisotropy of bond strengths.
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1. INTRODUCTION

The examination of the deformation characteristics of ordered and disordered alloys allows the comparison of their properties in relation to specific differences in the dislocation structure of the alloys in each state of order. This is particularly valuable for the study of fatigue damage for which dislocation models have been proposed by a number of workers.

The object of the present study was to investigate a number of alloys possessing ordered structures based on the body-centred cubic structure, to determine whether such alloys shared common fatigue and fracture properties, attributable directly to the structure type. The investigation was therefore divided into three parts:

1) The nature of fatigue damage.
2) The distribution of fatigue damage.
3) The orientation of the cleavage fracture plane.

The fundamental approach to the investigation was metallographic and therefore qualitative, but metallographic observations have been interpreted in terms of the cohesive and dislocation structure of the alloys. In order that these considerations should be related to the geometric implications of the ordered structure and to the different components in the alloys, attention has been given to these factors as well as to the movement of dislocations and the fatigue of crystals.
The author wishes to declare that the work reported in this thesis was carried out solely by him at the Battersea College of Advanced Technology and that all conclusions were derived independently by him, except where otherwise stated.
2.1 Crystal Structures and Phase Diagrams

2.1.1 The A2, B2 and DO₃ Structures.

The body-centred cubic structure, designated A2 in the Strukturbericht (1) classification, may be regarded as being made up of cubic blocks each of which has an atom located at the cube corners, and one at the cube centre, Fig. 1. The shortest distance between two atoms, labelled I, is one half of the cube diagonal, namely \(\frac{a\sqrt{2}}{2}\), where \(a\) is the length of the unit cube edge. There are eight atoms at this distance. Six second nearest neighbours are situated at a distance \(a\), labelled II, and twelve third nearest neighbours at a distance \(a\sqrt{2}\), labelled III.

In an arrangement of hard spheres the A2 structure is unstable to shears of the type \{110\} \langle110\rangle (2). One may conclude that crystals possessing this structure must have stabilising or attractive forces acting between neighbours, in order to prevent mechanical instability. Some suggestions as to the nature of these stabilising forces will be given in Section 2.3.3.
The caesium chloride or B$_2$ (l) structure is based on the A$_2$ structure, but is of lower symmetry. It may be regarded as being built up of two interlocking simple cubic sublattices, each of which is occupied by a different atom type, Fig. 2. In alloys which can be disordered at high temperatures, sublattices are occupied at random by both atom types, and the structure reduces to the A$_2$. As a consequence of the atomic arrangement in equiatomic alloys, some planes of the crystal will be composed of one atom type only, so that neighbouring planes of the same type will contain alternately atom type A, then atom type B, e.g. \{100\}, \{111\}, \{210\} while others will be made up of equal numbers of both atom types, e.g. \{110\}, \{211\}, \{321\}.

A perfect B$_2$ lattice may only be achieved when the two atom types are present in equal numbers. In alloy systems the structure can exist over a range of composition, the atom type of higher concentration having some nearest neighbours of its own kind.

The D$_{0}$$_3$ (l) structure, Fig. 3, is closely related to the A$_2$ and B$_2$ structures. It may be regarded as composed of four interpenetrating face-centred cubic sublattices, each of cube edge length 2a, where a
is the length of the cube edge of the $A_2$ structure to which the $D_0_3$ reduces on ordering.

Atoms of type $A$ occupy all sites of the $II$, $III$, and $IV$ sublattices, while atom type $B$ occupies sublattice $I$. The closest distance of approach of type $B$ atoms is $a\sqrt{2}$, and corresponds to a preference of these atoms to have unlike atoms as first and second neighbours. While in the $B_2$ structure the sublattices are entirely equivalent, in the $D_0_3$ structure $A$ atoms have different environments, depending on the sublattice they occupy. Those on sublattices $II$ and $IV$ have four $B$ atoms as nearest neighbours. Those on sublattice $III$ have only $A$ atoms as nearest neighbours.

2.1.2 The Copper-Zinc Phase Diagram

Literature on the phase equilibria in this system has been reviewed by Hansen 1958 (3). Fig. 4 is taken from this work. Addition of zinc to copper lowers the melting point and in excess of about 30 at.% renders the face-centred cubic, $Al$ (1), structure unstable, and stabilises the $A_2$ structure.

This phase field, centred on the copper-rich side of the equiatomic composition, extends at the solidus from 36 at.% zinc at $902^\circ C$ to 55 at.% zinc.
at 834°C. The solubility range becomes narrower with falling temperature. Below 460°C the homogeneous solid solution phase field tends towards higher zinc contents as the temperature decreases. Accurate determinations of phase equilibria near this region, (4), seem to indicate that all alloys of nearly equiatomic composition consist of two phases at some temperature, if equilibrium is achieved.

The transformation in the A2 solid solution near 460°C has been established as an order-disorder transformation to the B2 structure. The temperature dependence of this transformation with composition was first determined by Sykes and Wilkinson 1937 (5). They found that an alloy with 49 at.% zinc transformed at 468°C, while the 45 at.% zinc alloy transformed at 456°C.

It had earlier been postulated by Carpenter 1912 (6) that this transformation was of the eutectoid type. Recently, measurements of hot ductility and electrical resistivity (7) have been interpreted as showing that the ordered β'-phase is metastable under ordinary circumstances, but can be transformed to α + γ by deformation. The β'-phase is mechanically unstable under sufficient stress, but this does not necessarily indicate thermodynamic instability in the unstressed state. In his review of the copper-zinc
equilibrium diagram Hansen 1958 (3) concluded that available evidence indicated that the ordering reaction is homogeneous and not associated with a two-phase field. This question will be further discussed in Section 2.2.2.

2.1.2.1 The Copper-Zinc-Manganese Phase Diagram.

Imai and Kitazima 1951 (8) found that manganese was the only ternary addition of those they examined which lowered the order-disorder transition of the $\beta$-phase of copper-zinc, Fig. 5. This ternary system was extensively studied by Graham et al. 1949 (9) and the effect of manganese additions on the $\beta$-copper-zinc phase boundaries determined.

Manganese widens the $\beta$-phase field, Fig. 6, but it is not clear whether it acts as equivalent to zinc, substituting for zinc atoms in the B2 lattice, or whether both copper and zinc are replaced at random. The phase diagram indicates that the substitution is more or less random initially, since up to about 15 wt.% manganese the $\beta$-phase field extends normal to the copper-zinc binary side of the ternary diagram.
2.1.2.2 The Copper-Zinc-Gold Phase Diagram

No information appears to be available on the effect of gold addition on the \( \beta \)-phase boundaries of the copper-zinc system. However, since the gold-zinc system also contains a \( \beta' \)-phase centred on the equiatomic composition it suggests that gold acts in an analogous manner to copper in the ternary system, at least for low gold contents. Since the \( \beta' \)-gold-zinc phase retains its ordered structure to higher temperatures than the \( \beta' \)-copper-zinc phase, (Fig. 7 and Section 2.1.3), it is assumed that addition of gold to the \( \beta' \)-copper-zinc binary alloy would raise the order-disorder transition temperature, \( T_c \). Imai and Kitazima 1951 (8) found that nickel additions raised \( T_c \) very sharply, Fig. 5, and it is known that the equiatomic compound of nickel and zinc possesses the B2 structure up to 1040°C, (3).

2.1.3 The Gold-Zinc Phase Diagram

Literature on the phase equilibria in this system has been reviewed by Hansen 1958 (3). Gold and zinc form a phase diagram similar to that for copper-zinc, Fig. 7. However, a greater tendency to form compounds and ordered solutions exists in the gold-zinc system,
as shown by the atomic ordering which occurs in the α-phase about the composition $\text{Au}_3\text{Zn}$. This point will be further discussed in Section 2.3.3.

The $\beta'$-phase shows a peak in melting temperature at the equiatomic composition of $725^\circ\text{C}$, and maximum solubility limits from 36.5 to 57 at.% zinc at about $640^\circ\text{C}$. The $\beta'$-phase field narrows with falling temperature and at room temperature the single phase field limits are about $50 \pm 2$ at.% . Owen and Edmunds 1938 (10) have shown by an x-ray method that alloys in the $\beta'$-phase field are ordered at least up to $550^\circ\text{C}$. The degree of order at the melting point of the equiatomic alloy has been given as 0.7 (11).

2.1.4 The Iron-Cobalt Phase Diagram

Fig. 8 shows the binary phase diagram of cobalt and iron based on data available in 1957 (3). The limits of ordering in the α-phase have been indicated by measurements of the change of lattice parameter (12), specific heat (13) and recrystallization (14), (15). These latter investigations suggested that ordering also occurs in the region of the compositions $\text{Fe}_3\text{Co}$ and $\text{FeCo}_3$ and also that a transformation occurs in the region
of the equiatomic alloy at about 500°C. An anomalous decrease in the lattice parameter of these alloys at about 500°C. has also been detected by neutron diffraction (16). The nature of this transformation is not known, although a change in the magnetic properties has been reported to occur at this temperature (17).

2.4.4.1 The Iron-Cobalt-Vanadium Ternary Equilibrium Diagram

Although the phase equilibria have not been determined in detail, addition of vanadium to the equiatomic iron-cobalt alloy causes the γ → α transition temperature to be lowered, but the order-disorder temperature $T_o$ is not greatly affected. At room temperature a two-phase field of $α + γ$ is reported for alloys containing more than about 1% of vanadium (18). Fig. 9 gives the section through the ternary diagram from the equiatomic iron-cobalt alloy, with increasing vanadium content. The solubility limits of the α-phase field decrease sharply with decreasing temperature. However, vanadium is known to slow down the reaction rate (19), (20) and equilibrium becomes difficult to achieve below about 800°C.
2.1.5 The Iron-Aluminium Phase Diagram

Literature up to 1957 has been reviewed by Hansen 1958 (3). Fig. 10 taken from this work shows that aluminium forms a complete series of solid solutions up to 52 at.% aluminium, at high temperatures, based on the A2 modification of iron. The Al polymorphic form of iron is limited to a closed loop at low aluminium contents. Above about 35 at.% aluminium, alloys possess the B2 structure at low temperatures. If these alloys become disordered at high temperatures the disordered state cannot be retained by quenching (21).

Transformations below 600°C in the region of the composition Fe₃Al have been the subject of much attention, although their nature in thermodynamic terms has not yet been clarified, Section 2.2.2. Lütjering and Warlimont 1965 (22) have shown by transmission electron microscopy and electron diffraction, that ordering in alloys from 18.4 to 25 at.% aluminium takes place by a nucleation and growth process, and have proposed the equilibrium diagram for this region, Fig. 11. They determined the relative amounts of ordered phase, composition 25 at.% aluminium, to disordered phase by quantitative electron metallography of specimens quenched from various temperatures.
In general their work agrees with that of Erez and Rudman 1961 (23), Fig. 12, and the theoretical predictions of Rudman 1960 (24). Fig. 11 does not show a horizontal line separating a two-phase region of imperfect B2 order and Fe₃Al (existing above 510°C) from the low temperature two-phase region consisting of disordered α-phase and Fe₃Al. If the transformation from disordered α-phase to imperfect B2 order is considered as a classical phase change, Fig. 11 is inconsistent. However, Warlimont 1965 (25) states that no order was detected in the α-phase in the two-phase region below 560°C.

A diagram showing a peritectoid reaction at the ordering temperature 560°C has been proposed, (26), but the existence of a narrow range of solubility for the compound Fe₃Al is inconsistent with the electron diffraction evidence of Lütjering and Warlimont 1965 (22).

Davies 1963 (27) concluded that the phase field of imperfect B2 order completely surrounds the DO₃ phase field, and considered this to be in agreement with theoretical predictions, (24).

2.2 Order in Alloys

2.2.1 States of Order

In a homogeneous solid solution atoms may be
a) A random arrangement exists when lattice sites are occupied without distinction by all atom types in the solution. This implies that a plot of the number of A atoms acting as nearest neighbours to any lattice site at any instant results in a Gaussian distribution, the number varying from 0 to $z$, where $z$ is the nearest neighbour coordination number. A maximum frequency will occur at $\frac{1}{2}z$ for the case of an equiatomic alloy AB.

b) Short-range order in an equiatomic binary alloy is said to exist if the probability of finding an A atom as nearest neighbour on a particular site to any B atom is greater than $\frac{1}{2}$. No statement on the occupation of sublattices is made, and the possibility of the formation and disintegration of regions of short-range order is not excluded.

c) A state of long-range order occurs when sub-lattice sites are occupied consistently by one atom type over distances which are large compared with the lattice parameter of the structure. A degree of order, $S$, may be defined for a binary alloy as

$$S = \frac{D - r}{1 - r}$$

(28)
where $p$ is the probability that a site on the sub-lattice occupied by $A$ atoms in the fully ordered state will be occupied by an $A$ atom, and $r$ is the fraction of the total number of sites in the crystal occupied by $A$ atoms in a state of perfect long-range order. As order increases $S$ varies from 0 to 1. When the occupation of sites by an $A$ atom is equally probable, that is when $p = \frac{1}{2}$, then $S = 0$ for an equiatomic binary alloy. In this case the arrangement is random. In real crystals perfect long-range order through the crystal does not exist due to the presence of a domain structure, arising from the choice of one atom type of different sub-lattices for occupation in different parts of the crystal during the ordering transformation, (Section 2.5). In order to make the concept of long-range order meaningful, it is necessary either to consider the occupation of sub-lattices over distances smaller than the antiphase domain boundary spacing or to ignore the domain structure.

As an alloy with a high degree of long-range order is heated, the degree of long-range order falls with increasing rapidity as $T_c$, the critical temperature for ordering, is approached. Just above $T_c$ the arrangement of atoms is not random, but in general a state of short-range order exists. As the temperature is raised, the
tendency towards a completely random arrangement increases, until considerably above $T_c$ short-range order is virtually non-existent.

2.2.2 The Distinction Between First and Second Order Transformations.

This question is of importance since not only are thermodynamic properties different in the two cases, but mechanical properties may also be affected. In phase transformations an essential difference between those of the first and second order lies in the way the new phase is formed.

Thermodynamic distinctions in the case of order-disorder transitions have been given by Guttman 1956 (29). A first order transition (or transition of the first degree) is one in which the first derivative of the free energy, $G$, is not equal to zero, i.e.,

$$(\delta G/\delta T)_P = -S \text{ and } (\delta G/\delta P)_T = V$$

where $T = \text{temperature}$, $P = \text{pressure}$, $S = \text{entropy}$, and $V = \text{volume}$. A second order transition is one for which only the second derivative of the free energy is not equal to zero, i.e.,

$$(\delta^2 G/\delta T^2)_P = -(\delta S/\delta T)_P = -(C_p)/T \text{ and } (\delta^2 G/\delta P^2)_T = (\delta V/\delta P)_T = -\beta V$$
where $C_p$ is the heat capacity at constant pressure, and $eta$ the isothermal compressibility.

In practical terms this means that those transformations for which a latent heat of transformation exists, or those for which a discontinuity in volume exists, are first order transformations. Also, as pointed out by Rhines and Newkirk 1953 (30) in their paper supporting the view that all order-disorder transformations are classical phase changes, structure sensitive physical properties undergo a discontinuous change at a first order transition, but a continuous change at a second order transition.

Phases which form by a nucleation and growth process (which may or may not involve a change in composition) and which entail the movement of an interface of specific energy separating the product and matrix phases, are considered to be formed by first order transitions. If the transformation is a continuous and homogeneous process not involving the existence or movement of an interface, it is a second or higher order transformation.

It seems to be generally agreed (31) that all order-disorder transitions, excluding the A2 - B2 and A2 - D0$_3$ transitions, are first order, and their phase
diagrams are correctly represented by a two-phase region separating ordered and disordered phases. For the A2 - B2 transition the question is still open. Lütjering and Warlimont 1965 (22) have presented convincing evidence to show that the A2 - D03 transition is first order, but it is not clear whether the B2 - D03 transition is also.

Davies 1964 (32) investigated the ordering kinetics of an alloy containing 24.8 at.% aluminium by hardness measurements and the broadening of x-ray reflections to determine antiphase domain size, both by isothermal annealing and by slow-cooling followed by quenching. He concluded that in the slowly cooled alloys ordering takes place by a process of homogeneous formation, since no sharp discontinuity in the degree of order was found at $T_c$, while during isothermal annealing ordering takes place by a classical nucleation and growth process.

Beck and Smith 1952 (4) thoroughly examined the copper-zinc phase diagram in the region of the $\beta$-phase, and concluded that, within the experimental accuracy, there was no indication of a two-phase region, nor of discontinuities in the $\beta$-phase field boundaries at the transition temperature, both of which would be expected for a first order transition. Furthermore no discontinuity
at the ordering temperature has been found when measuring the change in the degree of order with temperature, (33).

In the iron-cobalt system a similar continuous change in the degree of order with temperature has been determined by neutron diffraction by Lyashchenko, et al., 1962 (16), (34), indicating that in this system also the ordering process in the neighbourhood of 50 at.% is second order. If this is the case the two-phase field indicated in Fig. 8 is incorrect. Chen 1964 (35) reported the transformation as first order on the basis of indications of grain refinement in ordering, and suggested that the transformation in iron-cobalt is either a marginal case of a second degree transformation which may be changed to first degree by addition of vanadium, or is a transformation of the first degree in which the volume change is small and the two-phase region apparently unresolvable.

A second degree order-disorder transformation is an example of a cooperative process. It is difficult to move one atom into a wrong site in a fully ordered alloy. However, the more atoms occupy wrong sites, the easier the disordering process becomes, until just below the critical temperature large changes in the degree of order can occur with small changes in temperature.
The available evidence indicates that the A2 - B2 transition is probably second order, but some doubt still exists and the question remains to be clarified.

The case of alloys in the aluminium-iron system near the composition Fe₅Al is somewhat more complicated. According to Fig. 11 (22) all transformations from the A2 or B2 structure in alloys with less than 25 at.% aluminium, must be first order since a change in composition is involved. From 25 to about 35 at.% aluminium transformations may be second order. No order-disorder temperature has been found for the equiatomic iron-aluminium alloy, but if it does disorder below the melting point, it is likely that it orders in a manner similar to β-copper-zinc or equiatomic iron-cobalt.

2.2.3 Kinetics of Ordering

In a disordered equiatomic alloy of the A2 structure each atom type is on average surrounded by four nearest neighbours and three next nearest neighbours of each atom type. Any volume somewhat greater than the unit cell of the structure should contain an equal number of each atom type, so that movement of atoms over distances greater than the lattice parameter on ordering, will not be necessary. It is likely that ordering to the B2 structure
can be a rapid process, particularly if no energy is required to move an interface between ordered nuclei and disordered matrix, i.e., if ordering is a second degree transition.

The rate of ordering of $\beta$-copper–zinc is known to be extremely rapid; the ordering reaction cannot be suppressed by quenching (3). Smith 1943 (36) studied the effect of quenching on the electrical resistivity and hardness of $\beta'$-copper–zinc. He concluded that quenching did not suppress the formation of essentially complete long-range order. This has been confirmed in general by other investigations (37), but Clark and Brown 1961 (38) have suggested that a small amount of disorder may be quenched into $\beta'$-copper–zinc, and that this is associated with a small concentration of wrong atom pairs in the ordered lattice.

Experiments on the increase of electrical resistivity of $\beta'$-copper–zinc on irradiation and subsequent annealing out (39) of the damage show that the activation energy for the ordering process must be low, since annealing out starts at temperatures below $-100^\circ$C. The same conclusion is suggested by the experiments of Imai and Kitazima 1951 (8). They were unsuccessful in finding a
ternary addition to $\beta'$-copper-zinc capable of suppressing the order-disorder transformation or of slowing it down significantly. Manganese was found to reduce the transformation temperature by about $20^\circ C$ for an addition of 6 at.\% manganese. A reduction, though somewhat smaller than this (5), would be expected even if the added element acted merely as a diluent. Aksenov 1963 (40) has reported that oxygen is capable of reducing the ordering rate.

Ordering is also rapid in the equiatomic binary alloy iron-cobalt. It has been reported (11) that a quenching rate of more than $6000^\circ C/sec.$ is necessary to retain the disordered state. In the iron-cobalt-vanadium ternary system, the ordering is slowed down by the addition of vanadium (20), (19), and experimental difficulties arise when a high degree of order is required.

In an early investigation of phase equilibria in the iron-aluminium system (21) it was shown that iron-rich alloys with compositions near 50 at.\% aluminium could not be retained disordered at room temperature by quenching from $700^\circ C$. Those alloys with less than 25 at.\% aluminium could be retained disordered by quenching from $600^\circ C$ and above, but alloys with more than 25 at.\% aluminium always possessed an imperfect B2 structure after quenching.
Investigation of the change of resistivity with degree of order in iron-aluminium alloys \((41), (42)\) have shown that partial \(D_0_3\) order may be retained at room temperature by quenching from below the critical temperature for ordering. Cooling rates of about \(1 - 2^\circ C/min.\) are adequate for retaining the equilibrium degree of order down to \(350^\circ C\) \((41)\).

2.2.4 Vacancies and Diffusion in B2 Alloys

Metals and alloys at temperatures near the melting temperature, \(T_m\), have a much higher concentration of lattice vacancies in equilibrium than can be supported in the lattice at low temperatures. It is estimated that the vacancy concentration in \(\beta'\)-gold-zinc at \(T_m\) is \(0.68\) at.\% \((43)\). Quenching from high temperature results in at least part of this excess concentration being retained in a metastable state, \((43)\).

Measurements of hardness and density of \(\beta'\)-copper-zinc specimens quenched from various temperatures show a minimum in the density and a maximum in the hardness associated with the critical temperature for ordering, Brown 1959 \((37)\). In this case the vacancy formation was attributed to the rapid ordering process, possibly by the
non-conservative movement of dislocation during the quench.

In a later note Brown and Cupschalk 1963 (44) suggested that a non-equilibrium concentration of vacancies is trapped in \( \beta' \)-copper-zinc after quenching, and that the rapid ordering is due to vacancies sweeping through the lattice at the instantaneous interface between the ordered and disordered regions. As a result a high concentration of vacancies is trapped at the antiphase boundaries (Section 2.5). On annealing these vacancies may collapse to form dislocations. Such a process presumably gives rise to dislocation loops.

Dislocation loops have recently been observed lying on \{100\} planes in quenched and annealed high purity molybdenum, (45) which lends weight to this argument.

The processes of annealing out of vacancies and of diffusion have not been clarified for \( \beta' \)-copper-zinc or other B2 structures and a number of interpretations of data have been proposed. For \( \beta' \)-gold-cadmium, which has a relatively strong ionic component in the bonding, vacancies have been suggested to move in pairs lying in the \(<111>\) direction, (46). In \( \beta' \)-copper-zinc vacancies have been thought to anneal out at jogs on dislocations (37). Diffusion in \( \beta' \)-copper-zinc has been suggested to take place either by a vacancy or interstitial mechanism (47), (48), by vacancies (49), and by interstitialcies (50).
Part of the difficulty lies in assessing the importance of retaining neutrality in the distribution of charge on lattice sites. The postulation that vacancies move in pairs can allow the distribution of charge in the ordered lattice to be retained.

A vacancy mechanism has been proposed for the recovery at room temperature of initially disordered samples of copper-25 at.% gold following deformation at low temperature (51). This may be correlated with the proposal that the movement of vacancies can provide a mechanism for ordering (52), (53). This is reasonable since the energy of the lattice may be lowered by ordering and by removal of non-equilibrium concentrations of vacancies. However, a single vacancy moving through a perfectly ordered lattice must produce a trail of disorder unless, in the case of the B2 structure, second nearest neighbour jumps can be made. It is possible that divacancies may be more stable than single vacancies in the noble metal B2 structures owing to the polar component in the lattice, despite a larger strain energy.

Because of the strain energy associated with vacancies it is likely that they will be annihilated where the local misfit at an atomic level is large, e.g., at grain boundaries or at dislocations which may even be locked by vacancy concentration (54).
2.2.5 Detection of Long-Range Order

Long-range Order may be detected by following changes in physical properties that take place during the ordering process. The nature of these changes depends on whether the transformation is of the first or second degree, (Section 2.2.2). For alloys forming B2 or D03 structures, the following methods have been used successfully:

- measurement of a) specific heat
  - b) electrical resistivity
  - c) change of lattice parameter
  - d) the intensity of superlattice reflections produced by x-ray or neutron diffraction.

  a) The change of specific heat with temperature was used by Sykes and Wilkinson 1937 (5) for the transformation in β-copper-zinc. A maximum is reached just below $T_c$.

  b) The change in electrical resistance on passing through $T_c$ has been used to study ordering in alloys near the composition Fe$_3$Al (41). In general resistivity is sharply reduced on ordering, since the regular arrangement of atoms on lattice sites leads to a reduction in the electron scattering.
c) Detection of the change in lattice parameter by x-rays, either at temperature or following quenching, has been used in the investigation of ordering in the iron-aluminium system (55). It is not a very accurate method for the determination of the degree of order because the changes in lattice parameter on ordering are usually small.

d) It was pointed out in Section 2.1.1 that the B2 and D0$_3$ structures are of lower symmetry than the A2 structure. Thus new reflections will appear when an A2 structure orders. Fig. 13 (28) shows \{100\} reflections from the A2 structure. Atoms on planes A, A$'$ and B are identical in their scattering factors for x-rays in this case and, because of the Bragg condition for reflection, reflection from plane B is exactly $\pi$ out of phase with reflections from planes A and A$'$, causing the total intensity, $I$, to be zero.

In the B2 structure atoms on planes A and A$'$ differ from those on plane B, Fig. 13. For this case complete interference in the \{100\} reflection will not, in general, occur, since it is to be expected that the scattering factors of the two atom types will be different.

$$I = c(f_A + f_B)^2$$, when \((h + k + l)\) is even and $$I = c(f_A - f_B)^2$$, when \((h + k + l)\) is odd.
where $I$ is the intensity of the reflected ray, $c$ is a constant, $f_A$ and $f_B$ are the atomic scattering factors for x-rays of the two atom types A and B, and $h$, $k$, and $l$ are the Miller indices of planes in the B2 lattice (28).

It can be seen from these equations that all reflections of the simple cubic lattice appear, but the intensity of superlattice reflections will be lower than that of principal reflections since the intensity of superlattice reflections depends on the difference of the scattering factors of the two atom types. The degree of order existing in a specimen may be calculated from measurements of the relative intensities of principal and superlattice reflections. The degree of order may be detected unambiguously by measurement of the line broadening of fundamental reflections, together with the intensity of superlattice reflections, since the existence of any two-phase region may be detected as a result of differences of the lattice parameter of the ordered and disordered phases, (56).

In some cases (copper and zinc, iron and cobalt) the difference of the atomic scattering factors is so small that superlattice reflections cannot be detected by standard means. This difficulty may be overcome by
using a radiation whose wavelength lies close to the absorption edge of one of the components. Such a method produces an artificial increase in the difference of the atomic scattering factors, and allows the intensity of superlattice reflections to be measured. This technique has been applied by Kittl and Massalski 1962 (57) to the detection of order in \( \beta' \)-copper-zinc using monochromatic Cu \( K_\beta \) radiation. Superlattice reflections from iron-cobalt alloys have been measured using cobalt radiation artificially to depress the scattering factor of iron (12).

Neutron diffraction has been used as an alternative method. Its success lies in part in the fact that the atomic scattering factors for neutrons are usually different from the atomic scattering factors for x-rays (58). Siegel and Shull 1949 (58) were the first to show that ordering in iron-cobalt alloys could easily be detected using neutron diffraction, but ordering in copper-gold alloys could not be detected using this technique since the neutron scattering factors for these atoms are almost identical.

Neutron diffraction techniques have been used to determine the degree of order in \( \beta' \)-copper-zinc (59) and cobalt-iron (16). The sensitivity of the technique for the latter case allowed the detection of order over a wide composition range and of an anomalous retardation
2.3 Electronic Structure and Bonding

The relation of the electronic structure of the elements and alloys to crystal structure and bonding has been examined frequently (60), (61) with a view to discovering a comprehensive theory. The related problems of cohesion and bonding have also been given detailed examination (62). At the present time many questions remain unanswered. Part of the difficulty lies in determining the electrons responsible for cohesive forces.

In the present study some indications of asymmetrical bonding strength have been given by the behaviour of the alloys examined, and this section deals with a simplified picture of the possible origin of this asymmetry. Ultimately a precise determination of electron distribution and interaction will depend on mathematical concepts, and it is doubtful whether a valid physical picture can be given.

2.3.1 Cohesion and Atomic Size

The stability of intermetallic phases may be considered from two points of view:

a) stability with respect to energy and

b) stability with respect to lattice rigidity.
Mott 1962 (62) has pointed out that the cohesive strength of a metal may be expressed with considerable accuracy in terms of volume alone. That is, to a first approximation cohesive strength is independent of crystal structure or coordination number. It is found that when the coordination number changes, the volume/atom remains constant rather than the interatomic distance, indicating that the former is the more fundamental property.

The change of volume on formation of a compound is related to the heat of formation (63), and should be a measure of thermal stability with respect to the components. Values of the heat of formation of some compounds considered here are given in Table 1.

Table 2 gives values of the volume/atom for a number of compounds of interest in this investigation. These have been calculated from values of the lattice parameter of pure metals (28), assuming that the nearest neighbour distance changes linearly across the phase diagram. Measured values of the lattice parameter of compounds were obtained from the references indicated. The calculated and experimentally determined values are compared. For the noble metal compounds the discrepancy is small.
transition metal—aluminium compounds it is much larger. For the equiatomic iron-cobalt compound a volume expansion occurs. These will be considered separately later.

Since the volume available/atom in a compound is important in determining its energy, relative packing efficiency expressed in terms of the volume occupied by the component atoms as elements will be of importance. Nevitt 1963 (70) has reviewed the known binary alloys having the B2 structure, and noted that the ratio of the atomic radii of the components, normalised to a coordination number 12 falls within the range 0.71 - 1.41. He concludes that since this range also represents almost the maximum range of radii ratio possible in that portion of the periodic table in which most B2 structures occur, relative size cannot be an important determining factor.

However, Evans 1964 (67) points out that the B2 structure in ionic solids will not be expected if the ratio of ionic radii lies outside the range 0.73 - 1.37, since overlap of the outer electron shell of the larger ions must occur in the <100> direction if this range is exceeded. Although the bonding in metallic B2 structures cannot be considered as primarily ionic, it is interesting that they should exhibit a closely similar range of atomic radii to
2.3.2 Electronic Structure and Electronegativity

The nature of bonding forces in metals and alloys depends intimately on the electronic structure of the component atoms. The simplest picture of a metal is an assembly of positive ions immersed in a gas of free electrons. In this case bonding forces are isotropic. The relative ease with which atoms in an alloy exchange electrons is obviously important for an understanding of alloy bonding.

The relative affinity of an atom for electrons is measured by the electronegativity. Table 3 is taken from Evans 1964 (67). The scale is not absolute, but relative, and depends on environment. A variety of values may be found in the literature.

In a binary compound the difference in the electronegativities of the two components is a measure of the electron transfer occurring between the atoms. If electron transfer occurs, the component giving up some of its electronic charge becomes positively charged, while the other component becomes negatively charged, and the bonding is said to be partly ionic or polar in character. Fig 14 shows the relation of electronegativity difference to ionic
character of the bond.

The electronic structure of elements of interest in this investigation are given in Table 4. Hume-Rothery et al. 1940 (71) considered as an empirical rule that the number of electrons available for bonding was given by the number outside the last complete electron shell. Thus Group I elements were considered to have one electron/atom available, Group II elements two electrons/atom, Group III elements three electrons/atom. The transition elements, having an incompletely filled inner d shell, formed a special group, and were considered to be of zero valency and capable of acting as electron acceptors.

Engel 1964 (61) has extended these concepts, relating the number of d, s and p electrons available for bonding to structure and cohesive strength. In silver for example, he considers 1.5 d electrons to be transferred to the outer electrons, allowing four electrons (1.5 d and 2.5 s and p) to form bonds. This is consistent with the moderately high cohesive strength of the noble metals, and with calculations based on bonding by s electrons alone which show the calculated cohesive strength to be consistently lower than that determined experimentally.

Alloyed with zinc or cadmium, the noble metals revert to bonding based on a single electron/atom owing to the stable filled d shells of the Group II elements.
This accounts for the lowering of the melting point of copper alloys with increasing concentration of zinc, Fig. 4.

2.3.3 Bonding in $\beta'$-Copper-Zinc and $\beta'$-Gold-Zinc

Hume-Rothery et al. 1940 (71) were the first to point out that the B2 structure occurred consistently in electron compounds having an electron:atom ratio of about 3:2. Three of the alloys examined in the present work may be described as belonging to the 3:2 electron compound group; $\beta'$-copper-zinc, $\beta'$-gold-zinc and iron-50 at.% aluminium.

If the convention of Engel (61) that A2 structures are based on the electron:atom ratio 1, and close-packed hexagonal A3(1) structures are based on the electron:atom ratio 2 is included, then the equiatomic iron-cobalt alloy may also be described as 3:2 electron compound. Engel's ideas have, however, recently been criticized by Hume-Rothery 1965 (72).

In the $\beta$ and $\beta'$-phases formed by Group IB elements (copper, silver and gold) with Group IIB elements (zinc and cadmium) one electron is said to be available for bonding from the Group I element and two from the Group II element. The charge density of the valence
electrons in the β and β'-phase alloys cannot be uniform. If this were so, the lattice polyhedron occupied by the zinc ion would contain a resultant charge of +0.5 e, while that occupied by the copper ion would contain a charge of -0.5 e in the case of β-copper-zinc, causing the energy of formation of the superlattice to be much greater than is observed (73), (74). It was concluded that the conduction electrons tend to cluster round the zinc ions and the surrounding polyhedral cells contain a total positive charge of 0.075 e each, with a corresponding negative charge round each copper ion. This gives a reasonable value for the ordering energy of β-copper-zinc, namely 0.040 eV/atom compared with the experimentally determined value of 0.043 eV/atom, (73).

The corresponding value for the β'-gold-zinc alloy is given as 0.058 eV/atom, (11). These values reflect the difference in the electronegativities of the atoms composing the two alloys - for copper and zinc, 0.3, and for gold and zinc 0.8, Table 3. According to Fig. 14 β'-copper-zinc should have about 7% ionic character in the nearest neighbour bond, and β'-gold-zinc about 16%.

In the 50 at.% alloys the total difference in charge between the two B2 sublattices will be a maximum
and will provide an important source of lattice stabilisation. The greater difference in ion charges in \( \beta' \)-gold-zinc results in the ordered structure being retained up to or near the melting point \( T_m \), while \( \beta' \)-copper-zinc disorders at 0.65 \( T_m \). Table 1 shows that the correlation of disordering temperature with electronegativity difference and heat of formation in this type of alloy is good. The stability of the B2 structure of \( \beta' \)-gold-zinc to higher zinc contents than \( \beta' \)-copper-zinc has been attributed by Hume-Rothery et al., 1951 (75) to the larger electronegativity difference between gold and zinc.

2.3.4 Bonding in Iron-Aluminium Alloys

The heats of formation of the transition metal - aluminium compounds are high, Table 1, despite a small difference in electronegativity, suggesting that the origin of bonding forces is different from that of the noble metal compounds.

The compound FeAl may be regarded as being based on the electron: atom ratio 3:2 if iron is considered to be zero-valent and aluminium as contributing three valence electrons per atom to the bonding. Nemnonov et al. 1960 (76) and 1962 (77) have considered the implications of such
electron transfer. If iron acts as an electronegative element relative to aluminium, this will lead to an increased localisation of the valence electrons about the iron atoms. Such a charge transfer must introduce considerable polarity to the structure, and this is reflected in the development of some form of order in alloys with as little as 16 at.% aluminium, (27).

In the perfect D0₃ structure a difference of environment exists between iron atoms on sublattice III(Fe I) and those on sublattices II and IV, (Fe II) (Section 2.1.1). The distribution of aluminium between the four sublattices with increasing aluminium content for both quenched and annealed alloys is shown in Fig. 15. The different environments are reflected in different properties of the two types of atom. Nathans et al. 1958 (78) have measured the magnetic moment of Fe I and Fe II atoms in this structure. Fe I atoms were found to have a moment $2.12 \pm 0.1 \mu_B$ and Fe II atoms $1.46 \pm 0.1 \mu_B$. The value for Fe I atoms is close to that for pure iron, indicating that transfer of electrons from aluminium atoms occurs only to nearest neighbours. Hence only iron atoms having aluminium nearest neighbours can accept electrons and take part in polar interaction.
Following considerations of charge distribution in β'-copper-zinc (Section 2.3.3), it is probable that the positive charge on the aluminium ion is partially shielded by the conduction electrons. If interactions between unlike atoms are strong - indicated by the change in volume given in Table 1 - it would be expected that ordering should appear in the region of 25 at.% aluminium, whereby aluminium atoms avoided a second nearest neighbour relationship. Such an arrangement would allow maximum transfer of charge.

The compound Fe₃Al is ferromagnetic below about 540°C (23) the magnetism being associated with the Fe I atoms. As the aluminium content is raised, and the Fe I atoms are replaced in the lattice, the ferromagnetic transition (Curie) temperature drops rapidly and falls below room temperature at about 32 at.% aluminium. Therefore ferromagnetic effects cannot contribute very much to the stabilisation of the structure.

It was concluded (41) from measurements of the change of resistivity with change in the degree of D₀₃ order in an alloy near the composition Fe₃Al that the freedom of conduction electrons is reduced as order increases.
Nemnonov et al. 1962 (77) considered that localised nonmetallic interactions are present in transition metal-aluminium alloys, as well as the predominantly metallic interaction. These effects increase with increasing concentration of aluminium and are responsible for the exceptionally short interatomic distances in some of the aluminium-rich phases. They suggest that resonance covalent bonds may be set up among a group of nearest neighbours. Such an arrangement should tend to be stable.

They have summarised the above considerations in the following way:

"Although the separation of the intermetallic binding forces into separate components is somewhat arbitrary, it may be assumed that the predominantly metallic interaction is supplemented by interactions of a covalent and resonance covalent type, with a certain amount of polarity, and that the binding electron cloud is repulsed towards the transition component."

2.3.5 Bonding in Iron-Cobalt Alloys

The A2 structure of α-iron-cobalt alloys is based on the stabilisation of the A2 structure of α-iron. A maximum in the phase stability with temperature is reached at about 45 at.% cobalt, Fig. 8. Addition of cobalt to
iron raises the magnetic ordering temperature of the A2 phase above the α-γ transition temperature, from 15 to 72 at.% cobalt.

A plot of magnetic moment/atom against the average number of electrons/atom of a range of ferromagnetic alloys, Fig. 16, shows a peak at about 2.6 μB/atom at iron-35 at.% cobalt, (79). This indicates an increase in the ferromagnetic interaction of iron and cobalt atoms up to 35 at.% cobalt.

Fine and Ellis 1948 (80) found a positive deviation from Vegard's law for this system, Table 2, and an anomalously low expansion coefficient in the neighbourhood of 50 at.% cobalt, particularly in the ordered alloy. They attributed these effects to more complete sharing of electrons between iron and cobalt atoms, leading to an increase in repulsive forces. If some interaction between iron and cobalt atoms is responsible for the observed effects, they should be more pronounced in the ordered than in the disordered alloy since in the former each atom is surrounded by unlike nearest neighbours.

A change in the electronic structure of iron-cobalt alloys at about 40 at.% cobalt has been detected by a study of the change of x-ray emission spectra with temperature and composition, (81). This change was
thought to be coincident with the peak in spontaneous magnetization occurring at about 35 at.% cobalt, Fig. 16.

The nature of the interactions between iron and cobalt atoms on alloying is not clear. It is possible that "electron sharing" of the type visualised by Fine and Ellis 1948 (80) involves a redistribution of electrons in the lattice. It appears to be impossible to differentiate clearly between magnetic, bonding and conduction electrons.

Little information can be deduced concerning directionality in bonding in these alloys, although both the appearance of ferromagnetic and crystallographic order may be accompanied by a change in the electronic structure, and may contribute to the stabilisation of the body-centred cubic structure.

2.4 Elasticity and Stability

2.4.1 Elasticity of β'-Copper-Zinc and β'-Gold-Zinc

It has been noted, (Section 2.1.1) that an A2 structure composed of hard balls is unstable to shears of the type \{110\} \langle\bar{1}10\rangle, nearest neighbour distances remaining unchanged to a first approximation. Zener 1947 (2) has pointed out that the resistance to shear in metals arises
primarily from two sources:

a) the exchange interaction between ions and
b) the electrostatic interaction between conduction electrons and ions.

According to Zener the former may be regarded as acting between nearest neighbours only, and will give a repulsion if the bcc lattice is composed of ions having closed electron shells, as is the case for \( \beta' \)-copper-zinc and \( \beta' \)-gold-zinc, giving a negative contribution to the elastic modulus

\[
\frac{1}{(s_{11} - s_{12})} = C'.
\]

(Elasticity relations are indicated in Appendix A.) The latter source of shear resistance was suggested to be independent of the structure of the ions, giving a positive contribution to \( C' \), depending on the charge on the ions and hence on the electronegativity difference of the component elements.

Zener regarded a low value of \( C' \) as typical for \( \beta' \)-phase alloys with closed inner shells and suggested that it will lead to a large amplitude of thermal vibration in this direction, resulting in a large entropy and the observed wide solubility field at higher temperatures, characteristic of the \( \beta \)-phase alloys.

The \( A2 \) structure is stable in the transition metals with from three to six electrons in the 3d shell.
In this case the exchange interaction provides a positive contribution to the shear modulus $C'$ and can contribute strongly to lattice stability, (Section 2.3.5).

Values of the elastic constants and associated functions for $\beta'$-copper-zinc and $\beta'$-gold-zinc are given in Table 5, together with those for the isotypic compound $\beta'$-gold-cadmium, demonstrating the generality of Zener's argument (2). Fig. 17 illustrates the change in elastic anisotropy measured as $E_{\langle111\rangle}/E_{\langle100\rangle}$ for $\beta'$-copper-zinc as a function of temperature, (83). Values given in Table 5 indicate that the elastic anisotropy of $\beta'$-copper-zinc is high, but do not show any consistent change with composition. The value of $\sigma_{44}$ given by Good (85) is recognized to be too low, and leads to the surprising result that Poisson's ratio for a stress applied in the $\langle111\rangle$ direction is negative, implying lateral as well as longitudinal extension in response to a tensile stress in that direction.

The elastic anisotropy of $\beta'$-gold cadmium is higher than that of $\beta'$-copper-zinc, and consistent with the occurrence of a diffusionless phase transformation in this alloy just above room temperature, (Section 2.4.3).

McManus' results 1963 (88), Fig. 18, indicate that the elastic anisotropy of $\beta'$-copper-zinc remains
constant or decreases slightly below 48 at.\% zinc. Jones 1952 (91) considered that the stability of \(\beta'\)-copper-zinc with respect to \(\{110\} <110>\) shears could be accounted for by the increase in Fermi energy which would result if the Brillouin zone were sheared. The same argument also suggests that a reduction in the zinc content would cause a reduction in the electron:atom ratio and hence of the stabilising effect. McManus 1963 (88) presents arguments to suggest that Jones' calculated values of the Fermi contribution to the elastic constants of \(\beta'\)-copper-zinc using a nearest neighbour approximation, are incorrect. He stated that a second nearest neighbour contribution term is necessary to explain both the observed composition dependence and the temperature dependence, even though the contribution from the Fermi surface overlap discussed by Jones, is probably considerable. These arguments have since been withdrawn as incorrect (92). Two of the alloys considered (88) (45.0 and 50.0 at.\% zinc) lie in a two-phase field, but the presence of second phase was believed not to be significant (92). The uncertainty in the relations between the elastic constants of \(\beta'\)-copper-zinc with composition and temperature might be resolved by an investigation using single crystals of metastable alloys quenched from the \(\beta\)-phase field and aged at room temperature, in order to
anneal out quenched-in defects and approach the equilibrium degree of order. This would provide a wider composition range and help to eliminate inaccuracies inherent in investigating a small range of composition.

Elastic data for $\beta'$-gold-zinc given in Table 5 indicate a low value of the elastic anisotropy. The elastic constants were estimated by an indirect method and are accurate only within 20%. The quantitative accuracy of any derived value, such as $C/C'$, must therefore be suspect.

2.4.2 Elasticity of Ferromagnetic Alloys.

Ferromagnetic ordering occurs on cooling a metal or alloy through the critical temperature $T_c$ (the Curie temperature), by a cooperative process involving the alignment of electron spins in neighbouring atoms. The temperature dependence of the process is similar to that of long-range order. The problem of the occurrence of both phenomena in the same alloy has been investigated theoretically (93), (94), and it has been shown that anomalies in the temperature dependence of both crystallographic and magnetic order can occur. It is known (94), (95) that both phenomena may have a considerable effect on the elastic properties of metals and alloys.

Unfortunately, very few data on the elastic constants of ordered and disordered ferromagnetic alloys are
available. Numakura 1961 (96) has reported work on the change of the Young's modulus with crystal orientation for an ordered and disordered alloy at the composition Fe$_3$Al. These results were obtained by a static method (three point loading of suitably oriented single crystals) and show that the Young's modulus in all directions is reduced on ordering. It was also shown that elastic anisotropy measured as $E_{[111]} / E_{[100]}$ is small (about 1.6) and is virtually independent of the state of order. No data are available for single crystals of cobalt-iron alloys.

In their investigation of the effect of heat treatment and magnetization on the Young's modulus of a range of polycrystalline iron-aluminium alloys Yamamoto and Taniguchi 1954 (97) found that the modulus was lower in the unmagnetized than in the fully magnetized state. Seliskii 1963 (98) concluded that the saturation magnetostriction of an alloy corresponding to the composition Fe$_3$Al was a maximum in the ordered state and a minimum in the disordered state.

An investigation of annealed polycrystalline iron-cobalt specimens in the unmagnetized state revealed a minimum in the Young's modulus/composition curve at 50 at.% cobalt (99). A quantitatively similar curve has been found for disordered iron-cobalt alloys (98).
However, a sharp increase in the Young's modulus on magnetization was found for annealed polycrystalline iron-50 at.% cobalt (99). Hall 1960 (100) investigated the magnetostriction and magnetic anisotropy of ordered and disordered single crystals of a range of iron-cobalt alloys. He describes the magnetostriction as large and positive in both states, though somewhat smaller in the ordered state. It was also found that the magnetic anisotropy passed through zero at about 40 at.% cobalt for the disordered alloy and at about 50 at.% cobalt for the ordered alloy. At this composition, no easy direction of magnetization exists in the crystal. An earlier report (101) has however suggested that magnetostriction increases on ordering.

These results illustrate the important changes that occur on chemical or magnetic ordering. They are however insufficient to deduce specific conclusions on changes of binding forces or of single crystal elastic constants that may occur as a result of these phenomena. Large positive values of the magnetostriction of both ordered and disordered iron-cobalt alloys and of iron-25 at.% aluminium may possibly imply an increase in repulsive forces between neighbouring atoms when electron sharing and spin alignment is more complete, but the question is almost certainly more complex than this.
It is noteworthy that the Young's modulus of iron-25 at.% aluminium is decreased on ordering, while for iron-50 at.% cobalt (102), copper-25 at.% gold, copper-25 at.% palladium and β-copper-zinc the Young's modulus increases (93). The relationship of ordering and magnetic properties could be further clarified by a detailed examination of single crystals, since results on polycrystalline material ignore the variation of magnetic and mechanical properties with crystallographic direction.

2.4.3 Phase Stability and Martensitic Transformations

Bilby and Christian 1956 (103) have defined a martensitic transformation as:

"A structural transformation during which the atoms on a primitive lattice, defined by a selected unit cell of the parent structure, move to positions on a primitive lattice defined by some unit cell of the product structure in such a way that the displacement constitutes a homogeneous deformation. This deformation may be different in adjacent small regions."

These transformations take place without diffusion although rearrangement of atoms, termed a "shuffle", may take place in a regular manner over distances shorter than the atomic spacing. For convenience of treatment and analysis
the atom movements may, in general, be regarded as being composed of three components:

a) a distortion known as the Bain distortion
b) a rotation and
c) a secondary shear

These do not necessarily have a direct physical interpretation since the component operations take place simultaneously. As a simple approximation the rotation and secondary shear may be regarded as being associated with the accommodation of the product in the parent lattice, that is with coherency conditions, while the Bain distortion contains the principal shear.

The Bain distortion largely determines the habit plane of the product, while the rotation and secondary shear are responsible for producing deviations of the habit plane from the plane of instability of the parent lattice. For example: it has already been pointed out that \( \beta' \)-copper-zinc is unstable to shears of the type \{110\} \<\bar{1}0\>, suggesting that martensite in this alloy would have a habit plane close to \{110\} \( \beta' \). In fact the habit plane has been determined as lying near \{211 12\} \( \beta' \), that is, about \( 7^\circ \) from \{110\} \( \beta' \), (104).

The close relation of mechanical twinning to martensite formation has been noted, (103), (105). Indeed,
Bilby and Christian 1956 (103) mention that mechanical twinning may, by the above definition, be regarded as a special case of the martensitic transformation. However, the interface of a twin with the matrix acts as a plane of reflection in the lattice, and twinning involves no change of structure. The usual twinning shear in the A2 lattice is of the type \( \{112\} <\bar{1}1\bar{1}> \). As pointed out by Laves 1952 (106) such a shear in the B2 lattice changes the relation of nearest neighbours, and the structure must then be described as \text{tetragonal} with unit cell dimensions \( a, a\sqrt{2}, a\sqrt{2} \), where \( a \) is the cube edge length of the B2 lattice. The increased difficulty of twinning on ordering has been investigated by Cahn and Coll 1961 (107) for ordered and disordered iron-aluminium alloys near the composition \( Fe_3Al \) impacted at \(-196^\circ C\). When the ordering parameter \( S \) has a value greater than 0.5, twinning is suppressed.

In 1948 Zener (108) proposed that the A2 structure should tend to become unstable at low temperatures because of the decrease in the vibrational entropy associated with the \( \{110\} <\bar{1}10> \) strain coordinates. As a result of investigations to test this prediction lithium and sodium were found to transform by a shear controlled process to more closely packed structures at low temperature, (109).
Martensitic phase transformations having a similar origin have been observed for the \( \beta' \)-phase alloys of copper, silver and gold with zinc and cadmium: gold-cadmium (110), copper-zinc (111), silver-cadmium (112), gold-zinc (113). These transformations are important in this context since they derive from the weakness of the parent lattice to shears of the type \{110\} \( \langle \overline{110} \rangle \).

Zirinsky 1956 (90) and Robertson 1965 (114) have related shear controlled transformations to the mechanical instability of the high temperature phase, measured by the elastic constants. The 46.0 at.% cadmium \( \beta' \)-gold cadmium alloy transforms at 90\(^\circ\)C, while the 50.6 at.% cadmium alloy transforms at 0\(^\circ\)C (115). This is consistent with the greater elastic anisotropy of gold-rich \( \beta' \)-gold-cadmium alloys reported by Zirinsky 1956 (90).

As indicated in Section 2.4.1, values for the elastic constants of copper-rich \( \beta' \)-copper-zinc alloys given in Fig. 17 are not consistent with theoretical predictions concerning the stabilising influence of the Fermi energy (91), nor are they consistent with the observed lattice instability measured by the change of martensite start temperature \( M_s \) with composition, Fig. 19.

\( \beta' \)-gold-cadmium, (115), \( \beta' \)-copper-zinc (116) and \( \beta' \)-silver-cadmium (112) all show a lowering of the
M_s temperature with increasing cadmium or zinc content. This has been interpreted as being due to the stabilising influence of increasing electron: atom ratio (117). This cannot be the only factor involved since the variation of M_s temperature with composition for beta'-gold-zinc Fig. 20 and for the A2 - A3 transformation of beta-silver-zinc is in the opposite sense, i.e., increasing zinc content raises the transformation start temperature. The additional factor is unlikely to be the long-range order parameter S, since if order has a stabilising influence in itself the M_s/composition curve should tend to be symmetrical about 50 at.%, the composition at which maximum order occurs. Zinc added to silver or gold produces a reduction in the lattice parameter and the volume size factor difference is negative, Table 2. It is possible that an increasing concentration of smaller atoms tends to encourage mechanical instability. If this is so, an increasing concentration of larger atoms as in the addition of zinc to copper cadmium to silver will produce a stabilising influence supporting that of the Fermi energy.

The martensitic transformation products of beta'-copper-zinc and beta'-gold-zinc belong to the group known as "thermoelastic martensites." Their formation is characterised by reversibility and low temperature hysteresis (31). Assuming that the shape of a growing plate remains
constant the increase in elastic energy of the matrix may be assumed to be proportional to the volume of the plate. However, edgewise growth will be restricted because of coherency conditions and the consequent rise in elastic energy may be greater than the decrease in chemical energy causing the transformation to proceed, and growth will cease. If this happens before the elastic limit of the matrix is reached the plate is held in an equilibrium between the chemical driving force and the surrounding elastic strain field. A change in the chemical driving force such as lowering or raising the temperature will change the equilibrium and cause the plate to increase or decrease in size. Similarly a change in the stress conditions around the plate cause the plate to grow or shrink.

Christian 1965 (31) suggested that thermoelastic martensite will be favoured when the chemical driving force is low, when the shape deformation has a shear component which is small and when the matrix has a high elastic limit. Fig. 19 shows the martensite start line $M_d$ under moderate or severe compressive deformation for $\beta'$-copper-zinc alloys. The transformation start line is raised dramatically by an applied stress, and runs approximately parallel with the $M_s$ line determined by cold stage microscopy.
A similar effect has been observed by Hull 1962 (118) who showed that thin films of 39% zinc $\beta'$-copper-zinc transformed spontaneously at room temperature, during electropolishing, if the film thickness was less than about 1500 Å. The same effect has also been observed by Ball and Smallman 1965 (119) in thin films of $\beta'$-gold-zinc. This effect was attributed to the removal of elastic constraints present in the bulk material, (118). The reversibility of the transformation under changing applied stress has been studied by Reynolds and Bever 1952, (120) who observed that plates could be made to advance or retreat without causing plastic deformation of the matrix.

Of the ferrous alloys of interest in this investigation, a martensitic transformation has been reported for an iron-aluminium alloy near the composition Fe$_3$Al possessing the D0$_3$ structure, (121). It was reduced 5% by rolling and examined by transmission electron microscopy. The elastic anisotropy of the compound Fe$_3$Al is very low (96) and it is therefore not likely that transformation occurred during thinning of the specimen. The reason for the transformation was given as the difficulty of deformation either by slip or twinning in the D0$_3$ lattice. Both of these processes will be associated with the creation of a certain amount of disorder. No corresponding transformation in the B2 structure of the equiatomic iron-cobalt alloy has been reported.
2.5 Domains in Ordered Alloys

In a perfect B2 or DO3 lattice each atom type occupies the same sub-lattice consistently through the crystal and perfect long-range order is said to exist, Fig. 2, Fig. 3. In practice, however, even highly ordered crystals possess a domain structure, such that the sub-lattice occupied by a particular atom type changes on passing from one domain to the next, while perfect order is retained within each domain. The shape and stability of this domain structure depends not only on the energy of the boundary separating one domain from its neighbour but also on the nature of the superlattice itself.

2.5.1 Origin of Domains

Domains, and the associated anti-phase domain boundary, may arise in two ways:

a) during formation of the superlattice from the disordered structure and,

b) during plastic deformation of the superlattice, (122) .

The second of these two possibilities will be considered in Section 2.7.3.

a) Ordered structures can be regarded as made up of two or more interpenetrating sub-lattices (Section 2.1.1). Disregarding the degree of the transformation by which ordering takes place, the process may conveniently be thought of as
being initiated from small nuclei of the ordered structure which appear at the critical temperature $T_c$. In the disordered state, sublattices are equivalent. However, as nuclei form, a particular atom type occupying one sub-lattice in one ordered nucleus may occupy a different sub-lattice in a neighbouring nucleus. The ordered regions grow by a cooperative process, eventually coming into contact. The region between these ordered domains will be characterised by bonds between neighbouring atoms which would be "wrong" in the perfectly ordered lattice. When nuclei, whose pattern of sub-lattice occupation is identical, come into contact, they coalesce to produce a single large domain.

2.5.2 Domains in the B2 Structure

The theory and experimental observation of domains in some ordered structures has been reviewed by Marcinkowski 1963 (122). He has described antiphase domain boundaries by means of a vector $\vec{p}$, where $\vec{p}$ is the displacement necessary to transfer atoms from sites on one sub-lattice to sites on another sublattice. For the B2 lattice this vector is $\frac{1}{2}a \langle 111 \rangle$, where $a$ is the lattice parameter, Fig. 2. To describe an antiphase boundary fully, the plane parallel to which it lies must also be defined. Fig. 21 shows two $\frac{1}{2}a \langle 111 \rangle \{110\}$ antiphase boundaries.
This diagram represents an unstable configuration, and is correct for first and third nearest neighbours, but not for second.

It is not possible for antiphase boundaries on \{100\} planes to cross, as shown in Fig. 22 which is a projection of the B2 structure on the (001) plane.

The direct observation of antiphase domain boundaries in the B2 structure was first reported by Marcinkowski and Brown 1961 (123), for an alloy near the composition Fe$_3$Al. This alloy possesses an imperfect B2 structure stable between 560°C and 800°C, Fig. 12. It was found that quenching from 900°C did not suppress the ordering but produced a small domain boundary spacing of about 250 Å. Annealing at 600°C for one hour, followed by quenching increased the spacing to about 900 Å. Lütjering and Warlimont 1965 (22) have reported observation of domains of the B2 structure in an iron-rich alloy near the composition Fe$_3$Al cooled at about 20°C/hr. having a spacing in the order of 20,000 Å. If a domain is to terminate inside a crystal of
B2 structure, it must be completely surrounded by the other domain, since only two different domains are possible. Although such an arrangement is possible, it is more likely that the two domains may be traced (intimately entangled) through the crystal. It is thus more meaningful to refer to antiphase domain boundary spacing than domain size.

If the B2 structure is regarded as resulting from a preference of atoms for unlike nearest neighbours, an additional energy will be associated with antiphase domain boundaries. Prolonged annealing will tend to reduce the area of boundary. Further, it might be expected that antiphase boundaries would favour orientation parallel with low index planes in the crystal.

Marcinkowski and Brown 1961 (123) found that this was not the case for imperfect B2 order in the alloy iron – 25 at.% aluminium and ascribed the fact to the independence of antiphase boundary energy with orientation in the crystal. In his theoretical analysis of contrast conditions Marcinkowski 1963 (122) presented arguments to show that because of the similarity in the scattering factors of copper and zinc, it should not be possible to detect antiphase boundary contrast in $\beta'$-copper-zinc. Hull (124) was unable to detect antiphase boundaries in $\beta'$-brass in agreement with this suggestion. However, recently
Warlimont 1965 (25) has observed antiphase boundary contrast in a thin film of 41.0 at.% zinc metastable $\beta'$-copper-zinc, and his results show that in this alloy domain boundaries are curved and show no tendency to lie along crystallographic planes. The domain boundary spacing varied from 100 to 5000 Å over very small distances. The origin of these contrast effects has not yet been determined. Aksenov 1962 (125) has reported a domain boundary spacing for $\beta'$-copper-zinc containing from 45 - 50 at.% zinc of about 300 Å determined during a nuclear magnetic resonance study of $\beta'$-brass.

No observations of antiphase domain boundaries have been reported for $\beta'$-gold-zinc or for iron-50 at.% cobalt.

2.5.3 Domains in the D0$_3$ Structure

Theory and experimental work have been reviewed by Marcinkowski 1963 (122). He points out that two distinct types of antiphase boundary can be produced in the D0$_3$ structure, associated with two different antiphase boundary vectors, Fig. 3. The first is essentially that of the B2 structure being $(1/4)a_o <111>$, where $a_o$ is the edge length of the D0$_3$ unit cell. Such a vector produces only "wrong" first nearest neighbour pairs, i.e., aluminium-
aluminium nearest neighbours. The second vector is of the type \( \frac{1}{2}a <100> \). This displacement results in "wrong" second nearest neighbour pairs, i.e., aluminium-aluminium.

Since four different sublattices exist in the DO\(_3\) structure (Section 2.1.1) four different domains may form. This provides a greater probability than may be expected in the B2 structure that growing nuclei will form antiphase domains and will not coalesce.

Marcinkowski and Brown 1961 (123) also examined domain boundaries in the DO\(_3\) structure of an alloy near the composition Fe\(_2\)Al. They found that the boundaries curved in a similar manner to those of the B2 lattice in this alloy, and that because of the B2 order existing before the formation of the DO\(_3\) structure, only two distinct DO\(_3\) domains could form within each B2 domain.

2.5.4 Stability of the Domain Structure.

The DO\(_3\) structure, possessing four distinct domain types, has the possibility of forming a metastable antiphase boundary structure, as pointed out by Marcinkowski 1963 (122). Such a structure has been likened to that of a foam (126). On this basis, corners require four types of domains, lines three, and surfaces two domains for stability. In this case Fig. 21 must represent an unstable
configuration. Marcinkowski 1963 (122) has suggested that the tangled arrangement of DO$_3$ domains occurring within B2 domains in the iron - 25 at.\% aluminium alloy might not occur if transformation to the DO$_3$ structure takes place directly from a disordered matrix. In this case more symmetrical and equiaxed domains are likely. This has been confirmed by Lütjering and Warlimont 1965 (22) for alloys of iron with 18.5 to 22 at.\% aluminium, which transform by a true nucleation and growth reaction.

It has been postulated that the region near a grain boundary in an ordered alloy might be disordered, presumably as a result of the energy associated with lattice mismatch across the boundary (127). Fig. 23 shows a grain boundary in an alloy near the composition Fe$_2$Al, demonstrating that antiphase domains run into the boundary and do not terminate in a disordered grain boundary layer.

2.6 The Deformation of Body-Centred Cubic Metals

2.6.1 The Appearance of Slip Traces

Maddin and Chen 1954 (128) have reviewed work on the deformation of single crystals and the appearance of surface deformation markings, in relation to crystal orientation.
They reported that extension of a single crystal of molybdenum just beyond the yield point gave rise to fine straight slip striations. After 18% elongation the appearance of the markings depended on their position relative to the active slip direction of the crystal. Viewed parallel with the slip direction, traces were wavy although parallel crystallographic directions delineating sections of the traces could be observed. Viewed perpendicular to the slip direction, traces were much straighter but showed some nonparallel segments. A similar distribution of slip markings has also been observed on single crystals of α-iron, (128).

2.6.2 The Slip Plane of Body-Centred Cubic Metals

Barrett 1952 (28) has reported the slip planes in the A2 structure as \{110\}, \{112\}, and \{123\}. These planes all lie in the \<111> zone. Elam 1935 (129) suggested that combinations of short slip traces on intersecting \{110\} planes could account for the appearance of slip markings apparently on planes of higher index lying in a \<111> zone. Maddin and Chen 1954 (128) have shown that the additional area of slip plane involved in this process is small: 13.4% for pseudo \{123\} slip and 15% for pseudo \{112\} slip. They suggest that if the stress to produce slip on the \{110\} plane is small, relative to the stress required for slip on \{112\} and \{123\} planes, composite slip of this nature is likely. However,
they also report work on single crystals of ingot iron which suggests that slip can occur on irrational planes in the \( <111> \) zone.

Keh and Weissman 1963 (130) have considered the relation of surface slip markings in iron to the dislocation structure revealed by transmission electron microscopy. They observed that most dislocations introduced into iron by deformation have screw orientations, change their slip plane very frequently and may move along paths not corresponding with low index directions in the crystal. Slip in iron–3 wt.% silicon single crystals has been shown to be controlled by the plane of maximum resolved shear stress in the \( <111> \) zone at low rates of strain, while at high rates of strain slip takes place on \( \{110\} \) planes only, probably due to the higher velocity of dislocations causing deformation, (131). The theory of intersecting slip on \( \{110\} \) planes has recently received support from a study of temperature and orientation effects on the deformation of iron 3% silicon single crystals (132).

Edge dislocations can move out of their slip planes only by climb, i.e., the diffusion of vacancies or atoms to the edge of the extra half-plane constituting the dislocation. A dislocation segment, either pure screw or having a screw component, can move into an intersecting plane if the direction of the Burger's vector is that of the zone described by the
two planes, (133). This process is known as cross slip. Such movement would provide a mechanism for the intersecting \{110\} slip suggested by Elam 1935 (129). A pure screw dislocation converts the lattice to a spiral whose axis lies along the core of the dislocation. The equilibrium configuration of atoms in the core will be determined by strain energy considerations. Displacement of the dislocation core in any direction will cause a rise in this energy, so that favoured directions of displacement will be those in which the rise in strain energy and the distance between energy valleys is a minimum.

2.6.3 The Effect of Temperature on Deformation.

The effect of temperature on the formation of slip markings has been reviewed by Maddin and Chen 1954 (128) and by Honeycombe 1961 (134). In particular, Ardley and Cottrell 1953 (135) studying yield in \(\beta'\)-copper-zinc crystals noted that at \(-196^\circ C\) slip took place entirely on the \{112\} planes, from room temperature to \(250^\circ C\) the slip system was \{110\} \<111\>, while above \(250^\circ C\) the slip markings became ill-defined and it was no longer possible to determine the slip plane. The slip system at \(-196^\circ C\) has also been determined as uniquely \{110\}<111> (136).
During their investigation of yielding and fracture in α-iron and its alloys with vanadium and cobalt, Stoloff et al. 1965 (137) have shown that wavy glide is suppressed by decreasing temperature. Similar results have been reported for α-iron deformed at −75°C by Keh and Weissman 1963 (130).

It has been reported that the linear work-hardening stage (Stage II) of the deformation of face-centred cubic metals at low temperatures is extended to higher strains than at room temperature, (138). Stage III is known to be associated with the occurrence of appreciable cross slip (138). All these results point to the general conclusion that cross slip, either in face-centred cubic or in body-centred cubic structures, is reduced if not suppressed as the temperature of testing is lowered below room temperature.

Dorn and Rajnák 1964 (139) have proposed that the observed sharp increase in flow stress with decreasing temperature, below room temperature which has been observed for a number of body-centred cubic metals and alloys, chromium, tantalum, vanadium, niobium, α-iron, molybdenum and tungsten (139), β'-silver-magnesium (140) and β'-copper-zinc (135), may be explained by the necessity of nucleating a pair of kinks in screw dislocations in order to move them from one energy valley
to the next. Such mechanism will be sharply dependent on thermal activation, and is closely related to the process of cross slip.

There seems no good reason why movement of dislocations on intersecting \{110\} planes should not take place over distances comparable with the lattice parameter, if cross slip is easy. If this is so, the distinction between slip on irrational planes of the \{111\} zone and intersecting \{110\} planes loses its significance.

2.6.4 Deformation Bands

The deformation of \(\beta'\)-copper-zinc (44.6 - 50.08% zinc) has been described by Elam 1936 (141), who reported slip markings and lenticular bands on the surface after elongation. These bands were thought to be twins with boundaries on \{100\}, but Laves 1952 (106) has since shown that twins are unlikely to form in the B2 structure. Greninger 1938 (142) observed bands lying close to \{110\} planes after deformation of \(\beta'\)-copper-zinc (48.1% zinc) in compression.

These bands, termed deformation bands (142), have been investigated by Bassi and Hugo 1958 (143) using an etch figure technique, on single and polycrystalline specimens deformed in compression to varying extents. Bands formed in the polycrystals after 5% strain, and were much more common in
polycrystals than in single crystals. It was concluded that deformation bands in $\beta'$-copper-zinc are formed by lattice tilting and result from dislocation pile-up, probably at grain boundaries. This view was supported by the observation that the boundaries of bands became sharp on annealing at a low temperature ($200^\circ\text{C}$), presumably by a dislocation climb mechanism similar to that proposed for polygonization, (144). It was further concluded that the formation of deformation bands represents a major mode of deformation in $\beta'$-copper-zinc.

Earlier investigations of deformation bands in aluminium, reviewed by Cottrell 1953 (145), established that deformation bands are composed of crystal rotated relative to the surrounding lattice. Further, they form early in deformation in tension or compression, but rarely during bending or shear, and are a source of asterism on Laue back reflection photographs. Barrett 1952 (28) has stated that deformation bands may be produced in all face-centred and body-centred cubic metals during deformation. The formation of deformation bands has not been noted in reports of the deformation of the equiatomic iron-cobalt alloy or of alloys near the composition iron-25 at.% aluminium, (146), (147).
2.7 Dislocations in the Superlattice

2.7.1 The Superdislocation

The lower symmetry of superlattice structures relative to the disordered structure implies that distances between equivalent lattice sites are greater in the ordered structure. Fig. 24A shows a two-dimensional disordered lattice, and Fig. 24B the corresponding ordered lattice. The distance between equivalent sites in the slip direction changes from \( a \) to \( 2a \) on ordering. The spacing of equivalent lattice sites in the slip direction will determine the magnitude of the Burgers vector \( b \) of unit perfect dislocations. A unit perfect dislocation is defined as the dislocation, having the smallest Burgers vector, which does not change the lattice following its passage, \((133)\).

If the distance between nearest neighbours does not change during the formation of the superlattice, the Burgers vector of the perfect superlattice dislocation will be a multiple of the vector of the perfect dislocation of the disordered lattice, assuming also that the slip direction is unchanged.

Fig. 24C shows a unit perfect dislocation of the ordered lattice. The condition that the structure is not changed requires the insertion of two extra half-planes to form the dislocation. Fig. 24D shows a unit perfect dislocation of the disordered lattice in the ordered structure. The motion of such a dislocation produces a trail of stacking
fault, in this case antiphase boundary, and the dislocation is imperfect. Koehler and Seitz 1947 (148) were the first to suggest that a dislocation arrangement whereby imperfect dislocations in the superlattice, moving in groups connected by antiphase boundary, might be energetically preferred to unit perfect dislocations. This prediction has been verified by recent transmission electron microscopy investigations of the dislocation structure of ordered alloys, (122).

Such a group of dislocations connected by antiphase boundary is called a "superdislocation", and the unit perfect dislocations of the disordered structure which terminate the antiphase boundary have been called "superpartial" dislocations, (149). This nomenclature will be used here.

2.7.2 The Relation of Superdislocations to Antiphase Boundary Energy

The equilibrium spacing of the superpartials composing a superdislocation is determined by an equilibrium between the energy of the stacking fault separating them and the energy associated with the strain field of two like dislocations on the same slip plane, (122). Alloys having a high antiphase boundary energy will contain closely spaced superpartials, while decreasing energy will allow the
separation to increase. The effect of this consideration on the slip mode of B2 structures has been investigated by Rachinger and Cottrell 1956 (150). It was found that in compounds where the ordering energy is large, e.g., $\beta'$-gold-zinc and $\beta'$-gold-cadmium (Section 2.3.3) the slip direction is $<100>$, while for compounds of lower ordering energy, e.g., $\beta'$-copper-zinc, the slip direction is $<111>$, i.e., that of the A2 structure. It was suggested that if the antiphase boundary energy is sufficiently high, the partials making up a superdislocation will be forced to coalesce, forming a unit perfect dislocation, Burgers vector $a<111>$. However, the $a<111>$ vector in the B2 structure is not the shortest possible, and dislocations with the vector $a<100>$ will be favoured. Such dislocations, being perfect, require no associated stacking fault in the superlattice.

The problem of the equilibrium separation of superpartials in the B2 lattice has been considered theoretically, using isotropic elastic theory, by Brown and Herman 1956 (151). They calculated the change in bonding energy on the formation of an antiphase boundary and the strain energy associated with a pair of like edge dislocations on the same slip plane, Cottrell 1949 (135). They estimated that the separation of superpartials in $\beta'$-copper-zinc is in the order of
15 atom spacings in the slip direction, taken to be \(<111>\).

Fig. 25 indicates the arrangement of the superpartials and
the stacking fault in the superdislocation of the B2 structure.
The angle \(\theta\) is the angle between Burgers vector and the
slip direction, and has the value \(90^\circ\) for a screw and \(0^\circ\)
for an edge dislocation.

Superdislocations in the \(\text{DO}_3\) structure have been
described by Marcinkowski and Brown 1961 (152). Their
analysis shows that the superdislocation will be composed of
four partial dislocations separated by different types of
stacking fault, Fig. 26. The Burgers vectors of the
superpartials and the antiphase boundary vectors are shown
in Fig. 3.

Marcinkowski 1963 (122) using Brown and Herman's
analysis 1956 (151) has estimated the spacing of partial
dislocations in the B2 lattice of \(\beta'\)-copper-zinc to be
\(88 \text{ Å}\) for edge partials and \(56 \text{ Å}\) for screws. Since this
analysis makes use of isotropic elastic theory, the results
are suspect in view of the elastic anisotropy of \(\beta'\)-copper-
zinc, (Section 2.4.1). The spacing of superpartials in
the imperfect B2 lattice of Fe\(_3\)Al is calculated to be infinite
(122), since the value of the antiphase boundary energy is
estimated to be zero. This is surprising in view of the
fact that the imperfect B2 ordered structure exists. However,
it is probable that antiphase boundary energy is small.

The spacing $r_1$ (Fig. 26) of screw superpartials in the $\text{DO}_3$ lattice was estimated to be $260 \ \text{"},$ and $r, 610 \ \text{"},$ (122). Transmission electron microscopy of thin films of Fe$_3$Al having the $\text{DO}_3$ structure revealed only imperfect dislocations having a Burgers vector $\frac{1}{2}a_0 \ <111>$, and not superdislocations as predicted by theory, (152). This was attributed to the low energy of antiphase boundaries in the $\text{DO}_3$ structure in iron-aluminium alloys, (152). In a later paper Marcinkowski and Fisher 1963 (153) questioned the validity of this conclusion, pointing out that the thinning process may allow edge dislocations to slip out of the foil, leaving a preponderance of screw orientations. Further, it is suggested that surface contamination may cause the creation of many $\frac{1}{2}a_0 \ <111>$ imperfect dislocations which would leave stacking fault trails. They concluded that indirect evidence from the plastic behaviour of alloys near the composition Fe$_3$Al supports the postulation of the existence of super-dislocations in these alloys.

Sainfort et al. 1963 (154) have reported the observation of dislocation pairs in an iron-40 at.% aluminium alloy, and state that the separation between superpartials decreases with increasing aluminium content, indicating an increase in the antiphase boundary energy with increasing aluminium content.
Superdislocations have not been identified unambiguously in \( \beta' \)-copper-zinc (124). However, resolution of the superpartials in this alloy may be difficult if the estimate of the spacing by Brown and Herman 1956 (151) is correct.

Transmission electron microscopy observations of superdislocations in ordered iron-50 at.% cobalt have been published (147). Paired dislocations with a spacing of about 125 Å were observed after low strains in an alloy in which the degree of order, \( S \), was 0.59. It was calculated that when \( S = 1 \), the superpartial spacing is reduced to about 50 Å. It is also concluded from the change of slip mode on ordering (cross slip is suppressed) that pairs of superpartials are responsible for deformation in the ordered structure, (147).

It was pointed out earlier in this section that owing to the change in slip direction in \( \beta' \)-gold-zinc, resulting from the high antiphase boundary energy, superdislocations will not exist in this structure.

The deformation modes of alloys examined in this work are listed in Table 6.

2.7.3 Interaction of Superdislocations with Antiphase Boundary

In his analysis of the deformation of superlattices,
Flinn 1960 (155) has shown that the interaction of a superdislocation with a thermally formed antiphase boundary will produce an increase in the area of antiphase boundary, Fig. 27. He suggested that at low temperature the nature of the deformation will be determined by such interactions, and that the work hardening characteristics should therefore be dependent on the domain size of the ordered structure.

Vidoz and Brown 1962 (149) have argued that this theory is inconsistent with experimental observations, and have proposed a work-hardening theory based on the formation and movement of jogs on superdislocations. The nature of these interactions depends on the geometry and the nature of the dislocations in the lattice. Fig. 28 shows schematically how a jog may be produced on a superdislocation. When the jogged dislocation moves it is forced to trail a double ribbon of antiphase boundary behind it. Other jogs may be produced on the superpartials themselves by dislocation interaction, and these may lead to more complicated faults when the jogged region is forced to move, (156).

2.7.4. The Plasticity of Ordered Alloys

2.7.4.1 The Flow Stress

It has been shown experimentally that the flow stress of ordered alloys is a function both of the degree of
order and of the antiphase domain boundary spacing. The inability to separate these two effects has caused some confusion in the interpretation of the role of order on the strength of alloys.

As originally suggested by Cottrell 1954 (157), the strength of ordered alloys reaches a maximum at some specific domain size. A maximum in strength has been found at about 40 Å for Cu$_3$Au by Ardley 1955 (158) and about 35 Å for Fe$_3$Al by Davies 1964 (32). Ardley 1955 (158) originally attributed this peak in strength to the fact that if domains are very large, little disorder is created by the passage of superdislocations, while if the domains are very small disorder may be removed from the lattice by the passage of dislocations. Hence at some intermediate domain size a strengthening peak occurs. Flinn 1960 (155) suggested that domain boundary energy rises with domain size producing an initial rise in the yield stress, but if the domain size is large, the chance of cutting a domain boundary is reduced, and the yield stress falls. This mechanism also gives a maximum at some intermediate domain size.

Stoloff and Davies 1963 (159) and Davies 1964 (32) have attributed the change in strength with domain size to a combination of strengthening produced by the creation of new antiphase boundaries with the strengthening due to the interaction of dislocations with short-range order, first
proposed by Fisher 1954 (160). It is known that both Cu\textsubscript{3}Au and Fe\textsubscript{3}Al order by an inhomogeneous process on isothermal annealing following quenching, (159), (32), so that domains of long-range order should be surrounded by disorder, or more probably short-range order, during domain growth. Short-range order may occur at room temperature following quenching, and its strengthening effect can be considerable, (147). Theories of short-range order strengthening have been reviewed by Cohen and Fine 1962 (161) and by Cahn 1965 (162).

No dependence of flow stress on annealing time after quenching was found by Brown 1959 (37) for \(\beta'\)-copper-zinc (47.9 at.% zinc) and it was concluded that no strengthening peak due to antiphase boundary spacing occurs in this alloy. However, it is possible that owing to the domain structure of this alloy (Section 2.5.2) the spacing of domains is larger than the critical value even after severe quenching.

Investigations into the effect of quenching temperature on yield stress measured at room temperature have shown that the yield stress reaches a maximum on quenching from just below \(T_c\), the critical ordering temperature. Such an effect has been observed by Brown 1959 (37) for \(\beta'\)-copper-zinc, by Stoloff and Davies 1964 (146), Davies 1964 (32) and Lawley et al. 1961 (163) for Fe\textsubscript{3}Al and for an equiatomic iron-cobalt alloy by Stoloff and Davies 1964 (146),
Marcinkowski and Chessin 1964 (147) and Marcinkowski 1964/65 (164).

Brown 1959 (37) found a maximum in the room temperature yield stress of 47.9 at.% zinc $\beta'$-copper-zinc after quenching from about 20°C below $T_c$. Although at this temperature the equilibrium degree of order, $S$, is about 0.55 little disorder is retained at room temperature, (Section 2.2.3). The peak in the flow stress was attributed to an excess of quenched-in vacancies annealing out at dislocations to form jogs. This conclusion was supported by a plot of the change of density on annealing at room temperature which showed a maximum for specimens quenched from just below $T_c$.

Lawley et al. 1961 (163) measured the flow stress as a function of quenching temperature for compositions in the range iron—24.8—27.8 at.% aluminium. Their results show that a maximum in the flow stress occurs at about $T_c$. However, for some experiments an oil quench was used and this may have allowed sufficient ordering to take place such that the flow stress peak was displaced to higher temperatures. One series of tests was made using a water quench, on an iron—25.5 at.% aluminium alloy, and these gave a flow stress peak above $T_c$. A tentative explanation of these results was given in terms of a mechanism of dislocation locking caused by local ordering in the stress fields of dislocations near $T_c$, originally proposed by Sumino 1958 (165), and of the Fisher 1954
short-range order strengthening mechanism.

The peak in room temperature flow stress of alloys near the composition Fe₃Al has been attributed by Stoloff and Davies 1964 (147) to a change in the type of dislocations producing the deformation. They suggest that as the degree of order increases on cooling from below Tₒ, on testing at room temperature unit perfect dislocations of the disordered lattice will be forced to leave a trail of disorder in their path, leading to an increase in the flow stress. As the degree of order increases further, the proportion of superdislocations increases, until, when the degree of order exceeds about 0.5, most of the deformation is produced by the movement of superdislocations. This theory also takes into account the effect of increasing short-range order as the temperature falls to Tₒ, since the room temperature flow stress/quench temperature curve starts to rise as Tₒ is approached from above.

Schematic flow stress/quenching temperature curves are shown in Fig. 29.

The flow stress of an equiatomic iron-cobalt alloy quenched from above Tₒ was found to be greater than that of the fully ordered alloy on testing at room temperature, Marcinkowski and Chessin 1964 (147). This difference was attributed to the retention of considerable short-range order at room temperature after quenching from above Tₒ. A peak in the room temperature flow stress/quench temperature curve just below
T_c was also observed. Similar results were obtained by Stoloff and Davies 1964 (146) on the equistatomic iron-cobalt alloy containing 2% vanadium, and accounted for by the change from unit perfect dislocations of the disordered lattice to superdislocations.

Although the theory that the flow stress peak in Fe_3Al is caused by a change from slip by unit perfect dislocations of the disordered lattice to slip by superdislocations is appealing and correlates well with experimental data, few superdislocations have been observed in the ordered structure. However, the evidence of Lawley et al. 1961 (163) and Davies 1964 (32) that strength also depends on domain size of the DO_3 structure points to the existence of superdislocations. It is difficult to envisage a mechanism whereby a peak in flow stress could occur if slip continued to take place by dislocations of the disordered lattice. The mechanism proposed by Brown 1959 (37) for the room temperature flow stress of β'–copper–zinc does not rely specifically on a change of the slip mode on ordering, but on the generation and movement of vacancies during the quench, and it is assumed that deformation takes place by the movement of superdislocations. In Fe_3Al and iron–50 at.% cobalt it is known that the equilibrium degree of DO_3 and B2 order respectively existing at any temperature can be "frozen in" by
quenching, so that it is unlikely that Brown's mechanism would apply to these alloys.

Flow stress experiments at temperature have been conducted by Ardley and Cottrell 1953 (135) on \( \beta' \)-copper-zinc, by Stoloff and Davies 1964 (146) on Fe\(_3\)Al, and on iron-cobalt alloys by Stoloff and Davies 1964 (146) and Marcinkowski and Chessin 1964 (147).

Ardley and Cottrell 1953 (135) found that the flow stress of \( \beta' \)-copper-zinc increased sharply below room temperature. This was interpreted as due to the difficulty of operating superdislocation sources at low temperature and to the locking of dislocations by an atmosphere of zinc atoms. This rise in flow stress with falling temperature was later attributed to the martensitic transformation, Brown 1960 (166). A peak in the at-temperature flow stress was also observed at about 200\(^\circ\)C by Ardley and Cottrell 1953 (135). Brown 1960 (166) rejected the earlier explanation connected with an anomaly in the elastic constants at 200\(^\circ\)C, and suggested that the peak was caused by an increase in the width of the antiphase boundary with increasing temperature. Although at this temperature long-range order is essentially perfect (33) moving superdislocations will nevertheless be forced to leave a trail of disorder and an increase in strength will be observed. At higher temperatures, approaching \( T_c \), it was
suggested that the degree of order falls, diffusion increases and a drop in the yield point with temperature results.

The observed peak in flow stress at temperature as \( T_c \) is approached has been explained by Stoloff and Davies 1964 (146) in terms of the change from single unit dislocations to superdislocations.

2.7.4.2 Work Hardening of Ordered Alloys

Differences occur between the work-hardening rates of ordered and disordered alloys, \( \text{Ni}_3\text{Fe} \) Vidoz and Brown 1962 (149), \( \text{Fe}_3\text{Al} \) Davies and Stoloff 1963 (167), iron-50 at.% cobalt Stoloff and Davies 1964 (146), Marcinkowski 1964/65 (164), and Marcinkowski and Chessin 1964 (147). The rate of strain hardening increases on ordering, except in the case of \( \text{Mg}_3\text{Cd} \) where new slip systems become operative, (168).

Marcinkowski and Chessin 1964 (147) showed that disordered iron-50 at.% cobalt exhibits profuse cross slip at all strains, and that the flow stress is strongly temperature dependent. They concluded that thermally activated cross slip is the controlling mechanism of deformation at low temperatures. The ordered alloys showed three stages of deformation, similar to those exhibited by face-centred cubic metals. During the first stage (designated Stage I) the
flow stress is nearly independent of strain. In Stage II the flow stress increases rapidly with strain and only straight slip traces were observed. Stage III produced stepped slip lines on the surface and the flow stress was nearly independent of strain. It was concluded that Stage II was a result of the non-conservative movement of jogs on screw dislocations and the absence of cross slip, and that Stage III was due to the ability of super-partial dislocations to cross slip independently although producing disorder in their path. These results were supported by the direct observation of superdislocations in Stage II, and mainly single dislocations in Stage III.

Stoloff and Davies 1964 (146) and Davies and Stoloff 1963 (167) have suggested that the rate of work-hardening may be correlated directly with the number of available slip systems, and deformation modes. If cross slip is suppressed on ordering, the rate of work-hardening should become greater, as is found experimentally, (146), (147).

Vidoz and Brown 1962 (149) proposed a theory of work-hardening for ordered alloys on the basis of jog formation on superdislocations and the creation of additional antiphase boundary as a result of the movement of the jogged dislocation. They showed that this mechanism should be nearly
independent of temperature at temperatures below $T_c$.
The rapid work-hardening stage of equiatomic iron-cobalt
(Stage II) is found to be almost independent of temperature,
(147).

The difficulty of cross slip in superlattices
was also discussed by Vidoz and Brown 1962 (149) with
reference to structures based on the face-centred cubic lattice.
They suggested that if cross slip originates from jogs on
super-partials cross slip of the whole superdislocation will
be very difficult, because jogs on the superpartials will lie
on different slip planes, generating antiphase boundary if
cross slip continues. If cross slip of the leading super-
partial takes place by a mechanism of constriction and
re-extension on the cross slip plane as described by Seeger 1957
(169) cross slip of both superpartials can occur only if the
second follows exactly the path of the first through the lattice.
They concluded that if cross slip takes place by the second
process it need not necessarily be difficult in ordered alloys.

The difficulty of cross slip in the ordered
equiatomic iron-cobalt alloy has been discussed by Marcinkowski
and Chessin 1964 (147). They point out that the results of
Keh and Weissman 1963 (130) indicate that cross slip in the
A2 lattice does not require dislocation pile-up as envisaged
for the Al lattice by Seeger 1957 (169). However, because
of the creation of new antiphase boundary cross slip in
the ordered structure will be difficult at low stresses (170).
During Stage III work-hardening of ordered iron-50 at.%
cobalt the stress level agrees with the calculated value
necessary for the creation of antiphase boundary, and
dislocations are shown to be of the type \( \frac{1}{2}a <111> \) which
cross slip singly, trailing a ribbon of antiphase boundary,
(147).

Davies and Stoloff 1965 (171) have suggested
another mechanism whereby cross slip can occur in an ordered
structure. Discussing the L1_2 (1) compound Ni_3Al, they
suggest that since the ordering energy is high, the
superpartials will be about 30 Å apart, and should be able
to move in a manner similar to an extended dislocation in the
Al structure (133), capable of cross slip. They accounted
for the widely spaced and wavy slip traces of ordered
Ni_3Al by this means. Such slip patterns are unusual for the
L1_2 structure, (172). Cu_3Au shows fine closely-spaced
slip traces, and superpartials are more widely spaced, (122),
apparently preventing cross slip of superdislocations in
this alloy.

Davies and Stoloff 1964 (146) have plotted
the relationship of superpartial spacing with degree of order
for Fe_3Al and the equiatomic iron-cobalt-2% vanadium alloy,
Fig. 30. They have suggested that separation of the superpartials producing independent cross slip becomes possible when the width of the superdislocation is in the order of 1000 Å.

Marcinkowski and Fisher 1963 (153) concluded from a theoretical study of deformation in metallic B2 structures, having a <111> slip direction, that slip will tend to be confined to {110} planes as the antiphase boundary energy is increased, since these planes have the smallest value of the antiphase boundary energy per unit area.

2.8 Grain Boundaries in Metals

2.8.1 The Structure and Energy of Grain Boundaries

A grain boundary in a metal may be defined as the region separating two crystals that differ either in crystallographic orientation, composition, or dimensions of the crystal lattice, (173). Grain boundaries and the properties associated with them have been fully reviewed by McLean 1957 (173). Theories of the structure of grain boundaries have been considered in the light of direct observation of the atomic arrangement near boundaries in refractory metals by field ion microscopy by Brandon et al. 1964 (174).

A general grain boundary has five degrees of
freedom (175), three of which describe the relative orientation of the crystals with respect to each other (in terms of two angles of tilt about axes at right angles to each other in the boundary, and a twist about an axis normal to the boundary) and the remaining two describe the orientations of the boundary with respect to the crystals.

Grain boundaries may be classified according to the degree and nature of the misorientation across the boundary:

a) low angle boundaries,

b) high angle boundaries

c) special boundaries.

a) Low angle boundaries are those for which the degree of misorientation is small and which can be described by a two dimensional network of dislocations, (174). A vertical array of edge dislocations of like sign produces a lattice tilt about the axis of the dislocations, and a cross grid of screw dislocations lying in the boundary gives a rotation about the axis normal to the boundary, (173).

b) High angle boundaries. The degree of misorientation across a boundary composed of an array of dislocations will increase as the dislocation density increases. In a high angle planar boundary atoms may be regarded as occupying sites of lowest energy representing a compromise between
the lattice sites of the two crystals.

c) Special orientations. As the angle of misorientation between two crystals increases from zero, orientations occur at which some sites are common to both crystals, (176). These "coincidence site" orientations result from the rotation of the grains about a common axis normal to a close-packed plane, (31). If the boundary between two crystals having a coincident site relationship follows the planes on which maximum density of such sites occurs the mismatch at the boundary will be small, and the energy will be a minimum, (174). Other special boundaries will occur when the crystals are twin related, (31).

If a boundary is composed of a vertical array of dislocations, having a period \( n \) atom spacings in length, the strain field of the array has been shown to extend a distance about \( \frac{1}{2}n \) on either side of the boundary, (173). The width of the boundary may be taken to be \( n \), implying that the width of a low-angle boundary is greater than that of a high angle boundary.

It has been shown (145) that the energy \( E \) of a simple tilt boundary is given by:

\[
E = K \theta (A - \ln \theta),
\]

where \( K \) is a constant depending on the material, \( \theta \) is the angle of misorientation and \( A \) is a constant proportional
to the energy of the core of dislocations composing the boundary. Fig. 31 shows the relative energy of a grain boundary in the simple cubic structure (expressed as $\sigma/\sigma_0 = E/K$) as a function of the angular misorientation, (175). The cusps occur at coincident site orientations. It can be seen that the energy of the boundary in general increases with $\theta$ to a wide maximum, and then falls to zero as the misorientation decreases.

Brandon et al. 1964 (174) have concluded from their experimental observations that the atoms near a low angle boundary possess higher energy than atoms remote from the boundary, shown by preferential evaporation of atoms from a strip on either side of the boundary. High angle boundaries are observed to be about 2 atoms in width, and a coincident site boundary is reported the width of which was in the order of one atom diameter. From these observations a model has been proposed (174) for high angle boundaries, based on the fact that such a boundary can have minimum energy if it is composed of small regions having a maximum density of coincident sites in the boundary, linked together by regions of bad fit.

The theory proposed by Wilkins 1962 (127), to account for the localisation of fatigue damage next to some grain boundaries in $\beta'$-copper-zinc, that a region about 10\mu wide composed of disordered or partially disordered
material exists round all grains in the equilibrium state appears to have no justification in view of the above considerations. No indication was given (127) as to the source of energy which would be necessary to maintain a layer about $3.10^4$ atoms wide in an incompletely ordered state.

2.8.2. The Effect of Grain Boundaries on Deformation

The plastic behaviour of polycrystalline aggregates has been reviewed by Nabarro 1950 (177) and by Dorn and Mote 1963 (178), the latter considering theoretical and experimental work on the deformation of face-centred cubic metals only. However, there is no reason why conclusions regarding the effect of grain boundaries on the deformation behaviour of face-centred cubic metals cannot be applied in a general way to the deformation of body-centred cubic or other structures.

Nabarro 1950 (177) drew attention to the importance of the inhomogeneity of the slip process. It was suggested that a strip next to the boundary in a deformed specimen, approximately equal in width to the spacing of the slip bands, would exist, in which high elastic stresses would be supported in order that coherency across the boundary could be maintained. The magnitude of these stresses was
estimated to be in the order of $\mu/30$, the theoretical yield strength. The observed region of disturbance at grain boundaries, reported as about $10^{-2}$ cm. wide (177), was explained as a region of high dislocation density produced by the pile-up of dislocations at the end of slip bands arrested by the region of high stress.

Transmission electron microscopy has shown that grain boundaries are also active sources of dislocations during deformation, as well as barriers to dislocation motion. Activity of grain boundary sources has been shown in stainless steel (179) and ordered Fe$_3$Al (152).

According to Elbaum 1960 (180) grain boundaries contribute no "strength" to a polycrystalline aggregate, but act by influencing the mechanism of deformation in adjoining grains. A series of aluminium single, bi-, tri-, and quadri-crystals, grown so that planar grain boundaries extended completely along the specimen, were deformed in tension. Mutual orientations within the multi-crystal specimens were arranged such that slip could propagate without difficulty across boundaries in some specimens (compatible multicrystals) while other specimens were composed of crystals having incompatible orientations. It was found that slip began at the same stress in all specimens, but that work-hardening was
greatest in the incompatible quadriocrystals. The compatible crystals showed no especially severe deformation next to the grain boundaries, while incompatible specimens did.

Livingston and Chalmers 1957 (181) investigated the tensile deformation of a number of isoaxial compatible and incompatible aluminium bicrystals, having boundaries along the specimen length. The incompatible crystals showed a total of at least four active slip systems, although some of these were localised to a region less than 1 mm. wide at the boundary.

These experiments indicate that grain boundaries do not affect the yield stress, but increase the rate of work-hardening by increasing the number of active slip systems. The region where multiple slip occurs is limited to a strip near the grain boundary, and the slip systems that operate in this region are usually, but not always, those also found in single crystals, (205) (178).

Head 1960 (182) has considered the effect of elastic anisotropy on the queueing of dislocations at the boundary of a bicrystal. He has shown that a dislocation at a distance $x$ from the boundary, situated in the crystal of lower shear modulus, experiences a repulsion from the boundary which can be attributed to an image dislocation of like sign
situated a distance \(-x\) from the boundary. The magnitude of the repulsion is dependent on \(x\) and the degree of elastic anisotropy. It seems reasonable to conclude that the converse of this arrangement is also valid, namely that a dislocation in the crystal of higher shear modulus experiences an attraction towards the boundary from an image dislocation situated in the crystal of lower shear modulus.

However, in a later analysis Head 1965 (183) has calculated the dislocation image force across boundaries in anisotropic cubic polycrystals for dislocations of \(<100>\), \(<110>\) and \(<111>\) Burgers vector. It is shown that when the elastic anisotropy \(C/C'\) is greater than unity, dislocations having a \(<100>\) Burgers vector experience a negative image force across a boundary composed of crystals of any mutual orientation, while for a \(<111>\) Burgers vector the image force is always positive. That is, \(<100>\) Burgers vector dislocations never experience a repulsive force due to the misorientation across a boundary, while dislocations having a \(<111>\) Burgers vector are always repelled from the boundary. This phenomenon is independent of cubic crystal structure, but increases with increasing elastic anisotropy, and with the crystal misorientation across the boundary.
2.8.3 Diffusion and Segregation at Grain Boundaries

Since grain boundaries constitute sheets of more or less severe atomic misfit, it is to be expected that diffusion along these paths should be greater than diffusion through the lattice. In a polycrystal, however, the relative distances through which diffusing atoms are able to move through the bulk and along grain boundaries from a free surface do not differ greatly, since atoms diffusing along boundaries are also able to diffuse laterally into the lattice (173). It has been shown that for diffusion times in the order of 100 hrs. the ratio of the grain boundary diffusion coefficient to the lattice diffusion coefficient must be in the order of $10^5$ in order that penetration should be twice as far along grain boundaries as through the lattice, (173).

The subject of segregation at grain boundaries has recently been extensively reviewed by Westbrook 1964 (184), who presents evidence to show that segregation at grain boundaries is a common effect, resulting in hardening detectable by careful microhardness measurements in a narrow strip next to the grain boundary. The intergranular brittleness of many intermetallic compounds is attributed to this phenomenon.

Specifically embrittlement of the compounds AgMg, NiAl and NiCa following heat treatment in an atmosphere containing
oxygen has been shown to occur, (185). If heat treatment is followed by a rapid quench from above a critical temperature, no grain boundary hardening can be detected. It has been suggested that oxygen atoms which have diffused into the compound exist in substitutional positions at high temperatures, but on moderately slow cooling an increasing proportion are forced to take up interstitial positions as vacancies anneal out at grain boundaries or free surfaces, (186). Occupation of interstitial positions produces lattice strains resulting in hardening, which is greater at the boundaries and free surfaces because of the effectiveness of these regions as vacancy sinks.

In view of arguments presented in Section 2.8.1 concerning atomic misfit at grain boundaries, it is likely that strain energy in these regions could be minimised by the segregation of larger or smaller atoms, as appropriate. However, it is probable that in any boundary, regions of both hydrostatic tensile and compressive stress exist on an atomic scale, so that the segregation of any one species of atom of a binary alloy uniquely to the boundary is unlikely. Since the width of grain boundaries is small, segregation for this reason would not in any case provide a region of the dimensions found experimentally, (184). Thermodynamic arguments for grain boundary segregation require only a monatomically thick grain boundary layer, if the
internal surface energy of the crystals meeting in a boundary is lowered by segregation, (184).

Microhardness techniques have shown an increase of about 6% in hardness at the grain boundary with respect to regions remote from the boundary, but this difference was not attributed with certainty to the grain boundary structure, (187). The effect of grain boundaries on deformation is to increase the number of slip systems operative, (Section 2.8.2).

It is doubtful whether a grain boundary will have much effect on the deformation produced by an indentor, which probably gives rise to multiple slip itself, except if the material tested exhibits marked plastic or elastic anisotropy. Increases of up to 60% in microhardness in the region of grain boundaries of single phase materials have been reported, (184). It is not conceivable that this increase is attributable to the influence of the boundary on the slip distribution alone.

2.9 Fracture

2.9.1 Cleavage Fracture

In this section brittle transgranular failure propagating on one or combinations of low-index crystallographic planes will be discussed in relation to fracture sources
and the conditions controlling the path of crack propagation.

2.9.1.1 Sources of Cleavage Fracture

It is now generally agreed, Low 1963 (188), that the initiation of cleavage failure in metals requires some plastic deformation before a crack can form, and all models postulate some interaction between dislocations, slip bands or twins, either with each other or with an obstacle, such that a crack may form. Mechanisms may be summarised as follows:

a) Crack nucleation at a blocked slip band, Zener 1948 (108).

b) Crack nucleation as a result of sudden localised shear forces before stresses can be relieved by plastic deformation, Kramer and Maddin 1952 (136).

c) Crack nucleation at the end of a piled-up group of edge dislocations, Mott 1953 (189).

d) Crack nucleation as a result of the stress concentration associated with the end of a dislocation wall produced by slip, Stroh 1958 (190).

e) Crack nucleation as a result of the coalescence of dislocations, Cottrell 1958 (191).

f) Crack nucleation as a result of stress concentration produced by the intersection of twins, Hull 1960 (192).
The mechanism originally proposed by Zener 1948 (108) of stress relaxation along one of a group of intersecting grain boundaries leading to a high tensile stress concentration and the nucleation of a crack at the junction has been generalised to cover the case of a slip band held up at a grain boundary. Such stress concentrations may either produce a crack in the boundary, or in a plane of weakness within one of the crystals forming the boundary. The nucleation of cracks as a result of slip band/grain boundary interaction has been observed in magnesium oxide and found to be dependent on the misorientation of the crystals composing the boundary, (193).

The mechanism of a stress concentration resulting from a sudden localised shear leading to the formation of a crack requires the existence of a yield point and a delay time for slip. The existence of sharp yield points in body-centred cubic metals is well known. Yield points have also been observed in ordered iron-50 at.% cobalt alloys (147) and in β'-copper-zinc, (135).

Kramer and Maddin 1952 (136) investigated the effect of temperature on the delay time for slip, after the application of a load, in aluminium, α-copper-zinc and β'-copper-zinc. They found no effect in the face-centred cubic structures but a strong temperature dependence in β'-copper-zinc (47.3 at.% zinc), such that the delay time for slip at a given value of the
resolved shear stress increased sharply down to $-196^\circ C$, Fig. 32. They concluded that brittle fracture during the loading of a specimen must ensue if the fracture stress is exceeded before the delay time for slip.

Mechanisms such as that proposed by Mott 1953 (189) based on the concept of large pile-ups of dislocations are not now thought to be operative in real crystals since the model requires a barrier capable of withstanding very high shear stresses, (187). Further, transmission electron microscopy has not revealed pile-ups of a sufficient size to cause fracture (130), particularly in crystals in which cross slip is possible.

The mechanism proposed by Stroh 1958 (190) for the formation of a crack at the end of a wall of dislocations has been observed by Gilman 1954 (194) in zinc bicrystals, in which the slip plane corresponds with the cleavage plane.

The mechanism proposed by Cottrell 1958 (191) is based on the coalescence of dislocations moving on the (101) slip plane of the A2 structure with those on the (101) plane leading to the formation of a pure edge dislocation in the (100) plane, the observed cleavage plane:

$$\frac{1}{4}a[111] + \frac{1}{2}a[\overline{1}11] = a[001]$$

Elastic energy is reduced by this reaction, and the incipient crack may be widened by the addition of more dislocations from
the slip planes. The analysis of Stroh 1959 (195) for body-centred cubic metals shows however that the \( a[001] \) dislocation will tend to dissociate before a propagating crack can be nucleated. However, such a mechanism has been shown to be operative in magnesium oxide, and was attributed to the pile-up of dislocations, (196).

Hull 1960 (192) investigated the conditions under which crack nucleation at the plane of intersection of twins in silicon iron occurred. It was found that cracks were nucleated only at those twin intersections lying in the cleavage plane normal to the axis of tension. Although this result is empirically reasonable, the exact explanation of the nucleation of the crack is not known. Hull 1960 (192) suggested that the cleavage plane may be weakened by a mechanism of dislocation combination at the common interface of the twins, while Low 1963 (188) has suggested a stress concentration mechanism resulting from the twinning shears.

2.9.1.2 The Propagation of Cleavage Cracks

The basic concept governing considerations of brittle crack propagation, due to Griffith 1920 (197), is that a crack will grow if the energy released due to the relief of elastic stresses at the crack tip is greater than the energy of the
new surfaces formed. This is true only if no work is done by plastic deformation at the crack tip.

Orowan 1949 (198) has pointed out that this latter term may be very significant in metals. In this case the original Griffith equation becomes:

\[ \sigma^2 = 2Ep/\pi c \]

for crack propagation, where \( \sigma \) is the fracture stress, \( E \) the Young's modulus, \( c \) the half-length of the crack and \( p \) represents the work of plastic deformation per unit area of new crack surface. Mott 1948 (199) has also emphasised that the kinetic energy of a moving crack also accounts for an additional energy term in the fracture equation, serving to increase the propagation stress \( \sigma \). Theoretical and experimental work on the plastic deformation associated with a propagating crack has been reviewed by Tetelman 1963 (200), (201). In particular the arrest and further propagation of cleavage cracks is considered.

The concept of the "cleavability" of crystals has been discussed by Gilman 1959 (202), who considered the factors determining the choice of cleavage plane in particular structures. The possibility that a mechanical criterion governs the choice of cleavage plane was explored starting from the classical Griffith criterion for crack propagation in terms of elastic modulus and surface energy. This concept appears to be only partially
successful in estimating the cleavage plane of crystals, including metals. Dislocation density and mobility were thought to be fundamental in determining the resistance of crystals to cleavage. That is, if slip occurs quickly and easily, stresses at a crack tip may be relieved and propagation in a brittle manner may not be possible.

An increase in the yield stress of α-iron, and a corresponding fall in values of the reduction in area with decreasing temperature as the ductile-brittle transition is approached have been noted, (203). This type of phenomenon has been linked with brittle fracture since the movement of dislocations is difficult at low temperatures in the body-centred cubic structure, (188). A similar rise in yield stress with falling temperature below 0°C has been noted for β' -copper-zinc (48.0 at.% zinc), (135).

Johnston, Davies and Stoloff 1964 (204) have argued that a rise in yield stress cannot in itself be the primary cause of brittleness in body-centred cubic metals. They have shown that the temperature of the ductile-brittle transition may be raised from about -100°C to +460°C on ordering an equiatomic iron-cobalt alloy containing 2% vanadium, even though the yield stress of the ordered material is lower than that of the disordered material, (Section 2.7.4.1). It was suggested that the
macroscopic slip mode and the ability to relieve local stress concentrations by cross-slip are the primary factors in the fracture behaviour of single phase solids. They point out that even when the equiatomic iron-cobalt alloy is ordered, Von Mises' criterion 1928 (205), that five independent slip systems must be available to allow a general strain in a polycrystal, is satisfied. In this case the ductile-brittle transition is a consequence of the temperature dependence of cross slip.

A similar conclusion has been reached by Stoloff et al. 1965 (137) concerning the ductile-brittle transition of iron, iron-vanadium and iron-cobalt alloys, containing up to 25% solute. The brittleness was attributed to the change from wavy to planar slip with decreasing temperature.

2.9.1.3 The Choice of Cleavage Plane in Body-Centred Cubic Crystals

Gilman 1963 (206) has discussed the cleavability of crystals in terms of the tendency of a crack to propagate parallel with a particular crystallographic plane without deviation, and also the question of the choice of cleavage plane in the A2 structure in terms of the energy density of broken bonds across the \{100\} and \{110\} planes. It was pointed out that a plot of surface energy of a crystal face with respect to some
angle of misorientation will give a series of low-energy cusps corresponding with low-index planes. It is to be expected that cleavage cracks will follow a path of low surface energy. Since the cleavage plane of the A2 structure transition metals is either \{100\} (tungsten, α-iron, molybdenum and niobium) or \{110\} (impure tantalum) the relative energy density of broken bonds across these planes in the A2 structure was investigated. Fig. 33 shows the arrangement of nearest neighbour bonds across the \{100\} and \{110\} faces. Since the cohesive strength of the transition metals is known to be high, (61) a coordination number of 14 was considered to be appropriate, including both first and second nearest neighbour bonds.

It was concluded that if the energy of a second nearest neighbour bond, Fig. 1 (bond II) is greater than 64% of that of the nearest neighbour bond, Fig. 1 (bond I), the broken bond energy density will be lowest on the \{100\} faces and cleavage will be favoured on this path. The details of this calculation will be considered and extended in the discussion (Section 5.5). The exclusion of third nearest neighbour bonds, Fig. 1 (bond III) may not be justified if the interaction energy is about one half that for second nearest neighbours, suggested for Fe₃Al by Wojciechowski 1959 (207).
2.9.2 Intergranular Fracture

Intergranular fracture at high temperatures is not uncommon, particularly under conditions of slow straining, (188), although Harper 1956/57 (208) suggested that fast straining in order to produce stress concentrations at the grain boundaries is essential for producing intergranular fracture at high temperature in β'-copper-zinc.

Intergranular brittle failure at low temperatures, i.e., room temperature and below, has been attributed to impurities associated with the region near grain boundaries, (209), (188), (56). McLean 1961 (209) considered mechanisms of grain boundary crack nucleation and propagation. He pointed out that according to the Griffith fracture criterion, a propagating crack will follow that path having the lowest surface energy. If the grain boundary region is enriched in some component by segregation, it is possible that the internal interface constituted by the grain boundary will possess a reduced surface energy and intergranular fracture will be favoured. If the grain boundary is weak relative to the grain itself, any mechanism involving stress concentration at the grain boundary will be capable of producing intergranular fracture. In this respect intergranular fracture need not differ in the initiation stage from transgranular fracture initiated by a process of stress
The intergranular fracture of an equiatomic iron-cobalt alloy in the fully ordered state reported by Marcinkowski and Chessin 1964 (147) may have been the result of intergranular embrittlement by impurities, but was attributed to micro-crack formation at high localised stress concentrations at the grain boundary resulting from the difficulty of cross slip. However, once microcracks are formed propagation will follow on the most energetically favourable path.

Chen 1964 (35) reported that cobalt-iron alloys near the equiatomic composition may be completely embrittled by traces of hydrogen or oxygen, leading to intergranular fracture. The adsorption of gas atoms at the grain boundaries was considered to be responsible.

Meyers et al. 1965 (210) suggested that the onset of cleavage fracture in body-centred cubic metals may be controlled by solid solution hardening at the grain boundaries limiting propagation of slip from one grain to the next, resulting in conditions favourable for cleavage. It is clear that inter- and transgranular brittle failure are closely related.
2.10. Fatigue of Crystals

Fracture may be produced in many crystalline solids by the repeated application of a stress below that required to fracture the material in a tensile test. The number of cycles to failure is related to the maximum value and range of the applied stress. All theories of such fatigue damage are based on the assumption that repeated dislocation movement takes place on the same or closely related slip planes.

The events leading to the fracture of a solid by fatigue may be conveniently divided into three stages:

1) the formation of slip damage
2) crack nucleation
3) crack propagation and final failure.

No great significance may be laid on the division of the process in this way. Observations of fatigue damage indicate that the process is continuous and all three stages may be taking place at various points in a specimen at the same time.

Wood and co-workers 1964 (211) have divided the curve of stress against number of cycles to fracture into three regions. The first, up to about $10^5$ cycles to failure is termed the H region and relates to high stress failures. The second, the F region, is the region of low amplitude fatigue failure. The third, the S region, is the safe
region concerned with lives beyond about $10^8$ cycles. Only damage in the F and S regions will be considered.

2.10.1 The Formation of Slip Damage

The typical features of progressive fatigue damage were first described for α-iron by Ewing and Humfrey 1903 (212). Slip bands formed early during the test and became more intense and broader as cycling continued. Cracks propagated from these regions of intense slip. The density of bands was found to be greater at higher stresses and cracks appeared earlier.

Investigations of a number of crystalline solids have established that the appearance of extensive slip damage during fatigue is related to the ease of cross slip of screw dislocations. McEvily and Machlin 1959 (213) have shown that lithium fluoride and sodium chloride which are unable to cross slip do not exhibit progressive fatigue damage, while silver chloride and a crystalline solid solution of thallium bromide and iodide, which possesses the B2 structure, both of which cross slip easily, exhibit progressive fatigue damage. McGrath and Thurston 1963 (214) have demonstrated that a close correlation exists between ease of cross slip and fatigue life of α-copper-zinc alloys; as the stacking fault energy decreased with increasing solute content the
fatigue resistance increased. Similarly Boettner and McEvily 1965 (215) have shown that extensive slip damage during fatigue is reduced as silicon is added to α-iron, and the ease of cross slip reduced. Alden 1963 (216) has shown that zinc, in which cross slip is difficult, hardens to high stress levels during fatigue stressing, but cadmium, which cross slips easily, does not. A high stress level for recovery during stressing is known to be associated with a high stress level for glide on the cross slip system, (138). The process of dynamic recovery has been specifically attributed to the mutual annihilation of unlike screw dislocations approaching each other on non-parallel slip planes and coalescing by cross slip, (217). Furthermore, the temperature dependence of the fatigue limit of face centred cubic metals, the stress below which fracture will not occur after a large number of stress cycles, has been suggested to be the same as that of the stress for the start of Stage III of the work-hardening curve, (217).

Studies of hardening during fatigue have shown that when cross slip is not easy the stress necessary to maintain a given strain amplitude reaches a constant value slowly, (218). The nature of this hardening has been investigated for copper by Broom and Ham 1959 (219) who showed that partially fatigued single crystals showed a yield point when
tested in tension, while the yield stress showed a strong temperature dependence. They concluded that point defects were responsible for the yield point by forming jogs on dislocations, and also by aggregation to form collapsed vacancy discs or clusters. These deductions have subsequently been confirmed by direct observation of dislocation arrangements in fatigued structures by transmission electron microscopy. Segall and Partridge 1959 (220) reported a high density of dislocation loops in fatigued aluminium and attributed this to the generation and condensation of vacancies during the fatigue process. In a later study of copper, nickel, gold and stainless steel, Segall et al. 1961 (221) suggested that loops were also produced by screw dislocations "pinching off" sessile jogs. Dislocation loops associated with heavily jogged screw dislocations have also been observed in α-iron, (222). Segall 1963 (223) was not able to find a direct correlation between the distribution of fatigue slip damage on the surface and the underlying dislocation arrangement. However, later studies of copper, Laufer and Roberts 1964 (224), and α-iron, Klesnil and Lukas 1965 (225) have shown a direct correlation, but only in films taken from within 40μ of the surface.

Forsyth 1953 (226) first reported observations of a special kind of surface roughening as a result
of fatigue deformation in which thin sheets of material were pushed up from slip bands, sometimes within a few cycles. These were termed "extrusions", and have since been observed in a large number of different materials. Wood 1959 (218) and Wood et al. 1964 (211) have used a taper-sectioning technique to produce virtual optical magnifications up to 30,000 times, and have observed intrusions or fissures related to extrusions and surface roughening in α-iron, α-copper-zinc and copper. These fissures were thought to be more important than extrusions in the process of crack formation because of the high stress concentration at the base of the fissure.

It was pointed out that extrusions can arise in a number of ways, including the exudation of metal debris and oxide from small existing cracks, as well as by mechanisms relying on dislocation interactions, (Section 2.10.2), (227). Extrusions and intrusions have been observed over a wide range of temperature. Cottrell and Hull 1957 (228) observed extrusions on copper fatigued at 200K and at room temperature, while intrusions have been reported in nickel fatigued in vacuum at temperatures up to 600°C, (229). The distinction between thin sheet-like extrusions, such as those reported by Forsyth 1953 (226) and surface roughening, also termed extrusion, observed by Boettner and McEvily 1965 (215) in iron-silicon alloys, is not clear. But surface roughening
does seem to be necessary for fatigue failure to take place. May 1960 (230) proposed that surface roughness itself may provide sufficient stress concentration at the base of fine notches to initiate cracks, without regard to special dislocation mechanisms. It was suggested that slip may take place in a random manner on closely adjoining planes, so that the original specimen surface is displaced in the slip direction in a manner determined by the random walk. May 1960 (230) calculated that stress concentrations sufficient to form cracks may be achieved after about $\frac{1}{2}$% of the fatigue life. Such a proposal does not indicate the factors which limit slip damage to intense slip bands on the surface nor can it explain why fatigue damage does not occur in those metals in which cross slip is difficult, nor how extrusions appear during the course of a few cycles, (226).

The problem of the localised distribution of fatigue slip damage has been investigated by Broom and Ham 1959 (219). It was found that when single crystals of copper were extended in tension following fatigue, deformation began in the intense slip bands, while the material between these bands yielded at a stress higher than that applied during fatigue. They concluded that hardening was due to the distribution of point defects. Roberts and Greenough 1965 (231) examined this problem using polycrystalline copper fatigued in push-pull. They found that fatigue striations reformed in the same regions
eleotropolishing. It was suggested that a large number of related dislocation sources was responsible for the development of fatigue slip striations. Many of these sources must be situated more than 60 µ under the surface of the specimen if slip striations are to be re-established after electropolishing. Alden and Backofen 1961 (232) found that the beginning of slip band intensification was coincident with the start of saturation of strain hardening. It is possible that intense slip striations represent zones where stresses are initially higher and on which intensification starts for this reason. Segall 1963 (223) reviewing work on the dislocation distribution caused by fatigue deformation concluded that slip spreads over the whole specimen very early in the fatigue life giving a uniform distribution of dislocation loops. Intense slip striations represent regions in which vacancies and dislocation loops are swept up by moving dislocations. Such a process would lead to the softening observed and correlate with the observation that intense slip striations are formed at the start of hardening saturation, (232). It is surprising that a direct correlation between intense slip striations and dislocation distribution has not been found at depths greater than about 4.0 µ. However, further away from the surface the region associated with the intense slip bands may become less well
defined and difficulties with respect to location in the electron microscope may occur because of the orientation of the bands relative to the specimen surface.

2.10.2 Fatigue Crack Nucleation

Careful studies by taper-sectioning techniques, Wood et al. 1964 (211), Boettner and McEvily 1965 (215) and by electron microscopy, Klesnil and Lukas 1965 (225) have shown that fatigue cracks are initiated at the edge of extruded regions and intense slip striations and from the bottom of intrusions or fissures.

Three types of mechanism have been suggested as responsible for crack formation:

1) Mechanical notching produced by random slip movements leading to an increase in local stresses, until fracture spreads from the base of the notch.

2) Vacancy condensation forming fissures associated with the regions of intense slip.

3) Dislocation mechanisms involving specific interactions which give rise to cracks directly or notches from which cracks can propagate.

Brittle crystals may fracture during fatigue stressing, but do not do so by the fatigue process, involving the slow nucleation and propagation of cracks. Failure is sudden, and
1) The process of extrusion and intrusion formation investigated by May 1960 (230) has been discussed. Investigations by Wood 1959 (218) and Wood et al. 1964 (211) on α-iron, copper and α-copper-zinc indicate similar conclusions to account for the initiation of fatigue cracks. Fissures formed in association with slip damage spread by a continuation of the slip process at the base, producing a narrow highly distorted sheet of material. A surface notch effect has also been observed in iron-2.9 wt.% silicon, (215). Cracks were observed to be initiated at the re-entrant angles of ridges on the surface.

2) Vacancy condensation has been considered as a major factor in the formation of fatigue cracks, Feltham 1961 (217). The heat evolved in the annihilation interactions of screw dislocations by cross slip at the start of work-hardening saturation was considered to provide energy for the continuation of such interactions in localised regions. Vacancies generated during this process were then thought to cluster and collapse into micro-cracks within the fatigue slip striations. The quantitative nature of this model has been criticised, (233). It is also considered unlikely on theoretical grounds that vacancies will condense to form crack nuclei, (188), and vacancy clustering can play no part in the development of fatigue cracks at 4.2°K, (234).
Clustering at higher temperatures cannot be excluded, however, and recently Klesnil and Lukas 1965 (225) have included the condensation of vacancies in possible mechanisms for the formation of micro-cracks 1–2 μm long at the boundary of regions of very high dislocation density observed in α-iron.

3) Dislocation interaction mechanisms for the formation of extrusions, intrusions, and cracks may be divided into those not requiring cross slip Fujita 1954 (235) and Cottrell and Hull 1957 (228), and those requiring cross slip, Mott 1958 (236), McEvily and Machlin 1959 (213), Kennedy 1961 (237) and Boettner and McEvily 1965 (215).

Fujita 1954 (235) suggested that unlike edge dislocations approaching each other on parallel planes less than about 10 Å apart experience an attractive force, causing them to align vertically, giving rise to a void between them. This void is then able to grow by the addition of more edge dislocations of the same sign. No observations of this mechanism have been reported.

The mechanism postulated by Cottrell and Hull 1957 (228) requires the alternate activation of two dislocation sources whose slip planes cross. Such co-ordinated action near the surface was thought to be able to produce extrusions and intrusions at the same time in a related manner. The experiments of McEvily and Machlin 1959 (213) showed that this mechanism
did not operate to produce either extrusions or intrusions in sodium chloride or lithium fluoride, even when favourable orientations were chosen.

The cross slip mechanism of Mott 1958 (236) requires the movement of a screw dislocation around a closed loop in the surface under the influence of the alternating stress field. No anchoring dislocation within the crystal was required when the dislocation terminated in a void, produced in a manner suggested by Fujita 1954 (235). As the dislocation completes each cycle, a tongue of metal is extruded from the surface, leaving a growing void beneath it. It was suggested that a propagating crack was able to grow from this void. No voids of this type have been observed beneath extrusions, and McEvily and Machlin 1959 (213) showed that cross slip provided a mechanism whereby material could be transported through the crystal from an intrusion, to form an extrusion, without the requirement of internal voids. The Mott mechanism has also been criticised since the mechanism whereby the cycling dislocation is prevented from returning on its path is not dealt with specifically.

Kennedy 1961 (237) has suggested that in face-centred cubic structures the alternate expansion and contraction of Cottrell-Lomer barriers can provide suitable "one-way" barriers. Specific mechanisms of this type may not be necessary in A2 structures in which cross slip is easy.
The mechanism suggested by Boettner and McEvily 1965 (215) as an extension of the Mott 1958 (236) mechanism is shown in Fig. 34. The continued cycling of a screw, or a number of screw dislocations, is facilitated by an angle greater than 90° between the primary and cross slip planes. This allows preferential movement around the path in one direction. The cyclic change from primary to cross slip plane is suggested as the explanation of the observation that intense slip striations, lie at some angle between the primary and cross slip traces on the surface, (215). Intense slip bands are thought to widen by the addition of new units of this basic mechanism. Such a mechanism cannot lead to the formation of intrusions, but very few were observed in studies of α-iron and iron-silicon alloys, (215) or in copper, (238). These results apparently disagree with other observations on copper (234), α-iron, copper and α-copper-zinc alloys (211). Since no voids of the type postulated by Mott 1958 (236) were observed by Boettner and McEvily 1965 (215) it was concluded that vacancy loops formed beneath the surface to compensate for the volume of material extruded. Cracks were observed to form at the re-entrant angles of intense slip ridges or extruded regions on the surface, apparently as a result of stress concentrations in these regions.
2.10.3 Crack Propagation and Final Failure.

General features of the propagation of fatigue cracks have been summarised by Forsyth 1961 (239) for aluminium and some of its alloys and by McEvily and Boettner 1963 (240) for face-centred cubic metals. Crack propagation appears to be a two-stage process.

Stage 1 is a continuation of the crack initiation process determined by shear stresses, and takes place in the slip plane. This may be identified with the process of fissure formation investigated by Wood 1959 (218).

Stage 2 involves the propagation of the crack under the influence of the tensile stress applied to the specimen. Propagation may take place by a ductile process involving blunting and sharpening of the crack tip during each cycle (241) or by a combination of ductile and cleavage processes (242). Final crack propagation may follow an inter- or transcrysalline path, depending on the temperature of testing, (243) and the applied stress, (244).

McEvily and Boettner 1963 (240) demonstrated that cross slip is important in both stages of fatigue crack growth. As pointed out in Section 2.10.2 cross slip is considered to be essential to the development of microcracks in fatigue slip bands. During Stage 2 the rate and mode of crack propagation are determined by the stresses at the crack tip,
and their relief by plastic deformation. It was suggested (240) that materials of low stacking fault energy, in which cross slip is difficult, are more resistant to crack growth than materials in which cross slip is easy. This evidence supports the fatigue crack propagation mechanism of Laird and Smith 1962 (241), which postulates plastic blunting at the crack tip during the tensile half-cycle. Cross slip also leads to the development of dislocation sub-structure (240) and propagating cracks have been observed to follow sub-structure boundaries, (245).

Christensen 1963 (246) considering aluminium alloys has shown that metal fragments may lead to reduced crack propagation rates by relieving stresses at the crack tip. Such fragments presumably arise by forking and division of the main crack, (247).

2.10.4 The Distribution of Fatigue Damage with Respect to Structural Features

While single crystal studies allow detailed examination of fatigue damage particularly with respect to crystal orientation, work on polycrystals has shown the importance of grain boundaries and annealing twins on the development and spread of fatigue cracks.

Hull 1957/58 (234) suggested that preferential
fatigue damage at twin boundaries in copper was due to the exaggeration of the extrusion and intrusion process at the interaction of twin boundaries and slip bands. Boettner et al. 1964 (238) noted that twin boundaries in copper are preferred sites for crack initiation if they are parallel with potential slip planes, and contain steps which may act as dislocation sources. They suggest that grain boundaries act in a similar manner if correctly oriented. Fatigue slip damage immediately next to twin and grain boundaries, leaving the boundaries undamaged, has been reported, (208).

An early study of aluminium bicrystals (249) sometimes showed slip concentrated at the grain boundaries, and demonstrated that the change in orientation across a boundary is important in limiting the spread of slip bands. Hempel 1959 (250) has shown that the fatigue resistance of single crystals of α-iron is lower than that of polycrystals of the same material. However, crack initiation in bi- and tri-crystals was observed to be associated with the grain boundaries, (250), indicating that crack propagation must be slower in polycrystals than in single crystals. This conclusion seems to be borne out by an investigation of the effect of grain size on the fatigue behaviour of α-copper-zinc, (251). Here it was found that cracks could be formed in individual grains of small-grained specimens, (grain size
0.016 - 0.04 mm.) below the fatigue limit, but these cracks did not propagate across grain boundaries. Large-grained specimens, (grain size 0.33 mm.) showed no cracks below the fatigue limit, above which cracks, when formed, were able to propagate without being held up at grain boundaries. These results suggested a correlation of critical crack length and the stress necessary to propagate a crack through a grain boundary.

A study of the effect of grain boundary misorientation on the initiation and propagation of fatigue cracks in copper tricrystals (252) showed that intergranular cracks formed in low-angle boundaries. It was suggested that dislocation interaction between crystals is most likely under these conditions and that cracks can form by the coalescence of vacancies produced by the interactions.

Intergranular fatigue crack initiation has been reported for a number of metals. Kemsley 1956/57 (244) fatigued copper at room temperature and found that the fracture path depended on the magnitude of the applied stress. At high stress failure occurred on an intercrystalline path, while at low stresses crack propagation was transcrystalline. Smith 1957 (253) found grain boundary cracks in aluminium, but not in copper. Testing at -73°C reduced the amount of intercrystalline crack initiation in aluminium. The difference
in behaviour was attributed to the higher melting point of copper. Forrest and Tate 1964/65 (251) briefly report work on the fatigue of aluminium and copper. Aluminium exhibited only intergranular crack initiation, while copper showed both inter- and transgranular initiation. Testing at $-196^\circ C$ completely suppressed intergranular initiation in copper.

A temperature dependence on the mode of crack initiation has been shown by May and Honeycombe 1963/64 (243) in magnesium and dilute magnesium alloys. At room temperature ($0.3 T_m$, where $T_m$ is the melting temperature in °K) cracks were initiated in slip striations and then spread in a largely transgranular manner. At $250^\circ C$ ($0.57 T_m$) crack initiation took place at triple points or by the linking of grain boundary cavities. Such failure is analogous to that found under creep conditions (188), and implies stress relaxation along grain boundaries, probably by sliding.

McEvily and Boettner 1963 (240) suggested that as the stacking fault energy of a face-centred cubic alloy is lowered, the resistance to transgranular initiation may increase, but at the same time the tendency for crack to be initiated in twin and grain boundaries is increased.
2.10.5 Fatigue of Ordered Alloys

The only published work on the fatigue of \( \beta' \)-copper-zinc reports the observation of fatigue slip markings, incipient cracks and extrusions next to some grain boundaries in material of unspecified composition. Cracks were reported as propagating into and across grain boundaries from the nucleation sites, \((254)\).

Boettner et al. 1965 \((261)\) have described the effect of fatigue deformation on an equiatomic iron-cobalt alloy containing 2 wt.% vanadium, and on a nickel-25.5 wt.% manganese alloy, in the ordered and disordered states. They show that the ordered iron-cobalt alloy has a superior fatigue resistance than the disordered alloy, Fig. 35 despite a lower flow stress. Crack formation is reported as associated with grain boundaries. The nickel alloy was similarly found to have a higher fatigue resistance in the ordered than in the disordered state. The difference was suggested to be due to the absence of surface notches caused by intense slip band formation, and a direct result of the difficulty of cross slip in these alloys when ordered. They tentatively suggest that grain boundaries may become preferred sites for crack initiation if suitable stress concentrations do not exist on the surface remote from the boundaries.
3. EXPERIMENTAL

3.1 Apparatus

3.1.1 The Fatigue Machine

The metallographic nature of this investigation suggested the use of flat sheet specimens. Fatigue could be applied either in reversed bending or in push-pull. In order to rationalise a choice between these loading systems a few preliminary experiments were carried out in push-pull using an Avery 660 lb. Midgit Pulsator Type 73N4 machine. The thinness of the sheet specimens precluded a compressive half-cycle and a stress range $0 - P - 0$ was used, where $P$ is the maximum cyclic tensile stress. This mode of testing was abandoned in favour of reversed bending, because stressing exclusively in tension produced considerable rumpling of the specimen surface, characteristic of tensile deformation Fig. 36, and masked the appearance of those effects characteristic of fatigue stressing. The Avery machine was also clumsy to use and insensitive to changes produced by the start of fatigue damage.

The reversed bending fatigue machine was based on that used in a previous investigation, (127), and depended on the forced vibration of a cantilever specimen at its
resonant frequency. A signal was taken from a beat frequency oscillator, amplified, and fed to two exciter coils, between whose poles the free end of the specimen vibrated, Fig. 37. These coils produced an alternating magnetic field which acted on soft-iron pole pieces attached to the free end of the specimen. The use of the resonant frequency allowed maximum amplitude of vibration to be obtained from a given power input. A signal frequency range from $0 - 2.10^4$ cycles/second was available but the frequency of vibration of the specimen was determined by its geometry (Section 3.3.1) and by the nature of the material composing it.

Two exciter coils were used in an attempt to produce a symmetric strain cycle at the specimen surface. In order to prevent the coils working in effective opposition it was necessary to render the magnetic field across the pole pieces asymmetric, Fig. 38. This was possible by polarising the fluctuating field with a strong permanent magnet. The strength of this magnet was not critical except in order to render the magnetic field asymmetric.

The form of the output of the exciter coils was checked on an oscilloscope, and the condenser bank on the amplifier output, Fig. 39, adjusted until waveforms approximating most closely to a sine wave were obtained. A list of components used in the amplifier is given in Table 7.
3.1.1.1 Mode of Operation at Room Temperature

A thin soft-iron pole piece was secured with "Araldite" adhesive to each face of the free end of the cantilever specimen, the other end of which was secured in the brass clamping block by four screws, Fig. 37. The pole pieces of the exciter coils were then adjusted to within 1 - 2 mm. of the pole pieces of the specimen, the polarising magnet set in position and the supply to the coils switched on. The resonant frequency of the specimen was determined by adjusting the oscillator signed frequency and fell within the range 100 cps for β'-gold-zinc to 500 cps for the iron-aluminium specimens. Vibration continued until fatigue cracking started. All tests at room temperature were carried out in air.

3.1.1.2 Mode of Operation at Low Temperature

A test rig was constructed of such a size that it could be contained within a wide-necked Dewar flask, Figs. 40 and 41. An aluminium specimen clamping block was used, and the specimen was set up as previously described. The whole block was then placed inside the vacuum flask, which was then filled with liquid nitrogen to about 20 mm. below the top surface of the test block. Heat was extracted from the block and specimen simultaneously. A control specimen
to which was attached a thermocouple showed that the specimen temperature fell quickly and reached the temperature of liquid nitrogen at the same time as the test rig. This showed that immersion of the specimen was not necessary. In general the frequency of vibration at low temperature was higher than that at room temperature, but this may have been due in part to the specimen vibrating on a harmonic of the resonant frequency.

3.1.1.3 Advantages and Limitations of the Technique

As previously indicated, flat specimens are easy to examine metallographically, and symmetric reversed bending produces no gross disturbance of the specimen surface. During bending compressive stresses are induced in the concave face of the specimen, and tensile stresses in the convex face. This difference leads to lateral strains in the specimen cross section, and stress concentrations at the specimen edges. It is known that the stresses are a maximum at the surface of a sheet deformed by bending, and that a plane exists in the specimen which does not suffer distortion. It was recognized that these geometric considerations could possibly affect the distribution of fatigue damage.

It was further recognized that the stresses in the specimen could not be determined when using this loading
technique. However, since the microscopic stresses produced by the mutual interactions of grains in a polycrystal are complex and seemed to be important in determining the distribution of fatigue damage in some cases, no great importance was attached to determination of the nominal macroscopic stress. All specimens were fatigued at a strain amplitude which ensured a life in excess of $10^5$ cycles. It was important, however, that the macroscopic strain (i.e., vibration amplitude) should remain constant as far as possible during the test, and this was achieved by choosing a suitable power input and by setting the pole pieces of the exciter coils a suitable distance apart.

Fatigue stressing of a specimen by vibration at resonant frequency without an automatic load maintenance device is unstable, because of changes in the resonant frequency of the specimen.

At the start of a test initial hardening took place rapidly, requiring adjustment of the specimen frequency, but a stable vibration was then maintained until sufficient fatigue damage occurred to render the system again unstable. This phenomenon served as a sensitive indicator of the start of damage. No feed-back system was used to maintain cycling until final failure. It was in general easier to determine the point of initiation of a crack under these circumstances,
than when testing was continued to complete failure.

3.1.2 The Quenching Furnace

In order to reduce the loss of zinc during the annealing of \( \beta' \)-copper-zinc and \( \beta' \)-gold-zinc, either by oxidation or by evaporation, it is necessary to anneal in an oxygen-free atmosphere containing a partial pressure of zinc. The quenching furnace consisted of a sealed quench and a vertical nichrome-wound tube furnace, Fig. 42, through the centre of which passed a second tube containing a roll of wide-mesh 70/30 brass in the hot zone of the furnace. Specimens were suspended by wire from the top of this tube and were quenched into iced 10% sodium hydroxide solution. Temperature could be controlled to \( \pm 5^\circ C \).

3.1.3 The Heat Treatment Furnace

Slow-cooling to establish order was carried out in a horizontal nichrome-wound tube furnace. This furnace contained three windings, the maximum current to each being determined by means of a variable ratio transformer.

Temperature control was achieved by using a platinum resistance thermometer next to the centre winding leading to an electronically controlled saturable reactor circuit. This achieved full proportionality control of the current to the
windings. Temperature settings were made by means of a helical potentiometer calibrated against temperature in the bridge circuit. This system was capable of controlling within 1°C. Slow cooling was controlled by continuous readjustment of the helical potentiometer by an electric motor driving through a reduction gear train.

3.2 Preparation of Materials

Alloys investigated in this work are listed in Table 8, together with the composition with respect to the principal components. Additional details of analysed impurities are given in each section.

3.2.1 β'-Copper-Zinc

This material was prepared from "Crown" zinc (99.995%) and OFHC copper and received as hot-rolled sheet either 2.8 mm. or 5.6 mm. section. It was then hot-rolled to about 1.2 mm. section using the minimum heating time to avoid zinc loss, about 5-10 minutes for the thicker sections at 700°C in air. Specimen blanks were then prepared from this sheet, (Section 3.3.1). These blanks were annealed at 830°C for 5 minutes in the nitrogen/zinc atmosphere furnace and quenched into iced 10% caustic soda solution. This treatment resulted in a β'-grain size of about 2 mm., so that specimens
were in general one grain thick. Since the lower zinc compositions required quenching to suppress the separation of \( \alpha \)-phase, it was decided that all compositions should be quenched in order to make the starting condition of all materials comparable.

Some tensile specimens were prepared in order to determine the ductility in the tensile test of an alloy near the stoichiometric composition and a copper-rich metastable alloy. These specimens were stamped out from 1.5 mm. thick hot-rolled sheet, heat treated and quenched. Owing to the softness of \( \beta \)-copper-zinc at high temperatures these specimens required support during the annealing and quench treatment. They were therefore heat treated in pairs on a jig which allowed free circulation of the quenching medium around the specimen gauge length.

No iron, aluminium, nickel, manganese or lead were detected by chemical analysis.

3.2.1.1 Copper-Zinc-Manganese

A 47 gm. ingot of this material was prepared by induction melting \( \beta' \)-copper-zinc stock and electrolytic flake manganese in a 10 mm. bore silica tube under a partial pressure of argon. Homogeneity was assured by inverting the tube a number of times while the contents were still molten,
and annealing for 24 hours at $750^\circ C$. A sound ingot was produced by passing the tube downwards through the induction coil and freezing the top last. The ingot was hot-rolled to 1.2 mm., fatigue specimens cut out and quenched, following a 5 minute anneal at $750^\circ C$. The nominal composition is given in Table 8.

3.2.1.2 Copper-Zinc-Gold

A 33 gm. ingot was prepared by induction melting copper rod containing 7 ppm. impurity, pure gold and zinc metal rod containing $1/10$ ppm. arsenic in a 10 mm. bore silica tube under a partial pressure of argon. The contents were mixed while molten, and the ingot annealed for 24 hours at $700^\circ C$. The ingot was then hot rolled to 1.2 mm. A slowly cooled sample showed only $\beta'$-phase. The nominal composition is given in Table 8.

3.2.2 $\beta'$-Gold-Zinc

An ingot was prepared by induction melting pure gold with zinc rod containing $1/10$ ppm. arsenic under a partial pressure of argon in a 10 mm. bore silica tube. The components were mixed during melting and the ingot annealed 24 hours at $640^\circ C$. Sheet stock about 0.8 mm. in section was then prepared by hot-rolling. The grain size of this
material was less than 1 mm., and a strain-annealing technique was used to obtain a larger grain size. Hot-rolled strips were strained in tension to give a plastic extension of 3%, using a Hounsfield Tensometer and a stress of about 9.3 kg./mm.², and then annealed for 8 minutes at 640°C. The resulting equiaxed grain diameter was in the order of 2 mm. Fatigue specimen blanks were cut from these strips, and the deformation induced by working removed by a short anneal at 400°C.

Spectrographic analysis showed the largest impurities to be 0.05 wt.% copper and 0.02 wt.% silver. The remaining impurities detected were 10 ppm. iron, 4 ppm. lead, 3 ppm. nickel, 2 ppm. cadmium, and 1 ppm. magnesium and palladium.

3.2.3 Iron-Cobalt-Vanadium

This material was received as sheet 0.7 mm. section. It had been prepared by vacuum induction melting, hot-rolling to 2.2 mm., quenching in iced brine from 850°C and cold rolling to 0.7 mm. The carbon content was determined as 0.0185 wt.%, (0.087 at.%). Specimen blanks were cut out and heat-treated to produce a disordered or ordered structure.

Disordered material was prepared by annealing specimens under vacuum in silica capsules for 1 hour at 830°C.
Some specimens were also prepared from material which had received an ordering treatment, to determine whether any difference existed between material prepared in this way and that prepared directly from the as-received sheet.

Specimens were ordered by sealing them individually in silica tubes under vacuum and cooling from 860°C to 430°C in 34 days. This represents a cooling rate of about 0.53°C/hour. A plot of temperature against time showed that the cooling rate remained constant over the temperature range. A separate tube for each specimen was found to be necessary to prevent specimens spot-welding together as a result of the prolonged vacuum anneal.

Electropolishing this material or mechanical polishing and etching revealed the presence of small second phase particles, particularly at grain boundaries. The nature of these particles was investigated using electron probe microanalysis. Fig. 43 shows an electron image of part of the surface, indicating the lines A – A' and B – B' over which line scans were taken. Fig. 44 shows the vanadium Ka x-ray image from the same area and indicates that particles were enriched in vanadium. The line scan results, Figs. 45 and 46 show that particles were enriched in vanadium and also deficient in iron and cobalt with respect to the matrix. It is believed
that these particles were carbides rich in vanadium. No attempt was made to determine the quantitative concentration distribution of components.

3.2.4 Iron - Aluminium (Fe₅Al).

This material was received as strip, about 1.2 mm. in section. An attempt was made to reduce the section by cold-rolling, but serious cracking was produced by a small reduction. The sheet was therefore annealed at 1100°C to induce grain growth, specimen blanks cut from the strip and ground individually on silicon carbide papers to reduce the thickness to 0.8 mm. The specimens were then annealed at 1250°C in air for 2 hours to remove the effects of shaping, and heat treated appropriately to produce a disordered or ordered structure.

A disordered structure was produced by annealing for 30 minutes at 800°C in air, followed by water quenching. Ordering was carried out by annealing the specimens in air at 800°C for 30 minutes, cooling in the furnace to 540°C and slowly cooling from this temperature to 210°C in 9 days, representing a cooling rate of about 1.5°C/hour.

All annealing treatments were carried out in air because of the protective properties of the oxide layer. Some
annealing treatments were attempted in vacuum in silica tubes, but a reaction took place between the aluminium and the silica leaving a brown deposit in the tubes, presumably as a result of the reduction of silica by aluminium at high temperatures.

3.2.4.1 Iron-Aluminium (FeAl).

The equiatomic iron-aluminium alloy was produced by induction melting high purity iron containing 0.006 wt.% carbon and oxygen with 99.99% aluminium in an alumina crucible under a partial pressure of argon. The ingot was annealed for 24 hours at 1200°C as a homogenization treatment and then furnace cooled. The ingot grain size produced was in the range 1 - 5 mm(607,523),(756,560). This material was used only to determine the orientation of cleavage fracture faces. The nominal composition is given in Table 8.

3.3 Specimen Design and Polishing

3.3.1 Specimen Design

In view of the relatively large grain size of the materials and the fact that only a limited number of gold-containing specimens could be produced, it was essential to use a specimen which allowed as large an area as possible to be subject to fatigue damage. The stress at any point on the
surface of a cantilever can be made constant by tapering the section to zero dimensions at the point of application of the load. For this reason a flat, taper-sided design was chosen. The specimen design is shown in Fig. 47, together with the relative stress distribution on the flat surface. The taper was not accurately machined, but served to extend the region of high stress concentration over a greater area than in the case of a notch of circular section. The numerical value of the stress at any point on the specimen surface is also a function of the specimen thickness, so that for specimens of varying thickness a range of deflections at the tip are required to produce a given value of stress on the surface.

The filing jig Fig. 48, was machined from steel and then surface hardened in an attempt to preserve the profile during use. Rectangular blanks were cut from the sheet material, drilled and assembled in the jig. They were then shaped to the jig profile using progressively finer files. This process produced a deformed layer at the specimen edge, but this effect was overcome by annealing.

3.3.2 Mechanical Polishing

The surface layers were removed from all specimens by wet grinding on silicon carbide papers from 220 to 600 grades in four stages, to remove the effect of
oxidation and give a surface suitable for electropolishing. The specimen edges in the notch region were also ground to remove oxidation, surface roughness and small recrystallized grains which tended to form during the heat treatment as a result of plastic deformation during the filing of the specimen profile. All specimens were then polished on 6 µ and 1 µ diamond polishing pads to give a fine mechanical polish.

3.3.3 Electropolishing

In order to produce a strain-free surface all specimens were electropolished after mechanical polishing. This treatment produced a surface on which deformation markings could be clearly observed and ensured that all specimens were in the same condition before fatigue stressing.

3.3.3.1 β'-Copper-Zinc and Copper-Zinc-Manganese

Heat treated and mechanically polished specimens were electropolished in concentrated orthophosphoric acid (Sp. Gr. 1.35). Each specimen was placed in a copper clip, and the surface covered in protective laquer "Lacomit", except for the specimen gauge length. The clip was placed in the polishing bath so that the specimen was horizontal. A flat sheet copper cathode was placed 10 - 20 mm. above the
specimen and the bath filled with electrolyte. The potential drop across the cell was maintained between 1.5 and 1.8 v. for the specimen area (~2 cm.²). The current fell from an initial maximum as a stable polishing layer was built up on the specimen surface. This layer was of greater density than the electrolyte and flowed from the specimen into the bottom of the polishing bath. A few minutes after the start of polishing a steady flow pattern was set up, which resulted in a distinctive wavy surface on the underside of the specimen. Both surfaces were polished, the top being quite smooth and flat. At the end of polishing the specimen was removed quickly from the bath and washed in a fast stream of cold water. Occasionally slight staining was produced if washing was insufficiently rapid. A polishing time of 6 hours was found to be necessary to ensure the removal of all surface deformation produced by mechanical polishing. Material was removed at the rate of 8 μ/hour. Orthophosphoric acid diluted with distilled water gave shorter polishing times, but the polish was less satisfactory than that produced by the concentrated acid.

The removal of surface deformation was shown by the change of etch-pit distribution with polishing time. Etch pits were produced by immersing the specimen for 30 minutes in a solution composed of:

30 mls. saturated aqueous ammonium molybdate
6 - 7 drops concentrated hydrochloric acid, (143).
Figs. 49, 50 and 51 show β′-copper-zinc (48.25 at.% zinc) specimens after 0, 1 and 6 hours electropolishing respectively. After longer polishing times the etch-pit distribution became more uneven, rows of pits formed in scratches were removed and the number of pits was reduced, presumably due to a drop in the dislocation density as the deformed layer was removed.

Care was required in using this electropolishing method. Air bubbles remaining on the surface prevented polishing beneath them. These could be wiped from the surface using a soft camel hair brush at the start of polishing. If the potential drop across the cell fell below 1.5 v. the specimen was etched, while above 1.8 v. pits were formed irregularly over the surface. Under some conditions, e.g., long polishing times, "growths" were produced on the specimen surface, Figs. 52 and 53. These extended in an approximately radial manner, even across grain boundaries without any deviation due to crystal orientation. The centres seemed to be associated with non-metallic inclusions on the specimen surface, so that the phenomenon may have been due to changes in the concentration of electrolyte in these regions, resulting in a reduction of the polishing rate in these areas.

Specimens of copper-manganese-zinc were polished without difficulty using this arrangement, and identical
polishing conditions.

Tensile test specimens for which a good metallographic finish was not necessary were polished vertically in a bath of 1:1 orthophosphoric acid (Sp. Gr. 1.35)/distilled water, using a vertical cylindrical copper mesh cathode, a current density of 12 Amps./dm.² and a polishing time of about 10 minutes. Vigorous stirring of the electrolyte was necessary to obtain polishing over the whole gauge length of the specimen.

3.3.3.2 α'-Gold-Zinc

Two electropolishing methods were used for this material. Neither was wholly satisfactory in that difficulties were encountered in producing an even polish over the whole area of the specimen.

The first was described by Reichert 1955 (256). Specimens were made anodic in a bath containing:

50 g./l thiourea

5 g./l. sulphuric acid

using a vertical cylindrical stainless steel mesh cathode. In addition about 0.1 mole zinc sulphate/mole thiourea was added to the solution in order to increase the throwing power of the bath, as suggested by Fischer 1955 (257). A current density of about 80 Amps./dm.² was required to give polishing,
but this was 12 to 25 times greater than suggested (256). The electrolyte was heated to $60^\circ C$ and stirred vigorously during polishing, which was continued for 2 - 5 minutes. Specimen edges, being subject to a higher current density than the centre of flat faces, were attacked more, and polishing also tended to produce grooving at grain boundaries. This latter point was considered to be a serious disadvantage, and a second method was therefore tried.

The electrolyte originally suggested by Morris 1949 (258) for electropolishing steels, and used by Ball and Smallman 1965 (119) for $\beta'$-gold-zinc, is composed of:

- 133 mls. glacial acetic acid
- 25 g. chromium trioxide and
- 7 mls. distilled water

Specimens were polished using a vertical cylindrical stainless steel mesh cathode and vigorous stirring. A current density of 20 Amps./dm.$^2$ was used and the electrolyte was cooled by an ice bath to prevent heating above the recommended temperature of $19^\circ C$. Although grain boundaries were not attacked preferentially, polishing again tended to be concentrated at the specimen edges. Polishing time was therefore limited to about 15 minutes to prevent excessive tapering of the specimen edge. The electrolyte was washed
off in cold running water.

3.3.3.3 Iron-Cobalt-Vanadium and Iron-Aluminium

Both the alloys CoFe-V and Fe₃Al were electropolished using the method described by Morris 1949 (258). Specimens were polished vertically in a bath cooled by ice, using a cylindrical stainless steel mesh cathode and vigorous mechanical stirring. Polishing was continued for about 10 minutes at a current density of 220 Amps./dm². After polishing specimens were washed in a stream of cold water. This method tended to etch up second phase particles in the iron-cobalt-vanadium alloy, but produced a smooth finish without preferential polishing at grain boundaries in the iron-aluminium alloy.

3.4 Observation Techniques

3.4.1 Light Microscopy

All photomicrographs were obtained using a Bausch and Lomb "Metallograph" using direct, oblique or polarised light. Interference patterns were obtained using a Watson two-beam interferometer and sodium light, wavelength 5890 Å.
3.4.2 Electron Microscopy

Surface fatigue damage was also examined by replica electron microscopy using an Akashi "Transcope" microscope operating at 50 Kv. Either "Formvar" or "Bexfilm" replicas were taken from the surface, in the manner described by Bradley 1956 (259). Carbon/platinum replicas were obtained by a two-stage evaporation process involving the deposition of a shadowing platinum/carbon film onto the stripped plastic replica in a hard vacuum (better than $0.5 \times 10^{-4}$ torr), followed by a backing coat of carbon evaporated in a softer vacuum (about $1.5 \times 10^{-4}$ torr). Both replicating plastics were found to be satisfactory, but "Formvar" was easier to use when a specific area on the surface was to be examined. In this case a support grid was "tacked" onto the surface in the correct position with a small drop of "Formvar" solution on a fine brush. A drop of solution was then placed on the grid which was prevented from moving and the grid and replica stripped off using "Sellotape". This technique was important for the examination of ordered iron-cobalt-vanadium specimens on which fatigue damaged regions were widely spaced.
3.4.3 Specimen Sectioning

Only \( \beta' \)-copper-zinc specimens were sectioned. Since fatigue damage was found to be rather localised, protection of the specimen surface and section edge during sectioning by electroplating a protective layer was excluded, owing to the difficulty of locating specific regions. Specimens to be sectioned were set in clear "Araldite" resin and gently mechanically polished to avoid damaging the specimen edge. This enabled observations of the section surface to be correlated with damage on the specimen surface. Taper-sectioning was also possible using this method. Specimens were ground at an acute angle to the surface to an extent determined by observations of the top surface through the Araldite. Section surfaces were usually not electro-polished since it was found that flow patterns caused grooving, and cracked regions were attacked preferentially causing cracks to be enlarged. Sections were generally either mechanically polished to 1 \( \mu \) diamond and examined unetched or lightly etched in alcoholic ferric chloride solution.

3.4.4 X-Ray Examination

3.4.4.1 Back-Reflection Photographs

The orientation of fracture facets and single
crystals in polycrystalline specimens was determined by the examination of Laue back-reflection photographs. The camera arrangement was a simplification of the system described by Holmes and Fuchs 1956 (260) and is shown in Figs. 54 and 55. Fracture facets were set up in approximately the correct orientation such that the collimated beam was normal to the surface, while specimens in which the specific orientation of a grain in the surface was required were set up relative to a fiducial line using a telescope and cross wires. The specimen was positioned 30 mm. from the film cassette, and the mirror, through the centre of which a hole was drilled at 45° to the surface, was set up at 45° to the path of the beam. Using the telescope to view the reflected image of the specimen, the position of the light beam which was shone through the collimator could be selected accurately, using the adjusting screws on the specimen support. Fracture facets appeared as bright spots when correctly oriented relative to the light beam. A film was placed in the cassette and the alignment re-checked, although in general no adjustment was necessary owing to the positive location of the cassette on the camera. All back-reflection Laue photographs were taken using white radiation from a copper target. Exposure times varied from ½ hour for β'-copper-zinc crystals, using a collimator
which gave a 1 mm. diameter area of irradiation, to
8 hours for iron-cobalt-vanadium fracture faces for which
a collimator giving a spot less than 0.5 mm. diameter was
required.

3.4.4.2 Lattice Parameter Determinations

Powder photographs of the iron-cobalt vanadium
alloy were obtained from the ordered and disordered states
using a 57.3 mm. diameter Phillips powder camera. A
square section rod 15 mm. long was cut from an ordered
specimen using a fine jewellers saw. The specimen was then
disordered and a second rod cut out. This process ensured
that both specimens were the same composition and contained
the same amount and distribution of second phase particles.
Material deformed by sawing was removed and the wires thinned
by dissolving in aqua regia. The wires were then given
4 hour exposures using cobalt Kα radiation, to depress
the atomic scattering factor of iron and show superlattice
lines, if present, (Section 2.2.5). The resulting powder
patterns are shown in Figs. 56 and 57. These patterns
show that the ordered material has a larger lattice parameter
than the disordered, since reflections occur at slightly
smaller values of θ, the Bragg angle, in agreement with
previous results, (12), (80). The relatively large grain
size (for a wire specimen) is indicated by the "spotiness" of the reflections.

The lattice parameters were determined using a Phillips PW 1010 diffractometer with copper radiation. Values of the lattice parameter, calculated from the \{211\} reflections are compared in Table 8. Since the diffractometer used copper radiation no extra lines corresponding to the simple cubic lattice were detected because of the similarity of the scattering factors of the components under these conditions and to the considerable fluorescence produced by iron.

The lattice parameter of the \(\beta'_1\)-gold-zinc alloy was determined using copper radiation in the diffractometer. Because of the different scattering factors of gold and zinc, superlattice lines from the primitive cubic lattice were detected without difficulty. The lattice parameter value determined from the \(\{321\}\) reflection is given in Table 8.

As a check on the structure of the cast iron-aluminium alloy FeAl a diffractometer trace was taken from sections of the polished ingot. Because of the large grain size not all reflections were present, but reflections corresponding to \(\{200\}\), \(\{211\}\) and \(\{310\}\) were detected. The lattice parameter calculated from the \(\{310\}\) reflection is given in Table 8.
An attempt was made to determine the change in lattice parameter with zinc content for the range of β'-copper-zinc alloys. Such a plot has been reported by Beck and Smith 1952 (4). However, because of the large grain size of the specimens high angle reflections could not be obtained consistently, and the question was not pursued.
4. RESULTS

4.1 Binary Alloys of $\beta'$-Copper-Zinc

4.1.1 Slip Traces

Slip lines appeared on the surface of fatigue specimens of all compositions during the first few cycles of deformation, and continued to grow in length and increase in number during the period before the appearance of cracks. The appearance of slip markings and their distribution varied greatly, not only from one composition to another but also from one specimen to another of the same composition, and even between neighbouring grains. This fact makes detailed comparison of the appearance of slip lines on the surface very difficult without specific information concerning crystal orientation and stress distribution. The present results can only lead to a qualitative explanation of the change in the appearance of slip traces with composition and deformation temperature. The results quoted are based on the observation of a number of specimens of each composition.

After the first few cycles of deformation macroscopic examination of a specimen showed that grain boundaries appeared to be associated with narrow regions in
which the deformation was more limited than elsewhere. No doubt this effect was due in part to the differing reflectivities of grains as a result of surface roughening due to the formation of slip steps, Fig. 58.

a) 42.5 at.% Zinc. This alloy frequently showed fairly widely spaced slip steps, particularly near the specimen edge, Figs. 59 and 60. As cycling continued these steps lengthened but no intensification, characteristic of fatigue damage, occurred, Figs. 61 and 62. Although slip lines were usually fairly straight, Fig. 63, this was not always the case, Fig. 64. Grain boundaries seemed to influence the distribution of slip, leading not only to the appearance of new slip traces in the grain boundary region but also to the limitation of slip traces approaching the boundary. Bending of slip markings on one side of a grain boundary to correspond with traces on the other side was also observed, Fig. 65.

b) 45.1 at.% Zinc. This alloy showed a generally similar distribution of slip markings to that observed on the 42.5 at.% zinc alloy. Slip lines were sometimes straight, Fig. 66, but curving slip markings, particularly in the neighbourhood of grain boundaries, were not uncommon, Fig. 67. However, well developed cross slip traces were also observed, Fig. 68.

One specimen of this composition showed needle-shaped bands in a grain near the specimen edge, Fig. 69. These
bands could conceivably have resulted from shear transformation of the $\beta'$-grain, or from lattice tilt during deformation. The latter view was supported by the observation of displacement of slip markings across the bands, at (A), by their relatively great length, about 1 mm., and by the fact that slip markings turned into the band at one end, Fig. 70. Further, no such bands were observed in other compositions following fatigue deformation.

c) 46.95 at.% Zinc. The influence of grain boundaries on the slip distribution is demonstrated in Fig. 71. Curving slip traces and the limitation of deformation next to the boundary may be seen. In general straight slip traces appeared to be closer together in this composition than those of lower zinc content, Fig. 72, and curving or wavy slip traces were also common.

d) 48.25 at.% Zinc. This composition showed cross slip traces on fatiguing at room temperature, Figs. 73 and 74. These appeared to be more clearly defined than in alloys of lower zinc content. Sharp bending of slip traces at grain boundaries was also observed, as in other compositions.

Only specimens of this composition were fatigued at 77°K, since transformation products were more likely to be formed in the binary copper-zinc alloys of lower zinc content. Further the 48.25 at.% zinc alloy showed curving and cross
slip traces most commonly and it was felt that the process of cross slip would be affected most by a reduction of the temperature of deformation. Slip traces formed during fatigue at $77^\circ K$ showed a significant difference from those formed in the same alloy at room temperature. Straight slip traces were predominant and the spacing wider following low-temperature deformation, Figs. 75 and 76. The appearance of slip traces and their distribution was similar to the 42.5 at.% zinc alloy fatigued at room temperature.

Summary

1) Decreasing zinc content from 48.25 at.% to 42.5 at.% caused slip traces to be straighter and more widely spaced.

2) Curving slip traces were observed throughout the composition range, but were most common and most clearly defined in the high-zinc alloys.

3) Fatiguing the high-zinc alloy at $77^\circ K$ changed the pattern of slip traces to that of a low-zinc alloy.

4.1.2 Ternary Alloys of $\beta'$-Copper-Zinc

In an attempt to rationalise these results in terms of the energy of the stacking fault between superpartial dislocations the two $\beta'$-copper-zinc ternary alloys were deformed at room temperature. Figs. 77 and 78 show the pattern of
slip traces on the surface of an electropolished \( \beta' \)-copper-manganese-zinc fatigue specimen. Slip traces are widely spaced and in almost all cases straight, although a few curving traces may be seen. The \( \beta' \)-copper-gold-zinc alloy on the other hand showed only wavy slip traces following mechanical polishing and slow deformation in reversed bending, Figs. 79 and 80. The implications of these observations will be discussed in Section 5.1.1.

4.1.3 Initiation and Propagation of Fatigue Cracks in \( \beta' \)-Copper Zinc

Fatigue deformation was found to initiate four types of crack:

1) Short cracks initiated at grain boundaries with little associated plastic deformation.

2) Short cracks initiated next to grain boundaries accompanied by intense plastic deformation.

3) Long, straight, transgranular cracks from grain boundaries accompanied by little plastic deformation.

4) Intergranular cracks.

The relative frequency of occurrence of these crack types, as well as the mode of crack propagation, depended on the composition of the alloy and the temperature of fatiguing. It was sometimes observed that two or even three types of crack
occurred in one area, and the arrangement of damage was such that it was difficult to attribute the cracking uniquely to one source. However, each of the four types was observed unaccompanied by other crack modes, so that each represents a possible form of initial crack. The results to be presented are believed to point to a single mechanism as responsible for the initiation of cracks during fatigue of $\beta'$-copper-zinc, but the types listed above will be considered as separate and distinct for the purpose of presentation of results.

a) 42.5 at.% Zinc. The classical mechanism of fatigue crack initiation by the progressive intensification of slip damage on the surface was not observed in this alloy.

A study was made of a specimen at various stages of its life by periodic microscopic examination to determine the change in the distribution of slip markings and cracks with continued cycling. Fig. 81 shows part of a specimen surface after $0.12 \times 10^6$ cycles at 200 cps. Neither cracks nor intense slip damage are visible, although typical widely spaced slip lines are present. Some rumpling of the boundary between grains 2 and 3 and between grains 3 and 4 may be observed. Fig. 82 shows the same area after $0.3 \times 10^6$ cycles. Slip lines lengthened in grain 5 and became more numerous in grain 2. Cracks were initiated at the boundaries between grains 2 and 3 and grains 2 and 5. Fig. 83
shows the boundary of grain 2 and the extent of the damage at this stage. Rumpling of the boundary is revealed by oblique illumination. The nature of the cracks at the boundary between grains 2 and 3 is shown in Fig. 84. Cracks extended from the boundary itself 10 to 15 μ into grain 3. Across the boundary the orientation of the cracks changed and their propagation was limited to a distance of 2 - 3 μ. The spacing of the cracks was regular, 7 - 13 μ, Fig. 83, and no slip traces may be observed between the cracks. Some dark protrusions may be seen emanating from all cracks.

After 0.56 \times 10^6 cycles damage extended away from the triple point along the boundaries of grain 2, Fig. 85. Arrows indicate the extent of the damage after 0.3 \times 10^6 cycles. Cracks along the boundary between grains 2 and 5 increased slightly in length. The same area is shown after 2.94 \times 10^6 cycles in Fig. 86. The arrow indicates the extent of the damage after 0.56 \times 10^6 cycles. Damage continued to extend along the grain boundaries, some new crack orientations appeared in grain 5 and cracks at the boundary between grains 2 and 3 started to join up at their tips. Black exudations appeared at the grain boundary between grains 2 and 5 and the crack continued to propagate intergranularly.

Other areas of Fig. 81 also showed damage at this
stage. Crack nucleation started from the triple point formed by grains 3 and 4, Fig. 87. Similarly damage was initiated at the triple point formed by grains 1, 4 and 5, Fig. 88. In general crack traces did not lie parallel with slip traces within the grains, Figs. 89 and 90. However, a few short slip lines having the same surface trace direction as the crack in Fig. 88 may be observed in grain 5 at the triple point with grains 1 and 4 in Fig. 81. This does not necessarily indicate that the crack and slip share the same plane.

Electropolishing specimens for a short time after fatiguing showed that short intense markings next to grain boundaries were indeed cracks, Figs. 91 and 92, 8µ removed, and 93 and 94, 4µ removed. Cracks formed at acute angles with boundaries and electropolishing back accentuated cracks linking the tips of those initiated at the boundary, Figs. 95 and 96, 8µ removed, and 97 and 98, 24µ removed. Crack linking in this way often produced a propagating crack leading to final failure, Fig. 99. This path appears to be composed of two orientations, neither of which are parallel with nearby slip traces. Short cracks formed at grain boundaries were sometimes spaced very closely and damage was intense, Figs. 100 and 101. Polishing back the specimen shown in Fig. 93 produced displacement of the cracks relative to each other along
the boundary, Figs. 94, 103, and 104. However, only traces of propagating cracks in the lower grain are displaced relative to cracks in the upper grain. Short markings at the grain boundary in the lower grain are not so displaced, indicating that these markings are formed on different planes from the long propagating cracks in the lower grain. It is noteworthy that the short cracks normal to the boundary, although spaced about 3 μ apart are still well defined after material has been polished from the surface to a depth of about 28 μ.

The orientations of straight propagating cracks were determined by observation of the traces made by cracks on two surfaces in the specimen. This required the orientation of each grain by the back-reflection Laue technique and the sectioning of each grain, usually on a plane at right-angles to the specimen surface. The technique is fully described in Appendix B.

Fig. 105 shows a heavily cracked specimen. Crack paths either lie along grain boundaries or are straight and transcrystalline. Orientation results for cracks of the latter type are given in Table 9 for the cracks indicated in Fig. 105 and for those in grains 2, 3, 4 and 5, Figs. 84, 87 and 88. These values are plotted on the standard stereographic triangle, Fig. 106 and
indicate that fracture paths are all of the type \{110\}. The scatter of \(\pm 3\) degrees is considered to be within experimental error.

Cracks not infrequently propagated through regions next to grain boundaries, Figs. 107 and 108. In such cases associated slip markings appeared to be connected with stress relief at the crack tip during propagation.

Examination of crack traces on sectioning planes normal to the specimen surface showed that cracks having a straight surface trace also showed a straight trace on the section plane. Fig. 109 shows such a section taken through grain 5 next to the boundary with grain 4, Fig. 88. Electropolishing has lead to rounding of the specimen edge, but all cracks may be seen to possess parallel traces. Progressive sectioning of this crack showed that its depth remained approximately constant at about 150 \(\mu\). As the tip was approached the depth decreased rapidly, indicating that the crack front curved down sharply from the specimen surface. A section on a plane normal to the surface but oblique to the grain boundary trace in the specimen surface, Fig. 102, is shown in Fig. 110. Electropolishing again led to rounding of the edge, and was abandoned for further sections. Parallel traces of short cracks extending from
the grain boundary may be observed together with an intergranular crack. Although specimen surface traces of cracks were spaced about 5 µ apart the section shows that these cracks extended some 40 µ into the grain from the specimen surface.

Figs. 111 and 112 show transverse sections through grains 6 and 8 respectively. Other flat fracture facets not positively identifiable with traces on the specimen surface are also visible. Straight crystallographic cracks propagated through almost the whole specimen thickness.

On one occasion only, propagation of a crack was associated with the appearance of transformation product revealed by a transverse section through the cracks shown in Fig. 107. This section is shown in Fig. 113. The nature of the product could not be determined but was presumed to be martensite arising from plastic deformation at the tip of the propagating crack.

Not all cracks formed during fatigue propagated over distances greater than about half the grain diameter, that is, comparable with the distance between triple points on the surface. This was in part due to the large grain size relative to the specimen width. Any crack which propagated through two or three grains rapidly produced complete fracture of the specimen and prevented the growth of other cracks.
Not infrequently a single type of crack damage spread along the whole length of boundary between two triple points. The mode of propagation changed at the triple points, Figs. 87, 95, 101 and 114. Fig. 101 shows a change from short cracks with little plastic deformation (type 1) to straight transgranular cracking (type 3) and intergranular fracture (type 4) along the boundary on which the original damage was formed. The cracking next to the boundary in Figs. 95 and 114 produced plastic deformation at the triple points and some intergranular fracture (type 4). The mode of crack propagation, Fig. 87 changed at the triple point to a ductile mode associated with considerable plastic deformation, similar to that in Figs. 107 and 108.

Short cracks formed parallel to each other along a boundary in general did not propagate into the grains but maintained a constant length of about 20 μ. The constancy of length and spacing of these cracks was a characteristic feature of this type of damage. Occasionally, however, some cracks propagated further than the majority, Fig. 102 and the crack path near the tip became ragged and showed few straight traces.

The propagation of straight crystallographic cracks was sometimes associated with exudations of dark material onto the specimen surface, grain 6, Fig. 105. This was
thought to be produced by the arrition of fracture surfaces, and therefore to succeed propagation of the crack tip. Although some cracks of this type showed little associated plastic deformation even when the crack was arrested remote from a grain boundary, Fig. 107, others showed a strip of slip markings associated with the propagation of the crack, Fig. 88. Plastic deformation at the tip would provide a means of stopping the propagation of such cracks.

Regularly spaced small ripples or folds were observed at a grain boundary, Fig. 115. At the triple point at one end of this boundary rumpling occurred in the grain not forming the boundary, indicating that some stress relaxation had taken place along the boundary. It is possible that ripples of this nature form the stress concentrations from which short markings along the boundary are produced. This suggestion was not confirmed since continued cycling to $2.9 \times 10^6$ cycles produced no change in these markings, which were present after $0.12 \times 10^6$ cycles.

**Summary**

1) Two types of crack were initiated during the fatigue of $\beta'$-copper-zinc specimens containing 42.5 at.% zinc; short cracks normal to grain boundaries with little interspersed plastic deformation and straight crystallographic cracks.
2) Crack propagation took place by three means; intergranular propagation through or from regions of short grain boundary cracks, transgranular propagation of straight crystallographic cracks and propagation of cracks on a zig-zag path associated with plastic deformation through a region next to the grain boundary.

3) Crystallographic cracks were found to lie on \( \{110\} \) planes.

4) Regions of short cracks normal to grain boundaries were observed to spread slowly along the boundary as cycling continued.

b) 45.1 at.% zinc. The initiation and propagation of fatigue damage was investigated in a specimen of this composition by periodic removal and examination of the specimen during the course of a test. Fig. 116 shows the first region of crack damage on a specimen following \( 0.59 \times 10^6 \) cycles. The region of crack initiation, (B), Fig. 116, and one triple point is shown in Fig. 117. Very short markings 2 - 3 \( \mu \) in length may be seen associated with the boundary. The appearance of these markings differs from those formed along grain boundaries in the 42.5 at.% zinc specimen, Fig. 84. In this case they are shorter, less well defined and more closely spaced. They were usually dark brown in colour and were apparently regions of intense plastic deformation.
An intergranular crack formed along this boundary and lead to plastic deformation at the triple point, Fig. 117. A further intergranular crack and a straight crystallographic crack then propagated from the triple point.

After $1.0 \times 10^6$ cycles the original crack (B) Fig. 116 propagated further and damage was initiated at a number of other points, Fig. 118. In all cases new cracks or intense slip damage were observed to be associated with grain boundaries. At point (A) a new propagating crack has been initiated in an identical manner to the original crack (B), i.e. an intergranular crack has been formed in association with short slip markings running from the grain boundary, Fig. 119. These markings are 4 - 5 μm in length and less than 1 μm apart even where they can be resolved. They do not appear to be separated from the boundary but are most intense in the region 1 - 4 μm from the boundary, Fig. 119.

At point (E) Fig. 118 very short markings formed along the boundary. These markings were intense and irresolvable and extended about 3 μm into the grain, Fig. 121. After $1.75 \times 10^6$ cycles straight crystallographic cracks were initiated from the deformed region, although the slip markings themselves did not lengthen measureably, Fig. 122. It may be noted that the grain boundary markings and the straight
cracks have different surface traces, and must have been formed on different planes.

The markings formed at (C), Fig. 118, consisted of intense deformation packets about 8 μ in length extending about 5 μ from the boundary, Fig. 123. A dark strip about 1 μ in width was observed parallel with the boundary, possibly in the second grain. Some markings indicated by the arrow Fig. 123 extend beyond the majority into the upper grain. After 1.75 \( \times 10^6 \) cycles Fig. 124 the intense markings did not grow, but a crack passed through the slipped region on a zig-zag path and then propagated into the grain near the triple point apparently along the marking arrowed in Fig. 123. Longer markings in Fig. 123 grew during the additional period of stressing, but only by about 5 μ during 0.75 \( \times 10^6 \) cycles.

A possible mechanism for the initiation of intergranular cracks from short slip markings at a grain boundary is indicated by Fig. 120. Some markings have become more intense than others, and cracks may be seen spreading from the root of these along the boundary. An intergranular crack can form by the linkage of these cracks. Short markings are again limited to a region about 5 μ in width from the boundary.

Propagation of the original crack (B) from 0.59 \( \times 10^6 \) cycles
to $1.0 \cdot 10^6$ cycles continued along straight crystallographic paths Fig. 118, and was associated with some exudation of material from the crack following a change in direction. Similar exudation of material from a crack may be seen in Fig. 119. During this time the crack propagated about 1200 $\mu$. Although this crack shows well-defined straight surface traces the rate of propagation was not rapid. Both in Fig. 116 and Fig. 118 the crack terminates within a grain.

In order to determine whether the segregation of one component to the region of grain boundaries could provide a reason for their apparent weakness, electron probe micro-analysis scans were made across the lines shown in Fig. 125, which shows an electron image of the triple point region at the right of Fig. 124. Two line scan traces are shown in Figs. 126 and 127. In no case could any deviation from the matrix composition be determined. The dark colour of the slipped region next to the grain boundary in Fig. 124 may be attributed to a change in reflectivity of the surface as a result of the formation of slip lines irresolvable by optical microscopy.

Summary

1) Fatigue cracks in 45.1 at.% zinc $\beta'$-copper-zinc have
been observed to be initiated at grain boundaries, usually accompanied by short slip markings in a region within 5 μ of the boundary.

2) Intergranular crack initiation without short slip markings at the boundary has also been observed.

3) Cracks may propagate initially on an intergranular path but straight crystallographic cracks were observed to propagate easily from intercrystalline cracks held up at triple points.

4) Electron probe micro-analysis indicated that no segregation, of either components occurred, to the boundary.

c) 46.95 at.% Mn. Only two modes of crack initiation were observed following fatigue of specimens of this composition:

the initiation of short parallel cracks in regions of intense plastic deformation next to grain boundaries; (type 2), and

the initiation of intergranular cracks, (type 4).

The initiation of straight crystallographic cracks (type 3) was not observed.

Figs. 128, 129, 130, 131, 132, and 133 show a number of regions next to grain boundaries in which short cracks have formed. Although these areas differ in the detail
distribution and appearance of the damage some common features may be observed. Damage appeared in general on both sides of the boundary, but was usually more intense on one side only. Frequently, it took the form of a strip of irresolvable markings, dark brown in colour and 10 - 15 µ in width, which was separated from the boundary by a region of relatively undisturbed material 1 - 2 µ in width, Figs. 131 and 132. These markings were tentatively thought to be regions of intense plastic deformation.

More intense markings, 20 µ or more in length, extended beyond the heavily deformed layer and were spaced at more or less regular intervals along the boundary, Figs. 128 and 129. Although in Fig. 128 markings in both grains are all parallel this was not generally so, Figs. 129 and 132. Longer markings often formed as pairs across the boundary, Figs. 128 and 132. Fig. 129 shows that near the most intense of these the surface damage was less than in regions remote from such markings. Although longer markings in any grain were more or less parallel, they frequently showed a tendency to change direction some 20 µ from the boundary, Figs. 128 and 132.

Optical microscopy seemed to indicate that longer markings were cracks which formed initially in regions of intense slip.
damage, separated from the boundary by a narrow strip of relatively undeformed material.

Selected area replica electron microscopy results confirmed these general features. Fig. 134 was taken from the damage in Fig. 129. The grain boundary lies out of the top right-hand corner of the picture. The region is composed of slip traces which are intense in the centre of the picture, but rapidly become less intense remote from the grain boundary. Apparent slight bending of the markings is probably due to bending of the replica. Part of one longer intense marking is also visible. The regions shown in Figs. 132 and 133 were also examined by replica electron microscopy. Fig. 135 shows an area of slip markings next to the grain boundary. Plastic deformation extends over the region 2 - 15 μ from the boundary, and is most intense about 5 μ from the boundary. Fig. 136 shows a region of more intense deformation. Although slip traces are not pronounced within 1.5 μ of the boundary, they may be discerned within 0.5 μ of the boundary, and are essentially straight in this region. Further from the boundary traces are wavy and much more intense.

The nature of longer intense markings is indicated in Figs. 137 and 138. The latter area is marked with an arrow in Fig. 132. Intense markings appear to have formed
within the region of intense slip about 4 - 5 μ from the boundary, and then to propagate in both directions, Figs. 138 and 139. These replicas indicate the existence of extrusions or intrusions (cracks). A series of white shadows along the intense marking at the right of Fig. 137 may be observed. The replicating technique did not distinguish specifically between extrusions and intrusions, but it seems likely that these shadows result from a crack.

Propagation of cracks from the region of intense slip across the grain boundary is indicated by the correspondence of longer cracks across the boundary. Fig. 138 shows that some intense slip markings did not produce a crack running up to the boundary, others produced a crack running only to the boundary, others a crack just crossing the boundary and the most intense markings gave rise to cracks propagating a few microns across the boundary. Propagation of the main crack into the grain involved a change in direction although slip traces in this region are parallel with those nearer the boundary. Similar deviation of longer intense markings from the original slip traces may be seen in Fig. 139.

The remarkable regularity of spacing of the more intense markings as illustrated in Figs. 137 and 139. In this case the spacing was about 2 μ. Fig. 133 shows that intense
markings 8 μ in length were spaced about 2 μ apart. Those 15 - 20 μ in length were spaced about 20 μ apart. A similar distribution of markings may be seen on Fig. 128.

Although indicated by surface observations, the fact that the more intense markings were indeed cracks was confirmed by sectioning regions of short markings on a plane normal to the specimen surface. The damage shown in Fig. 128 was sectioned on the broken line indicated. The distribution of cracks is shown in Fig. 140. The section surface was slightly etched in alcoholic ferric chloride solution to show the position of the boundary, and this has lead to some broadening of the cracks. Although maximum depths cannot be determined from a single section no crack on this section penetrated more than 15 μ into the grain. Cracks having a surface trace less than about 10 μ in length did not penetrate more than about 5 μ into the grain.

On a number of occasions intergranular cracks were initiated with little or no accompanying plastic deformation. These cracks propagated along the boundary for considerable distances. Typical examples are shown in Figs. 145, 146, 147, and 148.

Since short slip markings at boundaries and intergranular cracks appeared to be formed by some sort of interaction.
between grains across a boundary, a number of well-developed examples of each type of damage were chosen in order to determine the orientation of the crystals with respect to each other and to the applied stress on the specimen and also the orientation of the boundary with respect to the specimen. These results are shown in Figs. 141 to 148 together with micrographs showing the specimen axis N - S.

The orientation of the crystals were determined from Laue back-reflection photographs, and are presented such that the plane of the paper represents the specimen surface, and the line N - S the specimen axis. The orientation of each crystal in the pair, numbered 1 and 2, is represented by three 100 poles and the three <100> zones connecting them. The orientation of the grain boundary is inevitably very approximate, since few grain boundaries are planar, but is represented by the symbol ⊗.

The nature of the misorientation of the grains in these pairs is complex. No consistent pattern is obvious, except that the relative misorientation is high. This may be a necessary condition for the appearance of any sort of damage between grains of β'-copper-zinc during fatigue.

Not infrequently, cracks were initiated in association with a boundary terminating at the edge of the specimen.
Cracks initiated in this way were not considered to be representative of crack initiation in general, since grains at the edge of the specimen possessed two free surfaces and were more likely to be affected by artificial stress concentrations arising from notch effects at the specimen edge.

Specimens showing damage along a grain boundary were examined on both surfaces to determine whether the propagation of extensive damage from another source might have affected the stress distribution of the given grain pair. Cracks propagating through the specimen from one surface to the other provided non-typical conditions of stress concentration at the propagating tip. In general, both grains of a pair occupied the specimen thickness. Grain D1, Fig. 144 was however very shallow, and extended only about 100 μ into the specimen.

In order to determine the plane on which short markings and cracks next to the boundary formed, the orientation of a number of grains showing such markings was determined. Since many cracks showed surface traces less than 10 μ in length, and the depth of penetration into the specimen was even less, a single surface analysis technique, (Bowles 1951 (262)), was adopted. The method is described in Appendix C.
The result is shown in Fig. 149, and indicates that short cracks are formed on \{110\} planes initially. In view of the difficulty of measuring the angle of the surface trace of cracks less than 10 \(\mu\) in length, and the fact that not all markings at the same boundary were parallel, probably due to plastic deformation at crack tips, the scatter is not too large.

Short markings did not generally propagate more than 100 \(\mu\), Fig. 128, and in some cases did not propagate at all beyond the grain boundary region, Fig. 131. Fig. 128 shows that some markings produced exudation onto the specimen surface. The propagation of intergranular fracture through, and in association with, a region of short slip markings was observed, Figs. 141, 128 and 140.

Of the grain pairs showing intergranular crack initiation, only pair G, Fig. 147, did not show consistent intergranular propagation into the specimen, Fig. 150. Typical intergranular propagation is shown in Fig. 151, grain pair E.

Crack propagation usually took place on transgranular paths and was associated with considerable plastic deformation. Intergranular cracks changed to transgranular paths at triple points or when the boundary changed direction sharply.
Typical damage is shown in Fig. 152. Crack paths did not in general exhibit straight traces, but showed a tendency to propagate in or near to grain boundaries. Feature (A) shows a crack showing a straight surface trace. Taper sectioning this region, Fig. 153, shows that the crack did not occupy a planar path through the crystal, but branched and changed direction. Straight facets were sometimes observed on propagating cracks, however, Fig. 154.

Facets 2 - 5 μ in width were also observed on taper-sectioning feature (B) in Fig. 152, Fig. 155. Facets of this type are reminiscent of the classical faceted fatigue crack propagation mode.

Feature (C), Fig. 152, was a region of slip and crack damage next to a grain boundary, apparently accompanied by an intergranular crack, Fig. 156. This area was taper-sectioned, using a taper angle of about 5 degrees, allowing the depth of cracks to be determined accurately. Stages in the sectioning process are shown in Fig. 157. The taper angle was such that any point distant N μ from the taper edge lay N/10 μ beneath the original specimen surface.

Markings 5 μ or less in length did not penetrate more than 2 μ into the specimen. Longer cracks generated in slip markings did not penetrate more than 15 μ into the specimen.
The crack running along the boundary started to propagate transgranularly beneath the surface, Fig. 157 a) and finally, Fig. 157 d), showed no intergranular facets at all. Fig. 156 again shows that cracks formed in slip markings next to a grain boundary tended to turn, about 20 μ from the boundary, to a path at right angles to the normal stresses produced by bending of the specimen. Macroscopically, cracks followed paths transversely across the specimen.

Summary

1) Short cracks, which formed on (110) planes and lay approximately normal to the boundary were initiated in intense slip damage, in the region from 2 - 10 μ from some grain boundaries.

2) Short cracks propagated across and occasionally away from the boundary on a transgranular path whose direction was influenced by the normal stresses in the specimen.

3) Intergranular cracks were initiated without apparent accompanying plastic deformation.

4) The appearance of damage between a grain pair seemed to require a high angle of misorientation between the grains. No difference in orientation relationship was found
consistently between pairs showing short grain boundary markings and those showing intergranular cracks.

5) Propagation from both types of initial crack followed either a transgranular path associated with severe plastic deformation or an intergranular path.

6) Cracks frequently changed their path and became branched beneath the specimen surface.

d) 48.25 at.% Zinc.

a) Room Temperature. An attempt was made to study the relative orientation of grains showing intense short slip markings on their common boundary following fatigue at room temperature. This alloy exhibited a greater tendency for intergranular crack initiation than that containing 46.95 at.% zinc and the study was carried out on specimens of the latter composition, as described.

Crack initiation in short slip markings was observed following at room temperature, Fig. 158. The initial cracks share the same surface trace as the slip markings within the grain, which are probably therefore {110}. Cracks propagated transversely across the specimen on a microscopically random path associated with considerable plastic deformation, Fig. 159. Straight traces characteristic of type 3 cracks were not observed following fatigue at room temperature.
Summary

1) Intergranular cracks (type 4) and short grain boundary cracks formed in intense slip markings next to grain boundaries (type 2) were initiated during fatigue of the 48.25 at.% zinc alloy at room temperature.

2) Crack propagation was associated with considerable plastic deformation, and paths showed no tendency to form straight traces.

b) Fatigue at 77°K. Specimens appeared to be more resistant to fatigue when tested at 77°K than at room temperature. This impression was not confirmed quantitatively, although lives were generally in excess of $5 \times 10^6$ cycles. Fatigue deformation at low temperature not only changed the appearance and distribution of slip traces, but also the type of initial crack and its mode of propagation. Cracks were positively identified by sectioning normal to the specimen surface.

Two types of crack were formed initially:

1) Isolated long straight transgranular cracks always initiated at grain boundaries and accompanied by little plastic deformation, (type 3), marked (3), Fig. 161 and,

2) groups of closely spaced parallel cracks initiated from grain boundaries and unaccompanied by intense slip
markings, (type 1), marked (1), Fig. 161.

The distinction between these two types is arbitrary, since surface traces varied in length from a few microns, Fig. 162 to several hundred microns, Fig. 163. Isolated crystallographic cracks were frequently observed, Figs. 161 and 164. They were usually initiated either at triple points, Figs. 161 and 163 or where a grain boundary changed direction, crack (A), Fig. 164. Two surface analysis of these cracks showed that they were formed on \{110\} planes, Table 9 and Fig. 165.

Groups of parallel cracks were initiated at the grain boundary along which they formed, Figs. 161 and 166. Sectioning these regions normal to the specimen surface, e.g. along the line C-C', Fig. 161, showed that cracking was associated with considerable quantities of transformation product which appeared pink on etching in alcoholic ferric chloride solution, Fig. 168. Although some of these regions certainly contained cracks, the narrower markings did not. Comparison of traces on the two surfaces showed that the longer specimen surface traces were formed by true cracks, while the shorter markings were produced by transformation alone.

Markings 8 - 10 \( \mu \) in length were observed on the specimen surface along a grain boundary, Fig. 170.
This region was sectioned parallel with the broken line in Fig. 170 and showed what appeared to be parallel plates of transformation product. Selected area replica electron microscopy confirmed this view, Fig. 169. Each marking on the specimen surface corresponded with a marking on the section surface, indicating that the product was composed of parallel plates. Limited transformation occurred in the second grain, consistent with the very short markings on the specimen surface.

The habit plane of these plates relative to the $\beta'$-matrix was determined by two-surface analysis. Because of the small area of the grain in which the markings formed on the specimen surface, a Laue back-reflection photograph was taken from the section surface. The method of analysis, using this example, is given in Appendix B. The pole of the plates was found to lie 6 degrees from the $<100>$ zone and 2 degrees from the $<011>$ zone, corresponding very closely with $\{2\,1\,1\,1\,2\}_\beta$, the habit previously reported for martensite in this system, $(104)$.

Cracks frequently formed at acute angles to grain boundaries, Figs. 163 and 171, and a number of different crack trace orientations were observed within one grain, Fig. 167. The angles between cracks and grain boundaries were
measured and plotted on a histogram, indicating the frequency of observation, $f$, of cracks of a given angle to the boundary. Similar plots were made for the 46.95 and 42.5 at.% zinc alloys after fatiguing at room temperature. These results are shown in Fig. 173.

Cracks propagated on a transcryrstalline path showing straight surface traces and little associated plastic deformation, Fig. 164. Sectioning showed that these paths were not associated with transformation product. More random crack paths were observed, Fig. 172, but these also showed an arrangement of flat facets. Crack propagation along grain boundaries was infrequent, Fig. 174, and cracks showing straight facets were observed to propagate through grain boundaries, with little tendency to form intercristalline branches, Fig. 175.

Most crystallographic crack facets showed protrusions of dark material, Fig. 176. In common with the behaviour of specimens of other compositions, dark granular material was thrown onto the specimen surface in the neighbourhood of cracks, Fig. 177.

Summary

1) Only groups of parallel cracks, (type 1) and straight crystallographic cracks, (type 3), both unaccompanied
by intense plastic deformation were initiated during fatigue of the 48.25 at.% zinc alloy at 77°K.

2) A plate-like transformation product was found associated with short markings originating from some grain boundaries. The habit plane was determined as \{2112\}_\beta.

3) Crack propagation took place largely on straight transgranular paths, having \{110\} orientations, although occasional intergranular cracks were also observed.

4.1.4 Hardness and Tensile Test Results.

The hardness of quenched and electropolished samples of \(\beta'\)-copper-zinc in the composition range 48.25 - 42.5 at.% zinc was determined using a Vickers diamond pyramid machine with 5 kg. load. Values are shown plotted in Fig. 160. Despite a scatter of values of \(\pm 5\) points, the results show that the hardness increases with decreasing zinc content from a minimum value of 106 Hv.\(_5^\) for the 48.25 at.% zinc alloy to 117 Hv.\(_5^\) for the 42.5 at.% zinc alloy.

In order to correlate fatigue behaviour with mechanical properties, in particular ductility, specimens were fractured in tension, using an Avery 2000 kg. hydraulic machine, and values of ultimate tensile strength and elongation were recorded. The form of the tensile specimens is indicated
Two alloys were tested:
48.25 at.% zinc at 293°K and 77°K, and
39.8 at.% zinc at 293°K only.
Results are given in Table 10. For the
48.25 at.% zinc alloy elongation values were consistently lower,
and ultimate tensile strength values consistently higher during
testing at 77°K than at 293°K. The 39.8 at.% zinc alloy
showed consistently lower elongation and ultimate tensile
strength values than the 48.25 at.% zinc alloy when tested at
room temperature.

4.2 \( \beta' \)-Gold-Zinc
Specimens were fatigued after mechanical
polishing to 1 \( \mu \) grade diamond and also after electropolishing.
No difference was found in the distribution of fatigue slip
damage or crack paths after these two methods of preparation.
In order to determine the effect of temperature on the appearance
of fatigue slip markings and on crack propagation, specimens
were fatigued at room temperature and at liquid nitrogen
temperature.
4.2.1 Fatigue Slip Traces

a) Room Temperature. After a few hundred cycles, the position of some grain boundaries could be determined as a result of the rumpling of the specimen surface, Fig. 178. As cycling proceeded slip markings were formed on the surface. These markings took the form of lines, Fig. 179, bands, Fig. 180, or "packages", Fig. 181.

Slip lines were rarely straight, through a few such traces were observed, usually in association with grain boundaries, Fig. 182. Short slip lines on both sides of grain boundaries were not uncommon, Figs. 184 and 185. Very intense slip markings were observed associated with some grain boundaries, Figs. 186 and 187. Micrographs of the latter region under oblique illumination showed that bands of intense plastic deformation were raised above the specimen surface, Figs. 188 and 189.

An indication of anisotropy in the deformation characteristics was obtained by setting a Vickers diamond indent at a grain boundary, using a 5 kg. load, Fig. 183. One grain appears to have deformed more - or recovered, elastically, less - than the other.

After prolonged fatigue deformation, without altering the strain amplitude, new bands were seen to grow, and
those existing, to lengthen. The lengthening of a series of slip packages arising at a grain boundary was also observed, Fig. 190 after $3.5 \times 10^7$ cycles and Fig. 191 after $4.8 \times 10^7$ cycles. These regions had sharp boundaries, and increased in size apparently by the addition of new segments.

Slip bands running across grains were frequently observed, Fig. 192. Replica electron microscopy showed that slip traces were quite wavy and showed little tendency to contain any straight sections, Figs. 193, 194, 195 and 196. Slip appeared to be quite severe within the bands, Fig. 197, which were found to protrude from the surface by observation under oblique illumination, Fig. 198. Bands may be seen to be illuminated on the side facing the light source.

A number of regions showing fatigue slip bands were investigated by interferometry. The height of bands above the surface was calculated from the formula:

$$\text{Vertical height} = \frac{\lambda \cdot D}{2 \cdot W}$$

where $\lambda$ is the wavelength of sodium light (5890 Å), $D$ the lateral displacement of the fringe and $W$ the fringe width. Fig. 199 shows the general appearance of the displacement pattern on the surface of a crystal showing fatigue slip bands. Fig. 200 shows a series of parallel slip bands, the displacements of which have been calculated. Band heights at A, B,
Most bands were bounded by a slight depression on one side, indicated by a displacement of the fringes in the opposite sense to those on the bands, e.g. the band containing points C and D, Fig. 200. The ends of bands also seemed to be associated with a depression in the specimen. The irregular shape of the fringes on the larger slip bands indicates that they were composed of a number of segments, each contributing to the displacement above the specimen surface.

Some grains contained long and fairly straight bands and an attempt was made to relate the trace of such bands to the crystal orientation. Using the longitudinal axis of the specimen as the fiducial line N - S, the orientations of two crystals were obtained from Laue back-reflection x-ray photographs, crystal 1, Fig. 201 and crystal 2, Fig. 203. The back-reflection photograph from crystal 1 is shown in Fig. 205. Spots were rather diffuse, presumably as a result of the plastic deformation during fatigue.

In each case, the orientation of a typical band, marked "S", was measured relative to the specimen axis. The orientation of crystal 1 is shown in Fig. 202,

C and D were 0.7, 0.3, 0.75 and 4.2 μ respectively.
giving the 001 and O11 poles. The trace of the slip band in the surface, marked "band surface trace", (B.S.T.), is drawn on the projection. The pole of the surface trace must lie on the line marked "band pole trace" at right angles to this. This pole trace passes close to the pole O11, Fig. 202. Since β' -gold-zinc is known to slip on the {011} plane in the <001> direction, it was assumed that slip on the plane (011) must have contributed to the formation of the observed bands.

Dislocations slipping on the (O11) plane in the [100] direction can cross slip only on the (011) plane. The angular limits of slip traces formed by any combination of slip increments on the (011) and (011) planes are given by the arcs A - B and A' - B', Fig. 202. The line AA' is the trace in the specimen -surface of the plane (O11) and the line BB' the trace of the plane (O11). The orientation of all traces in the bands of the type "S" falls within these limits, Fig. 201. The formation of these bands is consistent with slip occurring on the planes (O11) and (011).

A similar analysis for the bands marked "S" in crystal 2, Fig. 203 (501) is shown in Fig. 204. In this case the surface trace angle of the bands is consistent with
slip on the planes (101) and (010) in the [010] direction. The straightness of most of the bands, together with the fact that they lie, in general, nearer to the trace AA', Fig. 204, is believed to indicate that the bands are largely composed of slip increments on the (010) plane, the contribution from the cross slip plane (101) being smaller.

(b) Fatigue at 77°K. The formation of fatigue slip markings was completely suppressed by reducing the temperature of testing to 77°K, although some rumpling of the specimen surface occurred. The resistance to fatigue deformation appeared to increase, indicated by the additional power from the amplifier necessary to produce extensive cracking.

Summary

1) During fatigue at room temperature intense slip markings formed both in association with and remote from grain boundaries.

2) Slip traces were almost always wavy.

3) The surface traces of parallel intense bands were found to be consistent with slip taking place on two {110} planes having a common <100> direction.
4) The formation of intense slip damage was completely suppressed by testing at 77°K although some surface rumpling was observed.

4.2.2. Crack Nucleation and Propagation

a) Room Temperature. The general distribution of cracks in a mechanically polished and an electropolished specimen is shown in Figs. 206 and 207 respectively. In each case the crack propagated from the specimen edge and was associated initially with a grain boundary. Both specimens revealed a marked tendency for cracks to be associated with grain boundaries, but in neither case was it possible to state that cracks were initiated only in an intergranular manner. Part of the difficulty lay in identifying cracks in regions of intense slip. For example, no crack was observed in the grain boundary surrounded by intense slip markings, Fig. 187, even though intense rumpling of the specimen surface had occurred, Fig. 208. Rumpling of the surface in this way gave rise to shadows at grain boundaries which had the appearance of cracks, when viewed in an optical microscope. In general, observation of the specimen during rotation under oblique illumination was capable of determining unambiguously that no crack existed.
Occasionally, however, lines at grain boundaries did not disappear during rotation, suggesting the presence of a crack, Fig. 209.

The possible existence of cracks associated with intense slip markings within grains was investigated by fatiguing, followed by electropolishing. Fig. 210 shows an area of intense slip markings, while Fig. 211 shows the same area following 20 seconds electropolishing. No cracks were visible within the grain after polishing, but considerable surface rumpling was evident.

The association of cracks with intense slip markings is also apparent in Fig. 212. Parts of the region of intense slip are shown in Figs. 214 and 215. It is likely that these slip markings were produced by the propagation of the crack and do not represent crack initiation points. Electropolishing this specimen showed that the region in which markings were most intense contained cracks, Fig. 213.

Transgranular crack paths were associated with considerable plastic deformation, Figs. 206 and 207, and showed little tendency to lie along specific crystallographic directions. However, the initiation of straight cracks was also observed, Fig. 216.
The propagation of this crack was probably fairly slow, since slip markings and very small steps may be seen along its length.

b) Fatigue at $77^\circ$K. The specimen edge remained as the preferred site for crack initiation during fatigue at low temperature. However, propagation was not observed to be principally associated with grain boundaries, Fig. 217. The point of crack initiation was not specifically determined, since cracks were either initiated at the specimen edge, Fig. 218, or showed fairly random paths crossing boundaries, Fig. 219.

An increased tendency for propagating cracks to form straight parallel facets was observed for specimens fatigued at low temperature. Fig. 220 shows the crack marked "A" in Fig. 217. The main crack contained a number of facets, not necessarily parallel with each other. No flat fracture faces comparable in size with the grain diameter were observed. Crystallographic cracks did not propagate far from the initiation point, and cracks generally showed fairly random paths, probably associated with plastic deformation, Figs. 218 and 219.

Summary

1) The nature of crack nucleation sites in $\beta'$-gold-zinc
was not positively identified for fatigue at room temperature or $77^\circ$K.

2) Following fatigue at room temperature, crack paths were observed to be associated with grain boundaries and with regions of intense slip.

3) Cracks formed during fatigue at $77^\circ$K were always associated with a grain boundary at some point.

4) Crack paths at $77^\circ$K showed some straight crystallographic surface traces but usually random paths associated with plastic deformation.

4.3 Iron-Cobalt-Vanadium

The average grain diameter of both ordered and disordered specimens was about 0.1 - 0.2 mm., so that about 25 - 50 grains made up the specimen width. As a result it was possible for cracks in the surface of the specimen to grow 2 - 3 grain diameters long without disturbing the resonance conditions of the specimen.

4.3.1 Slip Traces

A clear difference was found in the distribution of fatigue slip damage between ordered and disordered specimens.

a) Disordered Specimens. Intense dark bands of slip,
similar to those reported on $\alpha$-iron, spread across some grains, Figs. 221 and 222. These markings could not easily be resolved using optical microscopy, but their nature suggested that they were regions of intense cross slip, Fig. 223. While slip was observed to spread across some grains of the disordered alloy, damage was often initiated and localised at grain boundaries, Fig. 224. This micrograph shows the two distinct types of slip trace observed in the disordered alloy. The intense dark markings probably resulted from the cyclic motion of dislocations, characteristic of fatigue damage, while the wavy slip steps were probably associated with asymmetric bending of the specimen, either during the first cycle of fatigue deformation, or more probably, as a result of the fracture of the specimen taking place on one side only during the last half-cycle of deformation, leading to high bending stresses in unbroken grains. Other examples of this effect were observed, Figs. 225 and 226. The appearance of these traces indicates that cross slip is easy in the disordered alloy, and implies that slip intensification by such a mechanism should also not be difficult. Replica electron micrographs, Figs. 227, 228 and 229 show that the intense slip markings are wavy and do not reveal a
preference for slip on any specific set of planes.

Regions of intense slip occurred on one or both sides of some grain boundaries, Figs. 231 and 232. Slip markings usually extended up to the grain boundary, but occasionally a strip less than 1 µ in width could be observed at the boundary itself, Fig. 230.

b) Ordered Specimens. These showed relatively little damage on the specimens' surface, even after final failure. Fatigue slip damage was limited to narrow regions of intense slip next to occasional grain boundaries, Fig. 233. The same region is shown in Fig. 234 and in the electron micrograph, Fig. 235. Regions of intense slip formed along the boundary, but tended to occur as "packages" of damage. The nature of these slip packages is more clearly shown in Fig. 236, marked "A" in Fig. 234. Extrusions, intrusions or small cracks, indicated by the shadowed contrast on the relic, are associated with regions of intense slip.

Similar regions of short markings next to grain boundaries were observed in which a strip along the boundary remained relatively free of markings, Figs. 237, 238 and 239. The distribution of slip in Fig. 238 has arisen from stress relaxation along two grain boundaries at a
triple point, leading to stress concentration and slip within two of the grains. Asymmetric bending as a result of the fracture of the specimen produced only straight slip traces remote from the fracture faces. Straight slip traces were not observed on the specimen surface prior to the propagation of the main crack.

Summary

1) Disordered specimens showed dark fatigue slip damage both remote from and associated with grain boundaries.
2) Ordered material exhibited only very localised fatigue slip damage, always associated with grain boundaries.
3) In both cases replicas of this damage showed wavy surface traces when viewed in the electron microscope.
4) Wavy slip traces in disordered material, and straight slip traces in ordered material were observed following asymmetric banding of the specimen during fracture.

4.3.2 Crack Nucleation

Both inter- and transgranular cracks in the order of 1 - 2 grains long formed easily in disordered specimens, and appeared to be associated with regions of fatigue slip damage, Fig. 240. The high density of cracks
formed near the specimen edge indicated in this micrograph points to crack propagation as the rate-controlling factor in the final failure of the specimen. Some evidence of the importance of specimen shape in determining the distribution of fatigue damage is indicated in this micrograph. The regions of the surface near the specimen edge always showed a greater concentration of damage than the centres of the flat faces, indicating the existence of a stress gradient transversely across the specimen.

Both in the ordered alloy, Figs. 234 and 241 and the disordered alloy, Figs. 230, 232 and 242 the association of fatigue damage with grain boundaries gave rise to intergranular cracks, as far as could be determined. In disordered specimens no cracks were specifically observed to have been initiated only as the result of slip intensification within the grains.

Fig. 236 points to this mechanism as a possible source of micro-cracks or intrusions in the ordered alloy. But on no occasion could the source of fracture be identified as a region of fatigue slip damage after final failure of an ordered specimen. This was due to the initiation of a rapidly propagating crack from the specimen edge before the development of appreciable fatigue damage on the surface of the specimen.
Summary

1) Cracks appeared to be nucleated intergranularly in the disordered alloy, although the possibility of crack initiation through the intensification of fatigue slip damage cannot be excluded.

2) Grain boundaries and intense slip bands associated with grain boundaries both provided possible sources for the initiation of fatigue cracks in the ordered alloy. The initiation of the single crack causing final failure did not appear to be associated with fatigue processes.

4.3.3 Crack Propagation

Both disordered and ordered specimens eventually failed by the rapid passage of a cleavage crack transversely across the specimen at right angles to the tensile stress produced by bending.

a) Disordered Specimens. Initially these developed cracks which propagated only slowly, Fig. 240. The propagation of these cracks was associated with a considerable amount of plastic deformation at the crack tip, Fig. 242. The orientation of the crack in Fig. 242 is indicated relative to the longitudinal axis of the specimen, marked "N–S".
After the nucleation of the crack, propagation took place on a mixed inter- and transgranular path, Fig. 240. Transgranular propagation started when an initially intergranular crack reached a triple point. Transgranular cracks did not propagate rapidly initially. Final failure always occurred by the rapid propagation of a cleavage crack.

b) Ordered Specimens. Specimens of the ordered material showed no microcracks more than a grain diameter in length after the specimen had failed by the rapid propagation of a cleavage crack, Fig. 243. The source of this cleavage crack was not positively identified, but such cracks propagated from the edges of specimens.

Although propagation took place in one half-cycle of deformation, cracks produced deformation by slip, particularly when meeting an obstacle, Fig. 244, marked (A) in Fig. 243. The obstacle in this case may have been a grain of unfavourable orientation in the path of the propagating crack. The stresses were sufficiently high to produce intense cross slip and some rumpling of the surface as the crack changed direction. The direction of crack propagation is indicated in Fig. 243 by an arrow.

At (B), Fig. 243, a bridge formed across the crack,
and also a second crack parallel with the principal crack, Fig. 245. The fracture surface of this grain indicates how this bridge was formed, Fig. 246. The crack entered the grain below the specimen surface, from the left hand side, and the bridge was formed by the propagation of two closely parallel cracks, separated by a cleavage step.

**Summary**

1) Slowly propagating fatigue cracks have been observed in disordered iron-cobalt-vanadium. None was observed in the ordered material.

2) In both ordered and disordered material final failure took place by the propagation of a cleavage crack with relatively little associated plastic deformation.

4.4. **Iron - Aluminium (Fe₂Al)**

Specimens of ordered and disordered iron - 23.5 at.% aluminium were fatigued at room temperature and at 77°K.

4.4.1 **Fatigue Damage**

a) Room Temperature. No fatigue slip markings were formed on the surface of this material remote from the grain boundaries
in either the ordered or disordered state. Only after partial failure of a specimen could slip be observed, and this was believed to be the result of stress intensification following asymmetric bending of the specimen, Fig. 24-7.

Cracks in disordered specimens were always initiated in grain boundaries, Figs. 249 and 250. Fig. 249 shows three initiation points in the same boundary. Fig. 250 shows broadening of the markings at the boundary, which is shown in detail in Fig. 251. Short slip markings 2 – 3 μ long have been produced on one side of the boundary, but it was not possible to resolve any crack within the boundary itself.

In an attempt to determine whether the region near grain boundaries was associated with an increase in hardness, which might have been linked with the observed intergranular brittleness, rows of microhardness were made across grain boundaries of a disordered specimen, using a GKN microhardness tester with a 3 gm. or 10 gm. A typical series is shown in Fig. 248. No consistent variation in hardness values was detected. Apparently random variations in individual values occurred, and the method was considered insufficiently sensitive, and abandoned.
A similar crack initiation mode was observed in the ordered alloy fatigued at room temperature, Fig. 253.

Fig. 252 shows the grain boundary at "A", Fig. 253. A crack appears to lie very close to or in the boundary which is bordered by a narrow band of fine slip markings 2 - 3 μ long. Other markings 4 - 8 μ in length and normal to the boundary are also visible.

In both the ordered and disordered alloys cracks propagated along grain boundaries to triple points from which transgranular propagation could follow, Figs. 253, 254. Transgranular propagation was sometimes slow and associated with considerable deformation and zig-zagging of the crack path, Figs. 255 and 256. Complete fracture of a specimen was sometimes rapid however, and apparently associated with little plastic deformation, Fig. 257.

Often cracks produced dark granular material from the region away from the crack tip, but insufficient could be collected for examination. This was thought to be attrition product, Figs. 258, (9\times10^6 cycles) and 259, (12.6\times10^6 cycles). Final failure of the specimen usually occurred by the cleavage fracture of one or two grains on part of which propagation of a slow fatigue crack could be observed, Fig. 260.
If each ripple on this face is caused by one fatigue cycle, this crack propagated at about 2.5 mm./second, each ripple being spaced about 5 µ from the next.

Summary

1) No intense slip damage was formed in the regions remote from grain boundaries in ordered and disordered specimens.

2) Cracks were initiated intergranularly and were sometimes associated with fine slip markings normal to the boundary.

3) Crack propagation was governed by the normal stress distribution in the specimen and followed intergranular and transgranular paths, some of which showed associated plastic deformation.

b) Low Temperature. Since all cracks were initiated intergranularly at room temperature, fatigue at low temperature was investigated to determine the effect on crack initiation. Specimens were more resistant to fatigue stressing at 77°K than at room temperature, since it was found that barely enough power was available from the amplifier to produce fracture. Both ordered and disordered
specimens exhibited similar behaviour. No slip markings of any sort were observed. Fatigue cracks were initiated in the grain boundaries, Figs. 262 and 263. However, in both alloys the mode of propagation was changed relative to that at room temperature in that straight crystallographic non-branching cracks were formed from those initiated in the boundary, Figs. 264 and 265. Despite the presence of relatively large cracks no specimen failed completely, even after $10^7$ cycles, Fig. 265. All cracks, but particularly those in the ordered alloy, were associated with exudation of dark granular material, Figs. 261 and 265.

**Summary**

1) No slip traces were observed on the surface following fatigue stressing at $77^\circ$K.

2) Cracks were initiated intergranularly in both ordered and disordered specimens.

3) Crack propagation was slow and occurred on either intergranular or straight transgranular paths.

4.5 *Fracture Surfaces*

The nature of fracture surfaces was examined to
provide additional information on fatigue crack propagation. The orientation of flat fracture facets was determined by Laue back-reflection x-ray photographs to investigate the possibility of a change in crack habit plane with composition or changing degree of long-range order. All fractures were produced by fatigue deformation, except in the iron - 49 at.% aluminium alloy, single crystals of which were cleaved at 77^0K using a chisel.

4.5.1 \( \beta'\)-Copper Zinc

a) 42.5 at.% Zinc. The fatigue fracture surfaces of specimens of this composition showed large planar facets consistent with the formation of straight crack traces on the specimen surface, Fig. 105. Typical single crystal fracture facets are shown in Figs. 266 and 267. Both surfaces are partially obscured by dark granular material, which was found to adhere to the fracture surface, and was difficult to remove. It was not possible to collect sufficient to carry out a structure determination by an x-ray powder photograph. Scraping would certainly lead to the removal of some of the metal surface, and also to the formation of martensite by deformation.

The direction of crack propagation (from right to
left) is indicated in Fig. 266 by the convex crack front. The two pronounced curves are believed to have been formed when the specimen ceased vibrating and had to be tuned to a lower signal frequency, as a result of the fall of resonant frequency with progressive damage.

The Laue photograph taken from the facet in Fig. 266 is shown in Fig. 268. Spots are somewhat diffuse, probably indicating plastic deformation, during or after the formation of the fracture face. The orientation is \( \{110\} \). The orientations of fracture faces of all alloys determined by back reflection photographs are listed in Table II.

b) 46.95 at.% Zinc. No large fracture facets were observed in specimens of this composition, consistent with the absence of straight transgranular crack traces on the specimen surface. Fracture surfaces showed a considerable number of large steps, Fig. 269, or were non-planar, Fig. 270. No fracture surfaces sufficiently planar for orientation by means of Laue photographs were observed.

c) 48.25 at.% Zinc. Following room temperature fatigue, fracture surfaces were either highly irregular and associated with frequent changes in direction of the propagating crack, Fig. 271, or showed large areas of
intergranular fracture, top left, Fig. 272.

Following fatigue at 77°K fracture surfaces were found to be composed of large flat facets which were black when examined macroscopically. Microscopic examination showed that all faces were covered with an adherent coat of granular material, Figs. 273 and 274. Much more of this material was observed following fatigue of 48.25 at.% zinc specimens at 77°K than on 42.5% zinc specimens fatigued at room temperature, Figs. 266 and 267.

4.5.2 β'-Gold-Zinc

Fatigue at room temperature produced inter- and transgranular fracture faces, Figs. 275 and 276. Transgranular paths showed frequent changes of direction and no flat facets were observed.

Fatigue at 77°K produced a few flat facets, Fig. 277, but these were very small and could not be oriented by back-reflection Laue photographs. Transgranular fracture surfaces showed that the crack front did not lie in one plane, Fig. 278. Some intergranular regions were also observed, near the specimen surface, Fig. 279.

4.5.3 Iron-Cobalt-Vanadium

Disordered specimens showed intergranular fracture surfaces near the initiation region at the edge of the specimen, Fig. 280. Spots on this fracture surface were probably carbide particles. Remote from the region
of initiation of the single crack causing final failure
surfaces typical of rapid cleavage crack propagation were
observed, Fig. 281. Backreflection photographs showed
that the cleavage plane was \{100\}. Laue spots were sharp,
indicating that propagation of the cleavage crack was
accompanied by little plastic deformation.

Ordered specimens showed no intergranular
fracture, but only faces typical of rapid cleavage crack
propagation, Figs. 246 and 282. These show the
fracture surfaces of grains (A) and (B) respectively, Fig. 283.

The orientation of grain (A) relative to
the specimen surface was determined as very nearly \{100\}.
from a back-reflection photograph, Fig. 284. The sharpness
of the Laue spots was typical for photographs taken from
fracture faces, indicating that little plastic deformation
accompanied the propagation of the crack. The fracture
surface, Fig. 246, was observed to be normal to the specimen
surface, and a \langle100\rangle zone normal to the fracture surface.

The orientation of the fracture surface of
grain (B) was determined by analysis of measurements of
the relative angles of slip traces, known to be \{110\} in
the ordered alloy, to each other and to the fracture surface,
on a stereographic projection. Three sets of slip traces on the specimen surface are shown in Fig. 285. The lower traces in Fig. 285 corresponded with those on the specimen edge, Fig. 286, and allowed the orientation of the grain to be fixed.

4.5.4 Iron-Aluminium

a) Iron-25.5 at.% Aluminium. Disordered fatigue specimens showed intergranular fracture faces, Fig. 287, and large flat transgranular facets, Figs. 260 and 288. A back-reflection Laue photograph of the latter transgranular face is shown in Fig. 289. Spots were rather diffuse, indicating that fracture was accompanied by plastic deformation, consistent with the observation that fracture faces were not formed by the catastrophic propagation of a cleavage crack, and with the appearance of the fracture surface in Fig. 288. Contrast in the photograph was low, because of fluorescence produced by the use of radiation from a copper target with specimens containing iron. The orientation was \{100\}.

Ordered fatigue specimens showed fewer areas of intergranular fracture, and transgranular fracture surfaces often showed curving crack fronts, produced as the crack stopped and was restarted, Fig. 290. The back reflection
photograph showed it to be \{100\}.

b) Iron--49 at.% Aluminium. The ingot of this alloy, containing grains up to 5 mm. in diameter, was extremely brittle, and broke into single crystals without difficulty. These crystals were clamped at one end in a vice, cooled with liquid nitrogen, and given a sharp blow with a chisel. Under these conditions cleavage fracture was not difficult to produce.

Fig. 291 shows part of the fracture surface of such a crystal. Back-reflection Laue photographs from a number of crystals, consistently showed that the fracture plane was \{111\}. Fig. 291 also shows the three \{110\} traces in the fracture plane. A large proportion of the markings of the fracture surface correspond with these directions, and may therefore be formed on intersecting \{111\} planes. A typical back-reflection photograph is shown in Fig. 292. Spots were diffuse, and contrast lessened by fluorescence.
5. DISCUSSION

5.1 \( \beta'\)-Copper-Zinc

5.1.1 Slip in \( \beta'\)-Copper-Zinc. The present results show qualitatively that cross slip is more frequent — and therefore, presumably, easier — in alloys near the equiaxed composition than in copper-rich metastable alloys, during deformation at room temperature. Also, cross slip in a 48.25 at.% zinc alloy is less frequent during deformation at 77°K than at room temperature. Edge dislocations are only able to leave their slip plane by climb, so that only dislocations of screw orientation will be considered in this discussion.

For reasons discussed in Section 2.6 cross slip occurs very easily in metals possessing the A2 structure, providing that the temperature of deformation is not too low. The plane on which screw dislocations move in this structure often appears to be that containing the maximum shear stress in the most favourably oriented \(<111>\) zone.

Although the existence of superdislocations in \( \beta'\)-copper-zinc has not been specifically established by
transmission electron microscopy, the fact that slip takes place in the $<111>$ direction, despite the existence of a highly ordered structure below $400^\circ$C, points to the existence of pairs of $\frac{1}{2}a_o <111>$ dislocations, (157).

Theories of the deformation of crystals possessing the B2 structure (Section 2.7.4) emphasise the importance of the spacing of superpartials on the occurrence of cross slip.

Crystals of high ordering energy slip in the $<100>$ direction by the movement of $a_o <100>$ dislocations. These dislocations are unit perfect dislocations in the ordered lattice, and are free to cross slip in a similar manner to $\frac{1}{2}a_o <111>$ dislocations in the A2 structure. Since the observed slip direction in $\beta'$-copper-zinc is $<111>$ and not $<100>$, cross slip traces in $\beta'$-copper-zinc cannot be produced by the movement of $a_o <100>$ dislocations.

Marcinkowski and Brown 1961 (152) and Stoloff and Davies 1964 (146) have shown that cross slip can occur in B2 structure alloys which slip in the $<111>$ direction, by the movement of $\frac{1}{2}a_o <111>$ imperfect dislocations. The movement of these dislocations involves the generation of a trail of disorder, and is only possible if sufficient energy is available not only to deform the
crystal but also to create additional antiphase boundary in the lattice. Cross slip in this way has been observed in iron-25 at.% aluminium at low stresses, (152) and in iron-50 at.% cobalt at higher stresses, (147).

The independent movement of \( \frac{1}{3}a_o <111> \) superpartials in the ordered structure can be confirmed by the observation of dislocations trailing a sheet of antiphase boundary. No such observations have been reported for \( \beta' \)-copper-zinc, and the magnitude of the spacing of superpartials must be estimated by indirect methods.

Attempts at estimating the separation of superpartials in \( \beta' \)-copper-zinc have been made by Brown and Herman 1956 (151) and by Marcinkowski 1963 (122). Calculations are based on estimation of the elastic strain energy of the two superpartials and of the energy of the antiphase boundary between them.

Assuming isotropic elastic theory, the spacing \( r \) of superpartials in a superdislocation is given by:

\[
r = \frac{a_o^2 \sqrt{2} G b^2}{2 \pi k T_c S^2} \left[ \sin^2 \theta + \cos^2 \theta \right] (122)
\]

where, \( a_o \) is the lattice parameter of the structure, \( G \) the shear modulus of the material, \( b \) the Burgers vector of the dislocation, \( k \) Boltzmann's constant, \( T_c \) the critical
ordering temperature, \( S \) the degree of long range order in the structure, \( \Theta \) the angle between the slip direction and the Burgers vector of the dislocation, \( (90^\circ \text{ for screws, } 0 \text{ for edges}) \), and \( v \) is Poisson's ratio.

In structures of similar lattice parameter, the spacing of superpartials of the same type can only be affected by \( T_c \), the critical ordering temperature, \( G \) the shear modulus and \( S \) the degree of order.

A major difficulty in estimating the separation of superpartials in real crystals is that the above relationship is only valid for conditions of isotropic elasticity. Since the shear modulus of \( \beta'\)-copper-zinc varies by almost an order of magnitude with direction in the lattice, Fig. 296, quantitative estimations of the spacing must be suspect. Brown and Herman 1956 (151) using a value for \( G \) of 0.3 \( \times 10^{-12} \text{ dynes/cm.}^2 \) estimated the separation of edge superpartials to be 30 Å. The equivalent value for screws is 20 Å, taking \( v \) as 0.33.

Marcinkowski 1963 (122) estimated the separation of edge and screw superpartials in \( \beta'\)-copper-zinc to be 88 Å and 56 Å respectively. Although the details of this calculation are not given, it presumably involved the use of a higher value for the shear modulus than used by Brown and Herman 1956 (151). In an isotropic elastic
medium the shear modulus $G$ is given by $1/s_{44}$, which gives a value of $0.745\times10^{12}$ dynes/cm$^2$. According to the results for $\beta'$-copper-zinc of Artman and Thompson 1956 (89), Table 5, (see also Appendix A).

Since the distortion necessary to create a $\frac{1}{2}a_0 <111>$ dislocation, whether of edge or screw character, is in the <111> direction in the crystal, it is also arguable that the value of $G_{<111>}$ could be used in estimating the superpartial spacing. Table 12 gives values of $T_c$, $G_{<111>}$, $S_{max}$, and $G/T_c S_{max}^2$ for alloys of interest in this investigation. The value for $T_c$ for $\beta'$-gold-zinc is only an estimation and the value of $G_{<111>}$ given for iron-50 at.% cobalt and iron-25 at.% aluminium is that of $\alpha$-iron, (108). If these values are qualitatively accurate, the separation of superpartials in $\beta'$-copper-zinc is considerably smaller than the separation in iron-cobalt, for which calculated and experimental values agree, (147), and approaches that for $\beta'$-gold-zinc. However, $\beta'$-gold-zinc slips in the <100> direction, and it is presumed that pairs of $\frac{1}{2}a_0 <111>$ superpartials are unstable. This implies that the separation of superpartials in $\beta'$-copper-zinc is low, and may be near the minimum for slip in the <111> direction. Further, the calculated charge in each polyhedral cell in $\beta'$-gold-zinc is reported as 0.058 eV/atom, (11), while the corresponding value
for $\beta^\prime$-copper-zinc is 26% smaller, (73). This relatively small difference implies that the antiphase boundary energy is of a similar order of magnitude in the two alloys.

If these considerations are correct, i.e. superpartials in $\beta^\prime$-copper-zinc are closely spaced, the mechanism of cross slip must be approached from a new viewpoint. It is proposed that cross slip of a pair of \( \frac{1}{2}a_0\langle111\rangle \) superpartials should become easier as their separation approaches very low values. Cross slip in this way would involve both partials following atomically identical paths through the lattice, so that the trailing dislocation recreates order destroyed by the leading dislocation. If this does not happen, and the superpartials follow different paths, the dislocation pair would appear as in Fig. 28 D, and will be rapidly halted by the double sheet of antiphase boundary. Reactions of this type are believed to be responsible for the rapid work-hardening in Stage II and the suppression of cross slip, in ordered iron–cobalt alloys, (147).

Since a dislocation which destroys antiphase boundary must experience a gain in energy, the antiphase boundary trail left by the leading superpartial must form a preferred path for the trailing dislocation. If the superpartial separation is small, it is likely that both dislocations will follow the same path on an atomic scale.
It should be noticed that this mechanism does not require the coalescence of the superpartials to form a single \( a_0 \langle 111 \rangle \) dislocation for cross slip to occur, unlike the mechanism proposed by Seeger 1957 (169) for cross slip in the Al structure.

An additional factor favours the close approach of superpartials in elastically anisotropic crystals. Isotropic elastic theory predicts that screw dislocations possess no dilatation field. However, Chou 1965 (263) has shown that screw dislocations in an elastically anisotropic medium do possess a dilatation field, the magnitude of which increases with elastic anisotropy. This field possesses three-fold symmetry about the \( \langle 111 \rangle \) direction and consists of alternate sectors of expansion and contraction, in \{110\} planes. This factor should also lead to a reduction in the spacing of superpartials relative to the equivalent elastically isotropic solid.

For a given material, variation in the spacing of superpartials with composition may be produced by variations in the values of \( T_c \), \( S \), and \( G \). The nature of the variation in \( G \) for \( \beta^\prime \)-copper-zinc has not been established experimentally, Table 5, so that only changes in the value of \( T_c \) and \( S \) will be considered. The maximum degree of long range order possible in a non-stoichiometric alloy is
twice the atom fraction of the less plentiful element. Since the value of $r$ varies as $1/S^2$, the separation of superpartials will be very sensitive to changes in the degree of long-range order. The effect of composition on $T_c$ is more difficult to estimate. Experimental points show that $T_c$ drops more quickly than calculated values, (11). However, even if it is estimated that at 40 at.% zinc $T_c$ has a value in the order of $670^\circ K$ - obtained by an extrapolation of the curve through experimental points - the effect on $r$ is not great.

Fig. 293 shows a plot of the function $T_c^{50}/T_c^{50}_N$, $S^2 N$ against composition for $\beta'$-copper-zinc. $T_c^{50}$ is the value of $T_c$ at 50 at.% zinc, $(741^\circ K)$, $S_{50}$ the maximum degree of order at 50 at.% zinc, and $T_c^{50}_N$ and $S_N$ the corresponding values for an alloy containing an atom fraction $N$ of zinc, where $N$ is less than 0.5.

This curve shows that the spacing of superpartials should increase by about 72% in an alloy containing 40 at.% zinc with respect to the value for the equiatomic alloy, assuming that the value of $G$ remains constant.

Such an increase in the spacing of superpartials should make the cross slip of screw dislocations more difficult, and is consistent with the experimental observations reported in Section 4.1.1.
This conclusion is further supported by the hardness results for binary $\beta'$-copper-zinc alloys, Fig. 160. Although hardness measured in this way represents the combined effect of a number of factors, including flow stress and work hardening rate, it may be assumed that a low work-hardening rate gives a low hardness value, and a high rate, a high value. Since a decrease in the rate of work hardening usually implies an increased frequency of cross slip, (138), the results shown in Fig. 160 point to increasing difficulty of cross slip in alloys further from the equiatomic composition.

The slip patterns exhibited by the two ternary alloys confirm the above considerations. The alloys were made on the assumption that manganese lowers $T_c$, while gold increases $T_c$. This assumption is probably justified in view of the work of Imai and Kitazima 1951 (8), Fig. 5. The effect of these additions on the degree of order $S$ is not clear. It is possible that the maximum degree of order obtainable in the manganese alloy was less than unity if manganese acted only as a diluent. However, addition of manganese should lead to an increase in the superpartial separation, addition of gold to a decrease in the separation.

The cross slip of screw dislocations is regarded as a thermally activated process, (147), and should therefore
be sensitive to changes in the temperature at which deformation is carried out. Although cross slip in the 48.25 at.% zinc alloy was reduced by deformation at 77°K rather than 293°K, occasionally quite well-developed cross slip traces were observed, Fig. 166 at (A). Cross slip was thus not completely eliminated during low-temperature deformation.

The nucleation of kink pairs on screw dislocations, suggested to be the rate controlling mechanism for deformation of A2 metals at low temperatures, (139), should also control the ability of screw dislocations to cross slip at these temperatures. This mechanism will certainly require thermal activation, and should give rise to an increase in the flow stress (observed for β'-copper-zinc, (135)) and a reduction in the ease of cross slip with falling temperature.

The present metallographic results are consistent with a reduction in the ease of cross slip in 48.25 at.% zinc β'-copper-zinc during deformation at 77°K, with respect to deformation at 293°K, such that the deformation characteristics at 77°K are closely comparable with those of an alloy containing about 40 at.% zinc, deformed at room temperature.

Tensile test results, Table 10, on the 48.25 at.% zinc alloy, support the view that cross slip becomes more difficult on reducing the temperature of testing, since
the ultimate tensile strength is higher at $77^\circ K$, despite lower elongation values, than at room temperature. However, the results for both the 48.25 at.% zinc alloy tested at $77^\circ K$ and the 39.8 at.% zinc alloy at $293^\circ K$ are complicated by the ease with which deformation produced transformation. Such transformation may indicate that deformation by slip is difficult, but only if the strength is higher than at temperatures at which little transformation takes place. In view of the consistently lower ductility of the 39.8 at.% zinc alloy compared with that of the 48.25 at.% zinc alloy at room temperature, and the similarity in ultimate tensile strength, it appears that the applied stress for a given strain was greater for the low-zinc alloy. This may reflect an increase in the difficulty of cross slip in the low-zinc alloy. The effect of the transformation product on ductility is not known, however.

An additional factor that appears to be important in determining the appearance of slip traces independently of the alloy composition or temperature of deformation, is the crystal orientation. Fig. 118, part of a 45.1 at.% zinc specimen, shows a wide range of slip trace patterns — closely spaced, parallel, straight traces, widely spaced straight traces and quite wavy traces. Differences of this nature can only be
accounted for by orientation differences between the crystals.

The effect of changing orientation on the slip system of \( \beta' \)-copper-zinc crystals was investigated by Taylor 1928 (264). He found that the resistance to shear was least when the slip plane was \{110\}, but rotation away from this favourable orientation caused the shear stress necessary to produce slip to rise, and eventually slip was produced on planes other than \{110\} in the \langle111\rangle zone, in a manner similar to that for \( \alpha \)-iron. The distinction between slip on "non-crystallographic" planes described by Taylor and cross slip on intersecting \{110\} planes is not precise, (Section 2.6), but these results indicate that crystal orientation is important in determining the slip systems which become operative. If cross slip occurs between intersecting \{110\} planes in a common \langle111\rangle zone, cross slip should be easy when the resolved shear stress for slip is equal on two such planes.

5.1.2 Fatigue Crack Initiation

The nature and distribution of damage resulting from fatigue deformation will, in the most general terms, be determined by two factors:

1) The nature and distribution of stresses in the specimen
The present results are believed to indicate that the distribution of fatigue damage in β′-copper-zinc arises from regions of stress concentration of a similar nature in specimens of all compositions, and that the observed metallographic differences result from changes in the plastic properties with changing composition.

1) The Nature and Distribution of Stresses in the Specimen. Metallographic results show that the initiation of fatigue cracks in β′-copper-zinc is always associated with grain boundaries terminating either in the specimen surface or at the specimen edge. If it is assumed that damage occurs in regions of high stress, it is reasonable to conclude that the regions near grain boundaries are subject to stress concentration.

Analysis of the orientation of grain pairs showing damage along the common boundary in specimens of 46.95 at.% zinc indicates that the grains are separated by a high angle boundary.

A simple model to indicate the origin of stress concentrations at the grain boundary of a bicrystal whose grains have a large mutual misorientation has recently been
proposed, (265). The mechanism relies on a large difference in the elastic moduli of the two grains, and applies to a bicrystal composed of two blocks of elastically isotropic material of different moduli.

Fig. 294 shows the edge of a two-dimensional bicrystal of infinite length, and finite width. The grain boundary lies normal to the edge of the bicrystal, labelled "Datum (unstressed)". The crystal on the right has a Young's Modulus $E_2$ in the direction indicated, and that on the left a Young's modulus $E_1$, where $E_2$ is greater than $E_1$.

Under the action of a tensile stress, the bicrystal will extend normal to the boundary and contract parallel with the boundary. Remote from the boundary the "soft" crystal, modulus $E_1$, will contract to a greater extent than the "hard" crystal. If coherency is to be maintained across the boundary, the lateral contractions of both crystals at the boundary must be equal. The edge of the bicrystal will then show a profile similar in form to the lower full line in Fig. 294. Since the hard crystal is constrained by the softer to deform more in the region of the boundary a higher shear stress concentration must exist to the right of the boundary than remote from the boundary. Similarly, since the softer crystal is constrained less near the boundary than
remote from it, stresses will be lower immediately to the left of the boundary.

When the bicrystal is compressed, a similar distribution of lateral strain will prevail near the boundary, Fig. 294. In this case high stresses of the opposite sense to those produced during tensile stressing will be produced to the right of the boundary, while low stresses will be produced near the boundary in the soft crystal.

The relative magnitude of the lateral strains $e_1$ and $e_2$, either in compression or tension, will be given by:

$$\frac{e_1}{e_2} \propto \frac{E_2}{E_1}$$

Fig. 294.

The stress concentration arises as a result of the elastic constraint between the two crystals, and changes sign across the boundary, relative to stress conditions remote from the boundary. Such a stress concentration which reverses sign with the sign of the applied stress, should provide suitable conditions for the initiation of fatigue damage at the grain boundary.

This stress concentration may be relieved in three ways:

a) An intergranular crack may propagate along the boundary and destroy the conditions of constraint across the boundary,
b) short parallel cracks may form at some angle to the boundary or,

c) plastic deformation may take place in the hard crystal. If positive dislocations, say, move away from the boundary during the tensile half-cycle, either they will be constrained to return during the compressive half cycle, or negative dislocations will move away from the boundary. Considerations of this nature require knowledge of the flow stress, in both the hard and soft crystals.

Before considering the effect of the magnitude of the flow stress in the two crystals, with particular reference to β'-copper-zinc, some limitations of the model should be noted. The exact form of the edge of the curve described by the edge of the bicrystal is not known. However, the distance from the boundary over which the magnitude of the stress concentration drops to some small value will be of the order of magnitude of the length of the boundary. This point is not considered of major importance provided the maximum stress concentration occurs at the boundary. The model does not apply specifically to two elastically anisotropic crystals, but only to crystals of different moduli. The model is two-dimensional.
The stress applied along a given direction in a crystal, necessary to produce deformation on a given slip system, varies with direction, since slip is inhomogeneous, and takes place on specific planes and in specific directions in the crystal. Fig. 295 shows a crystal containing a slip plane (shaded). If \( T \) is the critical resolved shear stress for slip on planes of this type, \( \beta \) the angle between the slip direction and the crystal axis, and \( \alpha \) the angle between the normal to the slip plane and the crystal axis, the magnitude of the stress applied along the crystal axis to produce slip is given by:

\[
\text{Applied Stress } P = \frac{T}{\cos\alpha \cdot \cos\beta}
\]

A plot of relative values of \( P \) with respect to directions in the crystal may be drawn by calculating values of \( 1/\cos\alpha \cdot \cos\beta \) for the most favourably oriented slip plane, and plotting these against the cosine function \( F(\gamma) \), expressing directions in a crystal relative to fixed axes, (see Appendix A). \( F(\gamma) \) has the value 0 for \( <100> \), 0.25 for \( <110> \) and 0.33 for \( <111> \). Fig. 297 shows such a plot of applied stress against stress direction for slip on the system \( \{110\} <111> \). Values of \( \alpha \), \( \cos\alpha \), \( \beta \), \( \cos\beta \) etc. are given in Table 13. Values of \( 1/\cos\alpha \cdot \cos\beta \) represent relative values of the flow.
stress of any crystal which slips on the system \{110\} \langle111\rangle.

A series of stress-strain curves for the particular case of \(\beta\)-copper-zinc may be obtained by combining this plot with values of the reciprocal of Young's modulus with respect to crystallographic direction. Fig. 296 shows such a plot of \(1/E\) against \(F(\gamma)\), taken from the work of Artman and Thompson 1952 (89).

The combined plot is shown in Fig. 298. Relative values of the longitudinal elastic strain at the flow stress for any given direction of the applied stress may be read from this plot. Assuming that Poisson's ratio is independent of crystallographic direction, i.e. that longitudinal strain is proportional to lateral strain, independent of stressing direction, an attempt may be made to estimate the stress concentration at the grain boundary in a bicrystal composed of various hard and soft orientations.

Consider Fig. 299 (A). A bicrystal is composed of one crystal having a \(\langle111\rangle\) direction along the axis, the other the \(\langle100\rangle\) direction. The elastic behaviour of both crystals may be represented by elastic stress strain curves, Fig. 299 (A), OA for the \(\langle111\rangle\) crystal and OB for the \(\langle100\rangle\) crystal. If the bicrystal is subject to a tensile stress such that slip is just about to start in the \(\langle100\rangle\) crystal, the
relative lateral contraction in the two crystals remote from
the boundary is given by the ratio \(\frac{CD}{CB}\). At the boundary,
however, the ratio of the lateral strains in each crystal will
be inversely proportional to the moduli of the two crystals,
i.e. \(\frac{DE}{EB}\). Hence in the \(<111>\) crystal the lateral
contraction at the boundary will be proportional to \(CE\),
while remote from the boundary it will be proportional to \(CD\).
In the \(<100>\) crystal the corresponding values are \(CE\) and \(CB\).
This value of lateral contraction for the crystal \(<111>\) may
be thought of as equivalent to the imposition of an additional
tensile stress to the point \(F\). This indicates that in the
hard grain the flow stress will be exceeded, under these
conditions, by about 16%.

A similar analysis for the pair having moduli
corresponding with the directions \(<221>\) and \(<100>\) indicates
that the stress concentration factor may be as much as 64%,
Fig. 299 (B). The \(<321>/ <100>\) pair give a stress
concentration of 47%, Fig. 299 (C).

These calculations cannot represent conditions in
real bicrystals for a number of reasons. Real crystals are
three-dimensional, and show elastic anisotropy with respect
to different crystallographic directions in the lattice.
Further, because of symmetry considerations, the angle between
identical crystal directions is not always 90°. Indeed,
the distribution of stress concentrations of this nature will be impossible to determine for a real polycrystal. Nevertheless, it seems probable that high values of local stress can occur at grain boundaries in an elastically anisotropic metal, but the magnitude of this effect will be smaller than in the cases considered above. Since a polycrystal contains, in general, a random arrangement of crystal orientations pairs of grains suitably oriented for producing a high elastic stress concentration will not be very common. Also, surrounding grains will tend to reduce the magnitude of the effect. The ability of dislocations to cross slip freely on any plane in the zone of the slip direction will reduce the plastic anisotropy of the material, but conditions producing the elastic stress concentration will not be affected.

2) The Plastic Properties of the Material. The work of Johnston et al. 1964 (204), discussed in Section 2.9.1.2, shows the importance of cross slip in limiting the formation and propagation of cleavage cracks, and hence in retaining ductility in single phase materials. Similarly, Stoloff et al. 1965 (206) attributed the increased brittleness of iron and some of its alloys at low temperature to the increased difficulty of cross slip with falling temperature.
If these conclusions are generally true for body-centred cubic and related metal structures (B2 and D0$_3$), it is to be expected that the tendency for cracks to be nucleated and to propagate with little accompanying plastic deformation in β′-copper-zinc, should increase with decreasing zinc content from the equiatomic composition. Similarly the tendency for stress relief by plastic deformation alone should decrease towards the more meta-stable copper-rich alloys, and lowering the temperature of deformation should lead to an increase in transgranular brittleness, and a decrease in the prevalence of stress relief by plastic deformation alone.

The increased tendency for straight crystallographic cracking in alloys of low zinc content during fatigue at room temperature, and in the 48.25 at.% zinc alloy during fatigue at 77°C, is consistent with these conclusions.

In view of the above considerations of the nature and distribution of stresses in a polycrystalline fatigue specimen and the effect of the plastic properties on the fracture characteristics, it is possible to examine specifically mechanisms for the initiation of damage.

a) Sets of parallel cracks initiated at grain boundaries,
with little accompanying plastic deformation, Figs. 84, 93 and 101. Observation of the cracking in Fig. 84 showed that damage spread along the boundary from a triple point. Successive crack formation is also suggested by comparison of the crack spacing and crack depth. Figs. 102 and 110 show that even though the spacing of crack traces on the specimen surface is less than 5 µ, cracks penetrate up to 40 µ into the specimen. It is unlikely that these cracks could all have grown at the same time, since longer (and deeper) cracks stress relieve the material through which they pass, and therefore remove the conditions favouring the growth of shorter cracks near to them.

It appears likely that these parallel cracks have been formed in succession, in response to localised conditions of stress concentration along the boundary. All cracks of this type appear to be initiated at the boundary itself, which suggests that a brittle mechanism rather than a true fatigue mechanism involving localised intense slip damage is responsible for their formation. The increasing difficulty of cross slip in copper-rich alloys should favour brittle crack initiation. The atomic mechanism of crack initiation may be of the type proposed by Zener 1948 (108), involving crack nucleation by plastic deformation giving rise to local stress concentration, or of the type by
Kramer and Maddin 1952 (136) involving a delay time for slip. In either case crack initiation would be favoured when stress relief by plastic deformation is difficult. These conditions apply equally to the low-temperature deformation of the 48.25 at.% zinc alloy.

Once a single crack is nucleated propagation of the damage along the boundary should be fairly easy, as the stress concentration passes along the boundary, causing the formation of successive cracks. One striking feature of this type of damage is the similarity in the length of cracks formed parallel with each other. This suggests both the presence of a stress concentration at the boundary and also a mechanism for the arrest of cracks, (Section 5.1.3).

The 48.25 at.% zinc alloy also exhibited an additional mechanism of stress relief during fatigue at $77^\circ K$, which led to the formation of sets of parallel short traces along some grain boundaries, namely, the formation of parallel plates of martensite. It appears that the formation of martensite, unaccompanied by cracks, Fig. 169, represents an additional deformation mode, analogous to mechanical twinning in iron at low temperatures, (Section 2.4.3).

b) Straight crystallographic transgranular cracks, accompanied by little plastic deformation. Cracks of this type were formed predominantly in the 42.5 at.% zinc alloy,
when fatigued at room temperature, and in the 48.25 at.% zinc alloy when fatigued at 77°K. Long transgranular cracks were usually formed at triple points, Figs. 88, 89, 116 and 161 or where the grain boundary changed direction sharply, Fig. 164, point (A), indicating that cracks of this type were produced by localised high stress conditions at a point rather than along the length of a boundary. In alloys of high zinc content, such stresses could be relieved by plastic deformation, while in those of lower zinc content, in which cross slip is more difficult, cracks were nucleated. In this sense, cracks of this type differed from short parallel cracks nucleated along a grain boundary only in the nature of the stress concentration producing them, and no evidence was found to indicate that the process of crack nucleation was different in the two cases.

The mechanism proposed by Zener 1948 (108) for crack initiation could therefore also account for the formation of straight transgranular cracks. Suitable stress relaxation could occur by plastic deformation to give rise to a stress concentration at a triple point.

The brittleness of the 48.25 at.% zinc alloy during fatigue at low temperature could also be accounted for by the mechanism proposed by Kramer and Maddin 1952 (136),
involving a delay time for the initiation of slip. No evidence is available that a similar delay time for slip exists in alloys of lower zinc content when deformed at room temperature.

Fatigue stressing during the present investigation was carried out at a frequency of about 200 cps. This implies a loading cycle of less than 0.00125 sec. Loading times of this order are within the range suggested by Kramer and Maddin as capable of producing brittle failure at 77°K, Fig. 32. Nevertheless, fatigue specimens tested at 77°K all showed well-developed slip markings on the surface. This mechanism of crack initiation would be very sensitive to the frequency of the stress cycle during fatigue. No investigations of the effect of frequency were possible during the present investigation, since very careful control of stress amplitude would also be required, to ensure that any observed differences were due only to the effect of frequency change.

c) Cracks initiated next to grain boundaries accompanied by intense plastic deformation. This type of crack formation only occurred in alloys near the equiatomic composition. Although intense slip markings of this type formed along some grain boundaries of the 45.1 at.% zinc alloy, they were usually within a distance of 5 µ from the boundary. In the higher zinc alloys, markings were up to 15 µ in length. This again indicates that stress relief by plastic deformation was more difficult in the
The nature of the intense slip damage is revealed by the replica electron micrographs, Figs. 135 to 139. It appears that damage of this type— that is, crack initiation in regions of intense slip— represents the only true fatigue damage observed in alloys of β’-copper-zinc. The intensity and wavy nature of the slip traces in which cracks were formed indicates that this type of damage is the result of the cross slip of screw dislocations. The damage was characterised by the limitation of intense slip markings to a band about 15 μ in width displaced about 1—2 μ from the boundary.

Although cross slip of superdislocations in alloys near the equiatomic composition appears to be fairly easy, intense slip markings could be produced by the cross slip of superdislocations or of dissociated superpartials. Cottrell 1954 (157) has pointed out that the passage of successive superdislocations over the same path through a domain structure will lead to an increase in the antiphase boundary area by the mechanism shown in Fig. 27. If intense fatigue slip damage results from the movement of a relatively small number of dislocations through a large number of cycles, it is likely that the degree of order in these regions will be reduced considerably. Under such conditions the separation
of superpartials should increase, and cross slip become more difficult.

An estimate may be made of the additional stress necessary to move a $\frac{1}{2}a_0 \langle 111 \rangle$ superpartial through the ordered lattice to account for the energy of the antiphase boundary trail so created. The shear stress necessary for the creation of such a trail is given by,

$$ T_{S1}(APB) = \frac{E_o(110)}{b} \quad \ldots \quad (147) $$

where $T_{S1}(APB)$ is the shear stress necessary when the degree of order, $S$, is unity, $E_o(110)$ the antiphase boundary energy on the $\{110\}$ plane, and $b$ the Burgers vector of the $\frac{1}{2}a_0 \langle 111 \rangle$ superpartial. According to Flinn 1960 (155), the value of $E_o(110)$ is given by

$$ E_o(110) = \frac{4kT_0S^2}{a_0^2 \sqrt{2}} \quad \ldots \quad (148) $$

where $k$ is Boltzmann's constant, $T_0$ the critical ordering temperature, $S$ the degree of long-range order and $a_0$ the lattice parameter of the structure.

This gives a value for $E_o(110)$ for $\beta$-copper-zinc assuming perfect long-range order, of 83 ergs/cm$^2$, and hence a value of 32.5 kg./mm$^2$ for $T_{S1}(APB)$. This is
equivalent to an applied stress of 65 kg./mm$^2$, which is considerably in excess of the maximum tensile stress of $\beta'$-copper-zinc specimens, Table 10.

However, the value of the antiphase boundary energy is most sensitive to the degree of long-range order, $S$. When $S$ has the value 0.5, the necessary shear stress is reduced to 8.1 kg./mm$^2$. Arguments of this nature are of limited applicability in the present case, since the degree of long-range order in the intensely deformed regions is unknown, as also is the exact nature of the dislocation movements leading to crack initiation.

The reason for the precise limitation of the intense damage within a region about 15 $\mu$ from the boundary may also be determined by the nature of the dislocations causing the damage. If the intense slip markings are produced by the movement of superdislocations, the limitation of the damage near the boundary can only be a function of the stress conditions along the boundary, since superdislocations should be able to move away from the boundary without difficulty. If intense slip markings are produced by the movement of separated superpartials, the limitation is a function of the difficulty of moving superpartials into a highly ordered lattice. Replica electron micrographs of the extremities of
intense slip markings, Figs. 134 and 137 show that slip markings tend to form as discrete straight traces, but these do not point to the nature of the dislocations giving rise to the traces.

Intense slip markings next to grain boundaries in the 45.1 at.
% zinc alloy were observed to be much shorter than those in the 46.95 at.
% zinc alloy. Although the length of these slip markings will almost certainly be directly proportional to the stresses at the boundary, length may also be a function of the ease of cross slip of dislocations. If this is so, intense slip markings will be formed by the movement of superdislocations, since a lower zinc content should lead to an increased difficulty of cross slip and therefore shorter intense slip traces. If this damage were caused by the independent cross slip of superpartials, the length of intense slip traces should increase with decreasing zinc content, since superpartials should be easier to separate in alloys of low zinc content.

Two possibilities may be presented to account for the observation that slip markings are limited in intensity within about 1 – 2 µ from the boundary. Firstly, dislocations may be emitted from the boundary to relieve the stress concentration, and pass into the region next to the boundary. Here they should be free to move in a cyclic manner, limited by
the lower stresses remote from the boundary, and next to the boundary, by the difficulty of forming large slip steps immediately next to the boundary as a result of the coherency conditions at the boundary itself. In this case, the fine slip markings within 1 μ of the boundary, Fig. 136, would result from dislocations moving away from the boundary.

However, the theoretical work of Head 1965 (183) suggests a second explanation. Since all <111> Burgers vector dislocations experience a repulsive force as a result of the elastic anisotropy of β'-copper-zinc on approaching any grain boundary, boundaries should constitute barriers to dislocations. The repulsive force on the dislocation will increase as it approaches the boundary, so that the cyclic application of a stress should cause the dislocation to move nearer to and further from the boundary with each stress cycle. Conditions of this type should be favourable to the initiation of fatigue damage. Dislocations in this case do not originate at the grain boundary, but pile up against the energy barrier provided by the boundary following plastic deformation within the grains as a result of the stresses applied to the specimen.

Evidence for the limitation of the close approach of dislocations to grain boundaries is provided by micrographs of slip patterns in β'-copper-zinc, Section 4.1.1. The formation of slip steps was often considerably reduced within
a distance of about 25 μ from the grain boundary. However, if intense slip markings resulted from the cyclic movement of dislocations which produced slip remote from the boundary, and then piled up at the boundary, it would be expected that intense slip markings and slip within the grain would share the same traces. Although parallel traces of this type were observed, Fig. 128, intense slip markings also formed traces not observed elsewhere in the same grain, Fig. 142. This feature of intense slip damage has also been reported elsewhere, (254).

These considerations suggest that slip remote from the boundary, and intense slip markings are formed by different sets of dislocations, and that parallel slip traces next to and remote from the grain boundary result from the activation of dislocations sharing the same slip direction, but originating at different sources.

The nature of intense slip markings next to the grain boundary indicates that slip intensifies slowly along the whole length of the boundary. Fig. 129 shows that the region next to some of the longer markings is composed of less intense slip. Sectioning normal to the specimen surface showed that these longer markings were cracks, and it appears that these cracks have stress relieved a region extending about 5 μ on either side, and therefore caused
the limitation of slip intensification.

The nature of the process producing crack nucleation in regions of intense slip is not revealed by the present study. Replica electron micrographs Figs. 134, 137, 138, and 139 show that cracks are nucleated within regions of particularly intense deformation. It is possible that intense deformation leads to the formation of surface notches at which stress concentration can occur, leading to the slow propagation of the notch into the specimen. The regularity of spacing of cracks shown in Figs. 137 and 139 indicates that they may form in a successive manner similar to the progressive formation of short cracks unaccompanied by plastic deformation along the grain boundary. Such a process need not exclude the progressive intensification of slip along the boundary before cracks are formed, or the intensification of slip between cracks which have already formed.

d) Intergranular cracks. Intergranular cracks were initiated at the specimen edge in alloys of all compositions, but the initiation of intergranular cracks remote from the specimen edge without accompanying plastic deformation was limited to the zinc-rich alloys when fatigued at room temperature.

The bicrystal model considered earlier in this section indicates that the edge of the specimen should act as a favoured site for crack initiation, since the difference in
elastic strains between the two crystals at the boundary and remote from the boundary will be a maximum at the edge of the specimen. This difference is produced by reversing shear stresses along the boundary, the maximum shear stress occurring along the boundary itself. The boundary can be considered as a notch on an atomic scale, so that such conditions should favour the initiation and propagation of an intergranular crack, in the absence of stress relief by plastic deformation.

Once a crack has been initiated stress conditions at the crack tip should lead to its continued propagation on the same path, unless the stress conditions change, for example at triple points or where the boundary changes direction rapidly.

The atomic mechanism of intergranular crack initiation is not revealed by the present experimental observations. Electron probe microanalysis showed no tendency for segregation of either copper or zinc to the boundary on a massive scale. Vacancy condensation in the boundary might provide areas of weakness in the structure of the boundary. Quenching from high temperature should cause an excess of vacancies to be trapped in the lattice, but these should diffuse to sinks, at dislocations as well as grain boundaries. The concentration of vacancies diffusing to the boundary would depend on the mean free path of vacancies within the lattice, and this on the
dislocation density. A free surface, in this case the specimen surface, also provides a vacancy sink so that the concentration of vacancies near the specimen surface in a boundary, at which an intergranular crack is initiated, should not be so high as to render the boundary exceptionally weak. However, it is possible that vacancy condensation at boundaries could assist the propagation of intergranular cracks.

The observation that alloys of higher zinc content show much more intergranular crack initiation than those of low zinc content appears to imply that grain boundaries become weaker as the zinc content increases. Intergranular crack initiation in aluminium, but not in copper, during fatigue at room temperature has been interpreted as due to the relatively higher temperature of testing of aluminium, when temperature is expressed as a function of the melting point of the metal, (153). The melting points of $\beta$-copper-zinc alloys of high zinc content are somewhat lower than those of copper-rich $\beta$-phase alloys, Fig. 4, but this difference cannot be sufficiently large to cause the observed difference in behaviour.

There seems no good reason why the cohesive strength across grain boundaries should change significantly with zinc content. The observed difference in behaviour may
be accounted for by a lower fatigue resistance of the copper-rich metastable alloys, if it is easier to initiate straight transgranular cracks than intergranular cracks in these alloys. As the zinc content is increased, the initiation of brittle transgranular cracks becomes more difficult, and intergranular crack initiation becomes more common, implying that alloys near the equiatomic composition would have a greater fatigue resistance than the metastable copper-rich alloys.

An indication of the relative ease with which stress relief at a grain boundary occurs, either by the formation of an intergranular crack or of short parallel transgranular cracks is given in Fig. 173. If intergranular cracks are easily initiated, relative to transgranular cracks, transgranular crack traces making a small angle with the grain boundary should be observed infrequently. Similarly, if intergranular crack initiation is relatively difficult, transgranular cracks making a small angle with the boundary should be observed frequently. The results in Fig. 173 support this view. However, these results are only qualitative in nature, since no account is taken of the orientation of either the boundary or of the cracks relative to the specimen surface.
The orientations of grain pairs shown in Figs. 141 to 148 indicate that the initiation of damage requires a high-angle grain boundary between the grains. In an attempt to relate the specific grain orientations to the appearance of damage, values of the orientation function $F(\gamma)$ were calculated for each crystal in the directions normal to the specimen surface, axis 1, parallel with the specimen axis, axis 2, and normal to the specimen edge, axis 3. The angles between the three <100> crystal axes and the appropriate orientation axis in the specimen were measured from the stereographic projection. These values are listed in Table 14. Values of $F(\gamma)$ are related linearly to the value of Young's modulus, Fig. 296, so that $F(\gamma)$ values near zero represent low modulus values, while values near 0.33 represent high moduli.

No pattern of relative modulus values can be observed in Table 14 capable of distinguishing between conditions necessary for the initiation of intense slip damage or an intergranular crack. This might be taken as support for the suggestion that both types of damage originate from the same source of stress concentration.

A basic conclusion derived from consideration of the grain boundary stress concentration model, Fig. 294,
is that intense slip damage should begin in the grain which lies in the "hard" orientation to the applied stress, i.e. having a high value of $F(\gamma)$ in axis 2. The results shown in Table 14 are inconclusive in this respect. Damage probably started in grain 1 of grain pair A 1/2, Fig. 128. This grain has a higher value of $F(\gamma)$ only parallel with axis 2. Damage started in grain 1 of grain pair B 1/2, but this grain shows higher $F(\gamma)$ values on axes 1 and 3, but not parallel with axis 2. Grain pair D 1/2 clearly shows that damage began in grain 1, Fig. 132, nevertheless, grain 2 shows higher $F(\gamma)$ values in all directions.

Grain pairs showing intergranular crack initiation Figs. 145 to 148 all show a considerable degree of difference in the values of $F(\gamma)$ in the various directions, except pair H 1/2, for which the values are very similar, Table 14. Nevertheless Fig. 148 indicates that the misorientation is large. This suggests that a more meaningful approach to the problem of misorientation and its effect might be to relate values of $F(\gamma)$ to the orientation of the boundary. That is to consider misorientation parallel with and normal to the surface trace of the boundary, and normal to the specimen surface. Such
an approach might avoid cases such as \( D^{1/2} \) for which the grain in which damage was initiated always appeared to have a lower modulus value, in all directions considered.

An additional factor may also have contributed to the inconclusiveness of the present results. The fatigue specimens and method of stress application used in the present investigation are not the most suitable for an examination of the stress conditions between neighbouring grains. Since the specimen gauge length contained only about twelve grains, even if it is concluded that damage occurred at the boundary of the most favourably oriented grain pair in each specimen, it is most unlikely that the orientation conditions in every case were the most favourable possible. Possible alternative approaches to the problem will be considered in Section 6.7.

5.1.3 Fatigue Crack Propagation

The appearance of fracture surfaces and the paths of propagating cracks support the existence of a change in the ease of cross slip with zinc content and of special stress conditions at grain boundaries.

Short cracks formed along grain boundaries did not usually propagate and therefore did not in themselves give rise to the main crack producing failure of the specimen.
Those short cracks which did propagate further than their neighbours were observed to change direction about 20 μ from the boundary, Figs. 128, 138, 156 and 158. This change in direction is believed to be due to a change in the stress conditions, or of the mode of propagation, and is of the type reported by Forsyth 1961 (239) for aluminium. Cracks formed in intense slip markings were initiated by a ductile process, under the influence of local stresses, but propagation away from the boundary took place under the influence of the macroscopic bending stresses in the specimen, so that cracks tended to turn parallel with the E–W direction across the specimen, Figs. 141 and 156. When the component of the bending stress in the specimen was insufficiently large, short cracks did not propagate.

Both short cracks associated with intense plastic deformation and those not sometimes gave rise to a "mirror" pattern of cracks or deformation across the boundary, Figs. 102 and 128. Since both types of crack formed on {110} planes, the formation of such a pattern is believed to depend on the matching of {110} planes across the boundary. Such correspondence does not imply that both grains shared the same orientation. If {110} planes did not correspond, crack propagation across the boundary
was limited, Figs. 84, 93 and 131. In both high and low zinc alloys these cracks propagated across the boundary by a mechanism involving stress concentration at the crack tip. Although it is suggested that cracks of this type formed as a means of stress relief, complete stress relief at the boundary can only be produced by an intergranular crack. Such intergranular cracks were frequently observed, Figs. 86, 93, 101, 117, 119, 128 and 156, and their formation probably represents a stage of crack propagation succeeding the formation of short cracks.

Crack paths were frequently observed to follow grain boundaries. This is also believed to reflect stress concentration, since such cracks were frequently not intergranular, but transgranular, Figs. 91, 99, 107, 108, 114 and 152. This fact indicates that transgranular propagation was not especially difficult in any of the alloys. In those of low zinc content straight transgranular cracks on \{110\} planes were preferred. These cracks appeared very similar to cleavage cracks, but the fact that they did not propagate with very high velocity indicates that plastic blunting occurred at the crack tip. Some evidence for such deformation may be seen in Fig. 88, and from diffuse back-reflection Laue spots on photographs taken from fracture
faces, Fig. 268. In view of this it is perhaps surprising that little trace may be found of the crack front after each cycle of deformation on the fracture faces, although such traces may just be seen in Fig. 266. In high zinc alloys the observed transgranular ductile propagation, Figs. 155 and 159 reflects the greater ease of cross slip in these alloys, allowing stress relief at the crack tip by plastic deformation, leading in turn to the characteristic zig-zag path.

Crack propagation in the 48.25 at.% zinc alloy at 77°K, was similar to that in the 42.5 at.% zinc alloy at room temperature. However, the greater quantity of transformation product in the former case may indicate that its behaviour is more similar to an alloy of lower zinc content than 42.5 at.% . The large amount of transformation product associated with cracks formed parallel with each other along a grain boundary indicates that these cracks propagated under the influence of shear stresses, Fig. 168. It is not clear whether cracks or transformation product formed first, or whether they formed together. Fig. 168 points to the prior formation of transformation product, and it may be noted that the cracks show a slightly different trace from the habit plane of the transformed regions. This difference is probably consistent with the 7° difference in the habit planes \{110\} and \{2 11 12\} respectively. The tendency for isolated
straight transgranular cracks to show little or no transformation product may indicate that these cracks propagated by stresses normal to the crack path.

5.2 \(\beta'\)-Gold-Zinc

5.2.1 Fatigue Slip Damage

Fatigue at room temperature produced damage in individual grains, both specifically associated with grain boundaries, Figs. 179, 182 and 186, and remote from grain boundaries, Figs. 192, 200, 201 and 203. Damage of the latter type was observed to be non-uniform, in that intense fatigue slip bands formed in isolated grains, while neighbouring grains remained unmarked.

This distribution of damage is believed to result from the plastic anisotropy of \(\beta'\)-gold-zinc. A plot of the applied tensile or compressive stress necessary to produce slip on the system \{110\} \langle100\rangle may be constructed for various orientations of the crystal, Fig. 300, in the same way as for the \{110\} \langle111\rangle slip system, Fig. 297. The values of \(\alpha\) and \(\beta\) from which Fig. 300 was produced are given in Table 15. Fig. 300 shows that plastic deformation may be produced most easily by an applied stress along an axis in the
crystal near <111>. Stresses applied along an axis of the crystal contained within the triangle [311], [210], [100] must be greater than twice those for orientations near <111> to induce plastic deformation. Fig. 300 represents the stress required to produce slip on a single {110} plane. If fatigue slip bands are formed by cross slip of a<100> dislocations on intersecting {110} planes, indicated by the present results, the form of the curve would be changed for this case, since plastic deformation on two related {110} planes would have to be considered for each orientation of the applied stress. However, the resolved shear stress on all slip systems remains zero for an applied stress along the <100> direction, so that plastic anisotropy will be large even when cross slip is taken into account.

The stereographic projections of the crystals in Figs. 202 and 204 provide a check on the present suggestion that the formation of slip bands remote from boundaries is a function only of the orientation of the crystal and of the applied stress. During bending tensile and compressive stresses are produced parallel with the specimen axis, N - S . Measurements from the projection in Fig. 202 show the orientation function F(\gamma) in the direction N - S to be 0.3 , while that for the crystal
in Fig. 204 is 0.26. Comparison of these \( F(\gamma) \) values with Fig. 300 shows that slip may be produced most easily when \( F(\gamma) \) is greater than 0.25.

Localisation of damage along grain boundaries may be considered in terms of the mechanism of elastic stress concentration considered in Section 5.1.2. The only values available for the elastic constants of \( \beta' \)-gold-zinc (89), Table 5, do not allow the elastic anisotropy to be determined accurately. For reasons discussed earlier, it is probable that the elastic anisotropy of \( \beta' \)-gold-zinc is lower than that of \( \beta' \)-copper-zinc. The plastic anisotropy of \( \beta' \)-gold-zinc favours plastic deformation in the region of grain boundaries if some stress concentration exists in this region.

Consider Fig. 294. The elastically "hard" crystal, Young's modulus \( E_2 \), will have its axis near \( <111> \), while the elastically "soft" crystal will have its axis near \( <100> \). Inspection of Fig. 300 shows that these orientations are associated with a low and high flow stress respectively. Localisation of damage on one side of the boundary was observed, Figs. 186 and 199. The limitation of damage to a strip of fairly precise width next to the grain boundary, as in the case of \( \beta' \)-copper-zinc, was not in
general observed for \( \beta' \)-gold-zinc, supporting the view that local stress concentrations were less pronounced in the latter alloy.

Head 1965 (183) has calculated that dislocations having a \(<100>\) Burgers vector in a cubic crystal in which \( C/C' \) is greater than unity, always experience an attractive force due to the image dislocation across grain boundaries between two crystals of any orientation. Plastic deformation in the region of grain boundaries under conditions of cyclic stress may be favoured if dislocations are moved up and down a potential energy hill, by the changing sign of the applied stress. Unlike \( \beta' \)-copper-zinc, in which dislocations move up the energy hill when approaching the boundary, in \( \beta' \)-gold-zinc dislocations move up the energy hill when moving away from the boundary.

Both of these mechanisms - elastic stress concentrations at a grain boundary leading to localised plastic deformation, and the energy hill associated with \(<100>\) Burgers vector dislocations - are a function of the elastic anisotropy of the crystals. Since no second phase particles capable of giving rise to localised plastic deformation were observed in the grain boundaries, it seems reasonable to conclude that the appearance of slip damage
along grain boundaries during the fatigue of $\beta'$-gold-zinc at room temperature is a function of localised stress conditions produced by elastic anisotropy.

The analysis of the orientation of slip bands shown in Figs. 202 and 204 indicates that their formation is consistent with slip taking place on two intersecting \{110\} planes in a common \{111\} zone. The form of the trace of fatigue slip bands on the specimen surface will be a function of the angle at which the common slip direction, describing the zone of the slip planes, meets the surface of the specimen, in this case. The examples chosen for analysis consisted of fairly straight parallel traces, Figs. 200 and 203. The corresponding stereographic projections show that in each case the active slip direction lies at a small angle to the surface of the specimen. If the common slip direction lay in the specimen surface, the traces $AA'$ and $BB'$ due to each plane would be coincident, so that each plane would produce only a single common trace on the surface. Similarly, if the slip direction lay normal to the specimen surface, the traces of the slip planes would lie at right angles to each other, so that any orientation of surface trace could be produced by combination of small slip increments on the two slip planes. It seems reasonable to conclude that bands
which do not show sharply defined parallel traces are produced by slip in a \( <100 > \) direction making a large angle with the specimen surface.

Analysis of the displacement of interference fringes across bands of intense slip on the specimen surface, Fig. 200, shows that bands are raised above the surface. The magnitude of the vertical displacement varies within the wider bands, indicating that these are composed of separate regions of dislocation activity. Narrower bands, e.g. that containing point (B), Fig. 200, do not appear to be composed of separate regions, and may represent a single region of dislocation activity.

The nature of fatigue slip bands of this type has been discussed by Boettner and McEvily 1965 (215) with reference to iron-silicon alloys. They describe surface displacements of the present type as "extrusions", despite the fact that the height to width ratio of the bands was in the order of \( 1 : 5 \) to \( 1 : 10 \). The term "extrusion" was originally used by Forsyth 1953 (226) to describe thin sheets of material produced from fatigue slip bands, so that the use of the term to describe the observed bands in \( \beta' \)-gold-zinc will be avoided, since the height to width ratio is only about \( 1 : 10 \).
Boettner and McEvily 1965 (215) proposed the model shown in Fig. 34 to describe the formation of bands of fatigue damage composed of a number of sub-units, without the necessity of invoking the existence of sub-surface fissures, as required by the mechanism proposed by Mott 1955 (236). It was suggested that a high density of dislocation loops is formed beneath bands as a result of the cyclic movement of screw dislocations.

Bands were thought to widen by the addition of new sub-units of dislocation activity, (215), and this seems to apply in the case of β'–gold–zinc. Sub-units were thought to become dormant if one impinged on its neighbours, (215). This should lead to a maximum band height above the specimen surface equal to the height of a single sub-unit, since addition of new sub-units will lead to an increase in the total band width, but not the total band height. Examination of Fig. 200 shows that the height to width ratio of all bands is approximately constant at 1:10, independent of the band width. This implies either that dislocation activity continues near the centre of fatigue slip bands as new sub-units are added, or that the formation of new sub-units at the edge of a band produces sub-surface disturbance which causes the whole band to be
displaced upwards. The former possibility is probably more likely, since the widest band in Fig. 200 shows regions in which the deformation is not very intense, implying that dislocation movement should be able to continue in these regions.

If fatigue slip bands are formed by dislocation movement in limited regions, these regions must, by definition, be favoured regions for such activity. There is therefore little reason to postulate that dislocation activity within these regions ceases as a result of some work-hardening process. It seems more plausible that bands widen by the progressive "erosion" of neighbouring undeformed material. Also, if bands widen by the addition of sub-units dislocation motion must be related to the size of the sub-units and not to the width of the whole band.

The present results do not point to an explanation of the slight depression in the specimen surface formed at the end and at one side of the wider bands, Fig. 200. This is presumably a function of the dislocation movement, but a knowledge of the orientation of the slip planes and direction is required for such an explanation. It is possible that these depressions represent regions from which material has been moved, but this is unlikely if the distance travelled by single dislocations in fatigue slip bands is only in the order of 10 μ, (231). It is also unlikely that
depressions of this size can be formed by lattice coherency conditions.

Reducing the temperature of testing to $77^\circ\text{K}$ completely suppressed the formation of fatigue slip bands. However, surface traces of cracks, Figs. 217 and 218 and fracture surfaces, Figs. 278 and 279 show that crack propagation was associated with plastic deformation at the crack tip, and could not be described as a brittle process. It appears therefore that cross slip becomes more difficult at the temperature of deformation is lowered below room temperature, but that cross slip is still possible at $77^\circ\text{K}$. If the nucleation of a crack is not more difficult at low temperature than at room temperature, it is possible that the formation of fatigue slip bands may be masked by crack propagation.

5.2.2 Fatigue Crack Initiation and Propagation

All fatigue cracks were observed to be associated with grain boundary over some part of their length, following deformation both at $293^\circ\text{K}$ and $77^\circ\text{K}$. The crack producing final failure of the specimen was found to arise at a grain boundary terminating at the specimen edge, Figs. 206 and 207. Crack nucleation could occur by a
combination of stress concentration and grain boundary notching, similar to that proposed for β'-copper-zinc, Section 5.1.2. Grain boundary crack nucleation may also be favoured since the ionic contribution to bonding is known to be significant, Section 2.3.3, and grain boundaries in ionic solids are known to be weak as a result of the close approach of atoms of like charge resulting from lattice mis-match at the boundary.

Transgranular crack propagation, from an intergranular nucleus, may be favoured by easy cross slip at the crack tip, Figs. 276 and 278. As pointed out in Section 5.2.1, crack propagation at 77°K was associated with plastic deformation, although the ease of cross slip was reduced, with respect to that at room temperature. The appearance of some straight crack traces following low-temperature fatigue is also consistent with a reduction in the ease of cross slip.

5.3 Iron-Cobalt-Vanadium

The general features of slip traces formed on the surface of both ordered and disordered specimens during fatigue and fracture were found to be consistent with previous observations of slip traces in this alloy, (146) and
It will be assumed therefore, that slip takes place in the disordered alloy by the movement of \( \frac{1}{2}a_0 <111> \) dislocations which frequently possess screw orientations, as observed also in \( \alpha \)-iron, (309), and in the ordered alloy by the movement of superdislocations composed of pairs of \( \frac{1}{2}a_0 <111> \) superpartials, connected by a strip of antiphase boundary, at least in the initial stages of deformation.

The disordered specimens may have contained some short range order, either as a result of the anneal prior to quenching or formed in the quench itself, although only wavy slip traces were observed following fatigue deformation. The distribution and extent of intense slip damage on the surface may have been affected by the existence of short-range order, in that slip damage was not so widespread as has been observed for \( \alpha \)-iron, (250). However, crack initiation and propagation may also have limited the spread and intensification of slip damage.

Since no slip traces were formed on the surface of ordered specimens early in the fatigue life, the strain amplitude was not sufficient to produce plastic bending, so that damage appeared only at points where stresses were higher than average in the specimen. Replica
electron micrographs showed that fatigue slip damage in both the ordered and disordered alloys was wavy, consistent with the view that cross slip is necessary for its development. The limitation of this damage to very small regions in the ordered alloy is consistent with the difficulty of cross slip, (147). The distribution of damage in the ordered specimen indicates that stresses were higher at grain boundaries. The plastic anisotropy in this alloy is not great, Fig. 297, and it is doubtful whether plastic anisotropy alone would be capable of providing the necessary conditions along a grain boundary to cause local movement of dislocations.

There is no evidence to suggest that the elastic anisotropy of iron-cobalt alloys is high, (Section 2.3.5 and 2.4.2). However, even moderate values of the anisotropy may be sufficient to cause limited local plastic deformation, as discussed in Section 5.2. Very large stress concentration would not be required to initiate slip locally, and such a mechanism may explain the occurrence of a narrow strip of apparently undeformed material along grain boundaries showing damage, both in the ordered and disordered alloy, Figs. 232, 237 and 239. Alternatively, the formation of a strip of undeformed material at the boundary may only reflect the difficulty of dislocation
movement within 1 μ of the boundary, (177), and some other mechanism for the initiation of damage must be sought.

The surface of all specimens showed a number of second-phase particles, found to be rich in vanadium, Fig. 233. These particles were also observed at grain boundaries, Fig. 280, and were less than 5 μ apart. Such particles, if much harder than the matrix containing them, could cause local plastic deformation. Observations of this mechanism have been made by transmission electron microscopy on austenitic steels containing carbide particles, from which dense clusters of dislocations were nucleated during plastic deformation, (266). In the present case, the flow stress could have been exceeded locally in the neighbourhood of second-phase particles, allowing the damage to spread from grain boundaries. If this mechanism were alone responsible for the initiation of damage both in the ordered and disordered alloy it is surprising that so few damaged regions were observed on ordered specimens, Fig. 233. Despite some hundreds of grains in the gauge length, fewer than ten pairs showed any damage at all. This points to some alternative factor as governing the initiation of damage. This mechanism might be the elastic interaction between neighbouring grains.
In disordered specimens, Fig. 240, damage was initiated preferentially in the regions of higher stress near the specimen edge, but further from the edge, damage tended to be localised near grain boundaries. It may be that all damage was initiated at grain boundaries, but propagation away from the boundary was much easier in the disordered alloy, because of the ease of cross slip.

The development of fatigue slip damage in the ordered alloy probably required the independent movement of $\frac{1}{2}a_0\langle 111 \rangle$ superpartials in order for cross slip to occur. Although such movement requires high stresses in the tensile test, (147), this need not be so during fatigue. The development of damage in the ordered alloy may be thought of as the gradual "erosion" of the ordered matrix by imperfect dislocations, producing disorder. The fact that this process is slow is indicated by the advance of fatigue damage in Fig. 233, produced by $24 \cdot 10^6$ cycles.

Replica electron micrographs of both alloys, Figs. 227, 235 and 236 showed that surface roughening and possibly incipient cracks formed within regions of fatigue slip damage. The development of cracks by this process was limited, in the ordered alloy, by the slow propagation of the regions of fatigue slip damage, and the eventual failure
of the specimen by rapid cleavage, and in the disordered alloy by the ease with which intergranular cracks were formed. These cracks then spread on a mixed inter- and transgranular path associated with stress relief by plastic deformation, consistent with the ease of cross slip in the disordered alloy. Eventually crack propagation became too rapid for stress relief to occur, and final failure took place by the propagation of a cleavage crack. Grain boundaries in the ordered alloy were also probably weakened by the presence of second-phase particles Fig. 233, but the final cleavage crack was not found to be associated with fatigue processes. Presumably, after the initiation of a crack, propagation was governed by conditions at the crack tip, and not by intergranular weakness, so that rapid cleavage fracture resulted.

5.4 

Iron-Aluminium, $\text{Fe}_3\text{Al}$

Although specimens deformed during the course of this investigation have been referred to as "ordered" and "disordered", these terms require clarification. The alloy contained 23.5 at.% aluminium. Fig. 11 shows that the maximum degree of long-range order, $S$, of the $\text{DO}_3$
type obtainable in an alloy of this composition is about 0.76. Even when fully ordered, the alloy consisted of domains of the ordered phase, surrounded by regions of disorder. The disordered material was prepared by quenching from 800°C, through the phase field of B2 order. It is possible that these specimens contained some nearest-neighbour short-range order, produced either by the anneal or during quenching.

Slip traces produced by the bending of an ordered or disordered specimen following incomplete fracture were not distinguishable. Studies of the deformation of ordered and disordered iron-25 at.% aluminium by observation of slip traces, (146), and by transmission electron microscopy, (152), have shown that little difference may be detected between the deformation characteristics of alloys in either state of order.

The dominating characteristic of the fatigue of specimens of iron-25 at.% aluminium revealed in the present investigation was the preferential initiation of cracks in grain boundaries, and the lack of any fatigue markings remote from grain boundaries on the specimen surface. Metallographic examination of grain boundaries and intergranular fracture surfaces, Fig. 287, did not provide evidence for the existence of second-phase particles at the
grain boundaries. Nevertheless, because the weakness was so pronounced, it is believed that it resulted from contamination at grain boundaries, probably by gaseous diffusion during annealing, and possibly combined with the effect investigated by Seybolt and Westbrook 1964 (185), (186) discussed in Section 2.8.3, whereby gas atoms are forced into interstitial sites near grain boundaries when a polycrystal is cooled from high temperatures.

Iron-aluminium alloys may be inherently susceptible to intergranular crack initiation, since despite precautions to ensure that conditions during melting were suitable, the ingot of iron - 49 at.% aluminium was completely brittle intergranularly. The annealing treatment given to the iron - 23.5 at.% aluminium fatigue specimens probably allowed gases to diffuse into the specimens prior to final preparation, Section 3.2.4. Certainly, diffusion down grain boundaries would be faster than diffusion through the bulk of the material, even allowing for lateral diffusion from the boundaries into the bulk, (173). As mentioned in Section 4.4.1, an attempt was made to detect grain boundary hardening by placing a series of closely-spaced microhardness indents across a grain
boundary of an electropolished fatigue specimen, Fig. 248. The results were inconclusive, since the apparatus used was insufficiently refined to allow complete standardization in the indenting technique. Despite care in operation a large scatter of hardness values was produced, reflected in the variation of indent size in Fig. 248. Westbrook 1964 (184) has emphasised that great care is required in the determination of microhardness values near grain boundaries. Presumably, a suitable microhardness tester would include a delicate mechanical loading device to standardize the indenting procedure, together with a refined method of measuring the indent size.

An elastically isotropic polycrystal distorts elastically equally easily in all directions, and no stress concentrations can arise at grain boundaries without plastic yielding. The measured elastic anisotropy, $E_{111}/E_{100}$, of iron - 25 at.% aluminium is about 1.6, (96), and it is therefore surprising that cracks can be nucleated at grain boundaries, apparently without significant or observable plastic deformation. However, as pointed out in Section 5.1.2, elastic anisotropy can give rise to reversing shear stresses along the grain boundaries of a polycrystal during
cyclic deformation, if the grains composing the boundary are suitably oriented. It is a measure of the weakness of the boundaries in the present case, that intergranular cracks were formed at such low stresses relative to the plastic properties of the material. Crack nuclei presumably formed by the progressive breakdown of bonds across the grain boundary under the influence of reversing shear stresses. Once a nucleus formed stress concentration at the crack tip allowed propagation to continue.

During fatigue at room temperature of both ordered and disordered specimens very fine slip markings were formed along a few grain boundaries. Such slip markings were sometimes observed together with an intergranular crack, Fig. 252, and sometimes no crack was obvious, Fig. 251. It is possible that such markings represent the effect of plastic stress relief, in the case of Fig. 252. However, it is also possible that markings of this type formed without the stress concentrating effect of a crack tip, by the mechanism described in Section 5.1.2 to account for the formation of intense fatigue slip markings next to grain boundaries in $\beta'$-copper-zinc alloys of high zinc content. The slip
markings in Fig. 251 are only 1 - $1\frac{1}{2}$ μ in length, which indicates that the stress concentration must have been very small, and limited in extent. Also no plastic deformation could be observed elsewhere on the surface of the specimen, indicating that the overall stress at the surface was less than the flow stress. Slip markings of the type shown in Fig. 251 may therefore have been formed as a result of the local transcendence of the flow stress immediately next to the boundary. The analysis in Section 5.1.2 leads to the conclusion that those conditions favouring plastic deformation next to the boundary also favour intergranular crack initiation. The orientation of the boundary to the slip systems in the more highly stressed grain presumably also plays a role in determining whether plastic deformation will occur.

In general, both ordered and disordered specimens showed crack propagation on both inter- and transgranular paths. Intergranular cracks usually propagated up to a triple point before transgranular propagation supervened. Transgranular propagation at room temperature was associated with crack branching, Fig. 256, and intense plastic deformation at the crack tip, Fig. 255. These
observations are consistent with the observed ease of cross slip in iron - 25 at.% aluminium, both in the ordered and disordered state, (146), (152). Cleavage fracture was difficult to induce at low temperature, even when intergranular cracks ½ mm. in length were present, Fig. 263. This is in marked contrast to the transgranular brittleness of the ordered equiatomic iron-cobalt alloy during fatigue at room temperature, since in this case no microcracks were observed, except for very localised fatigue markings less than 10 μ in length. It is possible that plastic deformation at the tips of intergranular cracks arrested at triple points produced blunting, and so prevented the initiation of rapid transgranular cleavage. However, stable transgranular cracks in the order of ½ mm. in length were also observed, Fig. 265, following fatigue at 77°K. The propagation of this crack must have been very slow, since the specimen was unbroken after 70·10^6 cycles.

Change in the ease of cross slip can have two effects on crack propagation in A2 structures. If cross slip is easy, propagation of true fatigue cracks by a ductile mechanism, is favoured, (240). If cross slip becomes more difficult, fatigue crack propagation by ductile
blunting of the crack tip should become more difficult. At the same time stress relief at other highly stressed points also becomes more difficult, favouring brittle transgranular fracture, (204).

The number of steps on the surface of fracture facets of the iron-23.5 at.% aluminium alloy produced by fatigue at room temperature, suggests that dark exudations from cracks probably resulted from attrition of the fracture surfaces during crack propagation. This view is supported by Figs. 258 and 259, which show that exudations appeared only after the propagation of the crack. The large quantity produced during fatigue at 77°K may only be a function of the very long lives, well in excess of $10^6$ cycles. It is to be expected that loose material would be transported to the mouth of the crack, because of the statistical probability that particles will move away from the confined spaces associated with the crack tip.

5.5 The Choice of Cleavage Fracture Plane

The observation that single crystals of iron - 49 at.% aluminium cleave on {111} planes suggests that a reappraisal of the factors governing the choice of cleavage plane in metals possessing the A2 and B2
structures is necessary.

Gilman 1962 (206), considering the choice of cleavage plane in transition metals possessing the A2 structure, examined the energy density of broken bonds on the \{100\} and \{110\} faces, and also the symmetry of the broken bonds. It was suggested that broken bonds on the \{100\} face could be rearranged more easily than those on the \{110\} face following fracture, because of the four-fold symmetry of the nearest neighbour bond directions on \{100\} faces, Fig. 33.

Table 16, column 3 gives the number of bonds (type I, II and III, Fig. 1) for each atom in the planes \{100\}, \{110\}, and \{111\} of the A2 and B2 structures. The density of bonds in terms of the number on the area $a_o^2$ is given in column 4. Gilman 1962 (206) considered these values in the following way.

Comparison of the type I bond density on the planes \{100\} (4 bonds) and \{110\} (2 $\sqrt{2}$ bonds) shows that cleavage should be favoured on the \{110\} plane, since the bond density is lower. Cleavage of most A2 transition metals takes place on \{100\} planes, so that Gilman also considered the density of type II bonds, believing this to be consistent with the high cohesive strength of the
transition metals. If the total broken bond density is to be lower on \{100\} planes, one may write:

\[ 4(I) + (II) < 2\sqrt{2}(I + II) , \]

where I and II represent the bond strengths of I and II bonds respectively. This gives:

\[ (II) > 0.64(I) \text{ for } \{100\} \text{ cleavage.} \]

In view of the high cohesive strength of A2 transition metals it was thought likely that the strength of type II bonds would be greater than 64\% of the strength of type I bonds.

However, examination of Table 16, column 4, shows that, considering type I bonds alone, cleavage on \{111\} planes should be much more favoured than cleavage on either \{100\} or \{110\} planes, since the broken bond density value is very low, \((4/\sqrt{3} \text{ bonds})\). Even taking into consideration type II bonds, cleavage on the \{111\} face is favoured with respect to \{100\} cleavage unless the strength of type II bonds is greater than 186\% of the strength of type I bonds. On this criterion alone, \{111\} cleavage should always be preferred to \{110\} cleavage.

The rearrangement of bonds on the fracture
surface may be more difficult for the \{111\} plane than the \{100\} or \{110\} planes in view of the three-fold symmetry of the \{111\} atomic arrangement, Fig. 301. Information on the rearrangement of surface bonds, and possible atomic rearrangement in surface layers may be obtained from low-energy electron diffraction experiments, as suggested by Gilman 1962 (206).

The criterion of broken bond density alone is unsatisfactory also because it is not clear why cleavage should not occur on high index planes if the broken bond density is favourable. An arbitrary planar cut through a crystal of the A2 or B2 structure passes through only a limited number of type I, II or III bonds per unit area, so that an additional criterion to cover the indices of the plane appears to be required. If cleavage can be regarded in terms of the macroscopic process of forcing a knife edge between a pair of parallel planes, cleavage should be easier if the planes are widely spaced.

Table 16, column 5 lists values of the function $D$, the number of bonds on the area $a_{0}^{2}$ divided by the interplanar spacing. This relationship eliminates all planes of higher index than \{111\} from consideration as cleavage planes.
The significance of these values may be shown graphically. Fig. 302 shows a plot of the function $D$ with respect to the relative bond strengths. The most favoured plane for cleavage will be that showing the lowest value of $D$. The points I, II and III are those at which bonding is produced by type I, II or III bonds only. This graph may be shown as a ternary diagram, Fig. 303. Points within the area of the triangle indicate the relative strengths of type I, II or III bonds. The surface of lowest $D$ value can be seen to be divided into three planes, representing relative bonding strengths such that $\{100\}$, $\{110\}$ or $\{111\}$ cleavage is favoured. A plan view of this surface is shown in Fig. 304.

It appears that the cleavage behaviour of A2 and B2 crystals can be rationalised using the criteria of the energy density of first, second and third nearest neighbour bonds, together with the interplanar spacing. However, clarification of the concept of "bonds" as used in the above considerations is required.

The treatment given above could apply to an arrangement of balls connected by brittle spokes in the direction of type I, II or III bonds. It is unlikely that this type of model can describe the cohesive properties
of real metal crystals, since the cohesive strength of metals can be expressed qualitatively in terms of volume alone, (82). If the cohesive strength of a metal is largely independent of structure (62), directional components in the bonding cannot be very large. However, if anisotropic bonding components exist, they may be sufficient to determine the choice of cleavage plane in the manner considered above.

Huggins 1923 (267) listed three "rules" which he suggested govern the choice of cleavage plane in crystals:

1) Cleavage occurs so that the faces formed are electrically neutral.

2) Weak bonds will be broken in preference to strong bonds.

3) If all bonds are equally strong, cleavage will occur parallel with planes of lowest bond density.

It was emphasised that "bonds" in this sense were considered to be formed by the interaction of an atomic nucleus and an electron group or of two electron groups, and were not necessarily formed on the line between atoms in parallel planes.
Predictions of the directionality of bonding are probably simpler for ionic compounds than for metal crystals. Ionic interactions may be presumed to occur between nuclei, and in the case of order of the B2 type between first nearest neighbours only. It is more likely therefore that ordered alloys of the B2 structure will cleave on \{110\} planes than the corresponding disordered alloy, if ordering originates from electrostatic effects. It was this concept that suggested that the cleavage plane of ordered iron-cobalt or iron-aluminium alloys might be different from that of the disordered alloys. No such change was found.

Iron-cobalt is unusual in that it was the only alloy investigated which can be retained disordered at room temperature by quenching, but it probably was the alloy with the smallest electrostatic interaction, of those studied, (Section 2.3.5). Therefore a change in the cleavage plane on ordering was unlikely. Chen 1961 (268) has also reported \{100\} cleavage for both ordered and disordered iron-cobalt - 2% vanadium.

The changes occurring in the cleavage plane of iron-aluminium alloys with composition is particularly interesting, and may reflect changes in the charge
distribution with changing aluminium content, (76), (77), (269). In this case bonds can be considered as the product of the interaction between nuclei and an anisotropic electron distribution, which, at higher aluminium contents, leads to strong interactions in directions corresponding with third nearest neighbour directions. Bonding of this type need not reflect any interaction between the nuclei of third nearest neighbours.

Work on the orientation of fracture faces of high-purity chromium (270) has shown that flat fracture faces are not always formed during cleavage, even at 77°K. It is surprising therefore that determinations of the cleavage plane orientation in iron - 49 at.% aluminium single crystals always showed accurate {111} orientation. The markings on the cleavage face also showed <110> traces, which were probably formed by other {111} planes, Fig. 291.

It is probable that this treatment of the question of the cleavage plane of A2 and B2 alloys is incomplete, and only represents a simple model of some factors which may influence the choice. Bond symmetry and atomic rearrangement of surface layers following the formation of a new surface have not been considered. An additional factor which has been emphasised as important
Gilman 1959 (202) has suggested that cleavage will be favoured on a plane having minimum elastic stiffness normal to it. Since the elastic stiffness of $\beta'$-copper-zinc is a minimum in the $<100>$ direction the {100} plane should be more favoured than the {110}. Nevertheless, cleavage occurs on the {110} plane, which may reflect the importance of the electrostatic interaction of nearest neighbours. Any future study of the cleavage properties of the crystals considered in this investigation should nevertheless include a determination of the single crystal elastic constants.
6. CONCLUSIONS

6.1 The B2 Structure

The formation and propagation of fatigue damage in the alloys examined has been interpreted in terms of the elastic and plastic properties, and no phenomenon was found which could be described as typical of all the alloys. The localisation of damage at grain boundaries in some of the alloys was attributed to a common mechanism. This mechanism was not considered as characteristic of the B2 structure, since similar local damage was observed in disordered alloys of the A2 structure. In common with other metal structures the development of widespread fatigue damage in alloys of the B2 structure requires the easy cross slip of screw dislocations.

Cleavage fracture was found to occur on any of the three low-index planes of the B2 structure. In this respect also no consistent pattern of behaviour was observed.
6.2 $\beta'$-Copper-Zinc

1) Within the range of compositions studied, 42.5 to 48.25 at.% zinc, cross slip becomes more difficult with decreasing zinc content, or decreasing temperature. Cross slip is easier in ternary alloys with gold, but more difficult in alloy with manganese.

2) The increasing difficulty of cross slip was associated with increasing separation between pairs of superpartials composing superdislocations. In alloys near the equiatomic composition, or in ternary alloys with gold, the superpartial spacing may only be a few atomic distances, and cross slip takes place by the movement of pairs of superpartials having parallel screw orientations on an atomically identical path through the lattice.

3) The fatigue properties of $\beta'$-copper-zinc are primarily governed by two factors:

   a) The distribution of stresses in an elastically anisotropic polycrystal.

   b) The changing ease of cross slip with zinc content.

4) The localisation of fatigue damage at grain boundaries in binary alloys of all compositions studied is due to stress concentration along the boundaries resulting from
the elastic interaction between differently oriented elastically anisotropic crystals.

5) The ease with which these stresses can be relieved by plastic deformation determines whether cracks are formed directly by a brittle mechanism or whether they are formed by the intensification of localised slip damage.

6) The formation of intense slip damage localised in the region of grain boundaries is only possible when cross slip of superdislocations is easy. Such regions of intense slip damage are consistent with the cross slip of superdislocations.

7) When cross slip is difficult the formation of sheets of transformation product having a habit plane \(\{2 \ 1 \ 1 \ 2\}_\beta\) provides an additional deformation mode.

8) Fatigue crack propagation is largely ductile in alloys of high zinc content at room temperature, and largely brittle in alloys of low zinc content, or in high-zinc alloys at low temperature. These observations reflect the increasing difficulty of cross slip with decreasing zinc content or temperature.
6.3 \(\beta^1\)-Gold-Zinc

1) The distribution of fatigue slip damage is determined by two factors:
   a) The elastic anisotropy.
   b) The plastic anisotropy.

2) Elastic anisotropy is an important factor in determining the distribution of damage near grain boundaries, and exerts an influence either directly through stress concentration as a result of elastic constraint across the boundary, or through its influence on the image force on dislocations having an \(a_0 <100>\) Burgers vector.

3) Plastic anisotropy determines the distribution of damage remote from grain boundaries, in that some grains are favourably oriented for slip at low values of the applied stress.

4) The formation of intense slip damage is consistent with cross slip of dislocations between \{110\} planes sharing a common \(<100>\) direction. The form of the trace of damage on the surface is determined by the angle between the slip direction and the specimen surface.

5) The spread of fatigue damage takes place by the addition of new small regions of dislocation activity.
to areas already existing, but dislocation movement continues within existing areas.

6) Fatigue cracks are probably initiated intergranularly, but propagate transgranularly in a ductile manner as a result of the ease of cross slip, both at 293 and 77°K.

7) The lack of fatigue slip damage during fatigue at 77°K is due to the relative ease with which cracks are initiated rather than regions of intense dislocation activity.

6.4 Iron-Cobalt-Vanadium

1) Regions of intense slip fatigue damage in both the disordered and ordered alloy were formed by cross slip of dislocations.

2) The association of damage with grain boundaries in both the disordered and ordered alloy is due to a combination of elastic coherency stresses, assisted by local deformation nucleated at second-phase particles.

3) The rapid spread of slip damage across grains in the disordered alloy is consistent with the ease of cross slip of dislocations in this alloy. Regions of
slip damage were limited at grain boundaries by the difficulty of moving \( \frac{1}{2} a_0 \langle 111 \rangle \) superpartial dislocations independently through the ordered lattice.

4) Both alloys develop surface markings during fatigue consistent with the development of small cracks in regions of intense slip.

5) The initiation of intergranular cracks in the disordered alloy was assisted by the presence of particles rich in vanadium at the grain boundaries. Crack propagation was slow initially because of plastic deformation at the crack tip. When stresses reached a critical value, cleavage propagation supervened.

6) Rapid cleavage crack propagation in the ordered alloy was due to the difficulty of stress relief by cross slip at the crack tip.

6.5 Iron - 23.5 at.\% Aluminium

1) The lack of fatigue slip damage on either ordered or disordered alloy specimens was due to the weakness of grain boundaries resulting in intergranular cracks limiting plastic deformation on the surface.

2) Grain boundary weakness was possibly due to gaseous segregation.
3) The formation of very short slip markings along some grain boundaries in both the ordered and disordered alloy may have been due either to intergranular crack propagation accompanied by plastic deformation at the crack tip or elastic coherency stresses giving rise to localised plastic deformation.

4) Transgranular crack propagation was associated with plastic deformation at the crack tip, consistent with the ease of cross slip in this alloy in both the ordered and disordered state. However, the propagation of cracks on low-index planes in the crystal indicates that cleavage crack propagation was also significant during fatigue at 293°K.

5) Plastic deformation provided a means of stress relief at the tip of cracks initiated during fatigue of both alloys at 77°K, since stable inter- and transgranular cracks were observed.

6.6 Future Work

Three aspects of the present work require further investigation to test the proposals made in Section 5.

1) The nature of the dislocations and dislocation movement producing slip in β'-copper-zinc. If superpartials
in $\beta'$-copper-zinc are separated by only a few atomic distances, it is unlikely that superdislocations can be resolved into their component superpartials using transmission electron microscopy. However, if antiphase domain boundaries can be observed, it should be possible to determine whether dislocations in $\beta'$-copper-zinc produce an antiphase boundary trail during movement. If no trail of disorder is observed, and dislocations cannot be resolved into superpartials, it may be inferred that the superpartial spacing is indeed small. In this respect the examination of ternary $\beta'$-copper-zinc-manganese alloys would probably be useful. If the addition of manganese increases the superpartial separation, it is possible that superdislocations in these alloys could be resolved into superpartials. An examination of ternary alloys should also include determinations of the critical temperature for long-range order so that the examination of slip traces and superpartial spacing can be correlated with ordering energy.

2) The importance of orientation factors across grain boundaries in anisotropic polycrystals to the development of localised fatigue damage may be investigated in two ways. Firstly, by the examination of specimens in which a large number of grains are subject to fatigue stresses. If the stress
amplitude is small and constant, it is likely that only the most suitably oriented grain pairs will show damage. A large number of grains in each specimen would ensure that a wide range of relative orientations would be present. Those grain pairs showing damage would probably be representative of the most favourable conditions and a correlation of the most important orientation factors could then be made.

Secondly, bicrystals composed of grains of specific orientation, having a boundary of specific orientation, could be stressed under controlled conditions. However, without theoretical predictions of the most favourable orientations for the formation of damage, investigation of each of the variables in turn would entail a very long programme. Since the mutual orientation of two crystals and their common boundary involves five degrees of freedom, Section 2.8.1, the orientation of a grain pair to an applied stress involves seven degrees of freedom.

3) The nature and relative importance of factors governing the choice of cleavage fracture plane in A2 and B2 metals are not well established. Important factors include the elastic constants, the ease of dislocation movement and its geometry in the crystal, the nature of the binding forces between atoms and the nature and distribution
of impurities in the crystal. Since the cleavage fracture plane of iron-rich iron-aluminium alloys has been shown to change with composition, this system presents a good opportunity for further investigation of cleavage fracture in a system in which the nature of atomic interactions with changing composition have been investigated. Such a study should also include determinations of the single crystal elastic constants for each composition. It is doubtful whether the diagram shown in Fig. 303 could provide a useful approach to the problem, except possibly to emphasise the importance of an anisotropic bonding distribution as a factor in cleavage fracture.
APPENDIX A

Elasticity

The generalised form of Hooke's law for the elastic deformation of a solid relative to the axes $x$, $y$, $z$, may be expressed as:

$$
e_{xx} = s_{11}x + s_{12}y + s_{13}z + s_{14}x + s_{15}z + s_{16}y
$$

$$
e_{yy} = s_{21}x + s_{22}y + s_{23}z + s_{24}x + s_{25}z + s_{26}y
$$

$$
e_{xy} = s_{61}x + s_{62}y + s_{63}z + s_{64}x + s_{65}z + s_{66}y
$$

where, $e_{xx}$, $e_{yy}$, $e_{zz}$, $x$, $y$ and $z$ are the principal strains and stresses in the $x$, $y$ and $z$ directions respectively, $e_{ij}$ and $I_{ij}$ the shear strains and stresses on the plane $i$ in the direction $j$, and $s_{ij}$ the elastic compliance for the appropriate strain and stress. The symmetry of the cubic lattice leads to symmetry in these relations also, reducing the number of variables. The elastic compliances for the cubic lattice are specified by the matrix:

$$
\begin{bmatrix}
    s_{11} & s_{12} & s_{12} & 0 & 0 & 0 \\
    s_{12} & s_{11} & s_{12} & 0 & 0 & 0 \\
    s_{12} & s_{12} & s_{11} & 0 & 0 & 0 \\
    0 & 0 & 0 & s_{44} & 0 & 0 \\
    0 & 0 & 0 & 0 & s_{44} & 0 \\
    0 & 0 & 0 & 0 & 0 & s_{44}
\end{bmatrix}
$$
The coefficient $1/s_{44}$, usually written as $C$ or $G$, may be interpreted directly in terms of the structure. It is a measure of the resistance to deformation with respect to \{100\} $<010>$ shear. The coefficient $1/s_{11}$ is the Young's modulus $E_{100}$ in the $<100>$ direction in the crystal. The resistance to deformation under hydrostatic pressure is measured by the bulk modulus $K$, given by

$$K = 1/3(s_{11} + 2s_{12})$$

The resistance to $\{110\} <\bar{1}10>$ shear, $C'$, is measured as $1/2(s_{11} - s_{12})$. An anisotropic solid will have the same value of the shear modulus in all directions, so that for this case,

$$C = C'$$

Elastic anisotropy is usually measured as the ratio $C/C'$. However, some early reports on elastic properties use the ratio $E_{111}/E_{100}$. $E_{111}$, the Young's modulus measured in the $<111>$ direction is given by:

$$1/E_{hkl} = s_{11} - 2(s_{11} - s_{12} - s_{12} - s_{12} - s_{12}) F(\gamma),$$

while the shear modulus $G$ is given by:

$$1/G_{hkl} = s_{44} + 4(s_{11} - s_{12} - s_{12} - s_{12} - s_{12}) F(\gamma),$$

where $F(\gamma)$ is the orientation function given by

$$(l^2m^2 + m^2n^2 + n^2l^2)$$

where $l$, $m$ and $n$ are the cosines of
the angles of the direction of the applied stress with the crystal axes \( x , y \) and \( z \). This allows the value of \( E \) or \( G \) in any direction in the crystal to be calculated. Since the elastic compliances are constants, a plot of \( 1/E_{\text{hkl}} \) or \( 1/G_{\text{hkl}} \) against \( F(y) \) gives a straight line, e.g. Fig. 296.

In an elastically anisotropic crystal the deformation produced by an arbitrary stress in the elastic range will depend on the angle between the direction of application of the stress and the crystal axes. For a tensile stress, the ratio of the net transverse contraction to the longitudinal extension is given by Poisson's ratio, \( \sigma_{\text{hkl}} \). Depending on the direction of the applied stress this has the value:

\[
\sigma_{100} = \frac{3K - 2C}{6K + 2C}, \text{ for the } <100> \text{ direction and } \\
\sigma_{\text{111}} = \frac{3K - 2C}{6K + 2C}, \text{ for the } <111> \text{ direction.}
\]

Elasticity data are also quoted in terms of the elastic coefficients, \( c_{11} \), \( c_{12} \) and \( c_{44} \) which are related to the elastic compliances by the relations:

\[
c_{44} = \frac{1}{s_{44}} \]

\[
(c_{11} + 2c_{12}) = \frac{1}{(s_{11} + 2s_{12})} \]

\[
(c_{11} - c_{12}) = \frac{1}{(s_{11} - s_{12})} \]
APPENDIX B

Two-Surface Analysis

Two-surface analysis allows absolute determination of the habit of a plane in a crystal, within the limits of experimental error. A separate solution is obtained for each set of markings in non-parallel planes if the orientation of the crystal is known.

In the present example, the determination of the habit plane of the sheets of transformation product shown in Figs. 169 and 170, the surface traces of the markings appeared as in Fig. 305. The traces on the specimen surface made an angle N 27°W with the specimen axis N - S, while those on the section surface made an angle of 64° with the specimen surface E - W. This diagram shows that the pole of the habit plane must lie in the quadrant of the stereographic projection of the crystal described by the arc NE.

A Laue back-reflection x-ray photograph, Fig. 306, was taken from the section surface since the area of the grain in the specimen surface was too small to provide a unique solution. In order to obtain the crystal orientation relative to the specimen surface, the orientation obtained from the back-reflection photograph was rotated through 90° about the E - W
axis in the direction S. This resulted in the projection shown in Fig. 307. The pole O11 of the Laue photograph appears near the direction N in the NE quadrant.

The specimen surface trace N 27°W was then drawn on the projection, broken line, Fig. 307. The pole of any plane producing this trace must lie on the line at right angles to this, marked "pole trace". The angle of 64° was then measured off along the axis W - E, as indicated in Fig. 307. This point, together with the extremities of the surface trace line, fix the great circle containing the required habit plane. This great circle, dot-dashed line, Fig. 307, was then drawn on the projection. The pole of this circle must lie at 90° from the point of intersection of the circle with the line marked "pole trace".

The required pole lies at the point ®, Fig. 307. This point lies 6° from the <001> zone and 2° from the <011> zone, corresponding very closely with the observed habit plane of martensite in β' -copper-zinc, \{2 11 12\}, (104).

Values for the habit plane of straight crystallographic cracks were obtained by the same method. These results are listed in Table 9.
APPENDIX C

Single-Surface Analysis

Single surface analysis provides a method of determining the habit plane of markings appearing in a single surface of a crystal, when a large number of markings are available, and when the orientation of each crystal is known. It is not capable of providing a solution for each separate example, and is a statistical method, relying on the combination of a large number of results to eliminate inconsistencies. For this reason, some knowledge of likely solutions is required, or alternatively, some additional means of testing the feasibility of solutions offered.

In the present study, the method was used to determine the habit plane of intense slip markings or cracks appearing next to grain boundaries in 46.95 at.% zinc β’-copper-zinc specimens following fatigue at room temperature. These cracks were in the order of 15 μ in length and two-surface analysis was not feasible, since the depth of crack penetration into the specimen was small.

The orientation of each grain containing short markings was determined relative to fiducial line, the
specimen axis N – S, by means of a Laue back-reflection x-ray photograph. The angle between the fiducial line in the surface and the crack was measured and drawn of the stereographic projection of the crystal orientation.

The pole of the plane on which these markings were formed lay on the line at right angles to the surface trace. In order to correlate the results obtained from each crystal, all crystal orientations were rotated to standard 001 projection, together with all the pole traces, and plotted on a single stereogram, Fig. 308. If all these traces arise from markings on a plane \{hkl\}, each pole trace in Fig. 308 should pass through a pole of this type somewhere along its length. It is likely therefore, that points of intersection represent the required pole. However, this is not certain for two reasons:—Firstly, each pole trace cuts every other trace once, so that a large number of these intersection points must give spurious solutions. Secondly, in general, 24 variants of a given pole are available. This latter factor is eliminated by examination of stereographic triangles, each of which contains a single variant of every pole on the projection. Fig. 309 shows the standard 001 stereographic projection divided into stereographic triangles. Three distinct shapes of triangle,
all crystallographically equivalent, are shown, A, B and C. A standard triangle, corresponding to the shape of each of these types was drawn on tracing paper and placed over each triangle of the same type in turn. Those traces which appear to cluster near a particular pole, determined by inspection, were drawn on, more being added at each triangle. Such clustering of lines is shown near the 110 poles in Fig. 308. This indicates a probable solution. The three solutions obtained by investigation of the three types of triangle may then be combined by rotation into a single triangle. The solution \{110\} requires the rotation of the triangle type C to coincide with the other two, which need not be combined, Fig. 149. This diagram also includes some traces which do not pass near to any 110 pole. These may represent different solutions to the habit plane of the cracks, but are more probably the result of incorrect determination of crystal orientation, angular measurement or some other experimental feature. Such solutions may be ignored.
APPENDIX D.

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Vv2
### TABLE 1

Heats of Formation of B2 Compounds

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<tr>
<th>Compound</th>
<th>$-H_{m}^{o}$</th>
<th>$T_{m}$</th>
<th>$T_{c}/T_{m}$</th>
<th>Electronegativity</th>
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<td>AgZn</td>
<td>1.7</td>
<td>298</td>
<td>0.56</td>
<td>0.3</td>
<td>(64)</td>
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<tr>
<td>AgCd</td>
<td>2.17</td>
<td>304</td>
<td>0.73</td>
<td>0.2</td>
<td>(65)</td>
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<td>CuZn</td>
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<td>(64)</td>
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<td>AuCd</td>
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<td>298</td>
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<td>(64)</td>
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<td>AuCd</td>
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<td>&lt;1.0</td>
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<td>(66)</td>
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<td>AgMg</td>
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<td>~1.0</td>
<td>0.7</td>
<td>(65)</td>
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<td>AuZn</td>
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<td>~1.0</td>
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<td>AlFe</td>
<td>6.1</td>
<td>298</td>
<td>-</td>
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<td>298</td>
<td>0.57</td>
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### TABLE 2

Comparison of Values of Volume/Atom in Elements and Compounds

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<td>CuZn</td>
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<td>0.958 (4)</td>
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<tr>
<td>AuZn</td>
<td>16.077</td>
<td>15.302</td>
<td>0.952 (3)</td>
</tr>
<tr>
<td>AuCd</td>
<td>19.269</td>
<td>18.472</td>
<td>0.958 (68)</td>
</tr>
<tr>
<td>AgCd</td>
<td>19.316</td>
<td>18.489</td>
<td>0.955 (68)</td>
</tr>
<tr>
<td>AgZn</td>
<td>16.124</td>
<td>15.720</td>
<td>0.975 (68)</td>
</tr>
<tr>
<td>FeAl</td>
<td>14.186</td>
<td>12.297</td>
<td>0.867 (55)</td>
</tr>
<tr>
<td>Fe₂Al</td>
<td>12.731</td>
<td>12.144</td>
<td>0.953 (55)</td>
</tr>
<tr>
<td>CoAl</td>
<td>13.847</td>
<td>11.721</td>
<td>0.845 (68)</td>
</tr>
<tr>
<td>NiAl</td>
<td>13.767</td>
<td>12.032</td>
<td>0.873 (68)</td>
</tr>
<tr>
<td>CoFe</td>
<td>11.437</td>
<td>11.600</td>
<td>1.013 (69)</td>
</tr>
</tbody>
</table>

* Extrapolated Value

* Measured at 50°C
The electronegativities of the elements, from Evans 1964, (67)

<table>
<thead>
<tr>
<th>Element</th>
<th>Electronegativity</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>2.1</td>
</tr>
<tr>
<td>Li</td>
<td>1.0</td>
</tr>
<tr>
<td>Na</td>
<td>0.9</td>
</tr>
<tr>
<td>K</td>
<td>0.8</td>
</tr>
<tr>
<td>Rb</td>
<td>0.8</td>
</tr>
<tr>
<td>Cs</td>
<td>0.7</td>
</tr>
<tr>
<td>Fr</td>
<td>0.7</td>
</tr>
<tr>
<td>Element</td>
<td>At. No.</td>
</tr>
<tr>
<td>---------</td>
<td>--------</td>
</tr>
<tr>
<td>Al</td>
<td>13</td>
</tr>
<tr>
<td>Mn</td>
<td>25</td>
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<td>Fe</td>
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<td>Co</td>
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<td>Ni</td>
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<td>Cu</td>
<td>29</td>
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<td>Zn</td>
<td>30</td>
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<td>Ag</td>
<td>47</td>
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<tr>
<td>Cd</td>
<td>48</td>
</tr>
<tr>
<td>Au</td>
<td>79</td>
</tr>
<tr>
<td>Alloy</td>
<td>Composn. at. % Zn or Cd.</td>
</tr>
<tr>
<td>-----------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>$\beta^+$-CuZn</td>
<td>-</td>
</tr>
<tr>
<td>46.6</td>
<td>-</td>
</tr>
<tr>
<td>47.2</td>
<td>0.578</td>
</tr>
<tr>
<td>48.26</td>
<td>1.22</td>
</tr>
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<td>44.8</td>
<td>1.344</td>
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<td>48.25</td>
<td>1.265</td>
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<td>50.0</td>
<td>1.36</td>
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<tr>
<td>$\beta^+$-AuZn</td>
<td>-</td>
</tr>
<tr>
<td>$\beta^+$-AuCd</td>
<td>47.5</td>
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TABLE 6
Slip Modes in Some Ordered Alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Structure</th>
<th>Slip Mode</th>
<th>Slip Traces</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>β ′ - CuZn</td>
<td>B2</td>
<td>{110} - {112} &lt;111&gt;</td>
<td>Cross slip and straight traces.</td>
<td>(141)</td>
</tr>
<tr>
<td>β ′ - AuZn</td>
<td>B2</td>
<td>{110} &lt;100&gt;</td>
<td>Very easy cross slip</td>
<td>(150)</td>
</tr>
<tr>
<td>Fe₃Al</td>
<td>B2</td>
<td>&lt;111&gt;</td>
<td>Easy cross slip as α-iron</td>
<td>(152)</td>
</tr>
<tr>
<td>Fe₃Al</td>
<td>D0₃</td>
<td>&lt;111&gt;</td>
<td>Easy cross slip as α-iron</td>
<td>(152)</td>
</tr>
<tr>
<td>FeCo</td>
<td>A2</td>
<td>&lt;111&gt;</td>
<td>Easy cross slip as α-iron</td>
<td>(147)</td>
</tr>
<tr>
<td>FeCo</td>
<td>B2</td>
<td>{110} &lt;111&gt;</td>
<td>Straight slip traces, cross slip difficult.</td>
<td>(147)</td>
</tr>
</tbody>
</table>
### TABLE 7

Components used in fatigue machine power amplifier; Fig. 39

<table>
<thead>
<tr>
<th>Resistors</th>
<th>Capacitors</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1$ 470K pot. 3W</td>
<td>$C_1$ 8 micro F</td>
</tr>
<tr>
<td>$R_2$ 10K 1/2W</td>
<td>$C_2$ 50 micro F</td>
</tr>
<tr>
<td>$R_3$ 1K 1/2W</td>
<td>$C_3$ 50 micro F</td>
</tr>
<tr>
<td>$R_4$ 10K 1/2W</td>
<td>$C_4$ 50 micro F</td>
</tr>
<tr>
<td>$R_5$ 100K 1/2W</td>
<td>$C_5$ 50 micro F</td>
</tr>
<tr>
<td>$R_6$ 100K 1/2W</td>
<td>$C_6$ 8 micro F</td>
</tr>
<tr>
<td>$R_7$ 270 ohm 1/2W</td>
<td>$C_7$ Variable</td>
</tr>
<tr>
<td>$R_8$ 47K 1/2W</td>
<td>$C_8$ Variable</td>
</tr>
<tr>
<td>$R_9$ 47K 1/2W</td>
<td>$C_9$ 8 micro F</td>
</tr>
<tr>
<td>$R_{10}$ 100 ohm 1/2W</td>
<td>$C_{10}$ 8 micro F</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Valves</th>
<th>Transformers</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_1$ 6J5</td>
<td>Mains 350 - 0 - 350</td>
</tr>
<tr>
<td>$V_2$ 807</td>
<td></td>
</tr>
<tr>
<td>$V_3$ 807</td>
<td></td>
</tr>
<tr>
<td>$V_4$ UU8</td>
<td></td>
</tr>
</tbody>
</table>

$S_1$ switch

$L_1$ choke approx. 18 H
### TABLE 8
Composition and Lattice Parameter of Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition (at.%)</th>
<th>Lattice Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta'$-Cu/Zn</td>
<td>42.5 zinc</td>
<td></td>
</tr>
<tr>
<td></td>
<td>45.1 zinc</td>
<td></td>
</tr>
<tr>
<td></td>
<td>46.95 zinc</td>
<td></td>
</tr>
<tr>
<td></td>
<td>48.25 zinc</td>
<td></td>
</tr>
<tr>
<td>Cu/Mn/Zn</td>
<td>50 copper</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.5 manganese</td>
<td></td>
</tr>
<tr>
<td></td>
<td>42.5 zinc</td>
<td></td>
</tr>
<tr>
<td>Cu/Au/Zn</td>
<td>46.6 copper</td>
<td></td>
</tr>
<tr>
<td></td>
<td>43 zinc</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.4 gold</td>
<td></td>
</tr>
<tr>
<td>$\beta'$-Au/Zn</td>
<td>50.3 gold</td>
<td>3.149</td>
</tr>
<tr>
<td></td>
<td>49.7 zinc</td>
<td></td>
</tr>
<tr>
<td>Fe/Co/V</td>
<td>49.6 iron</td>
<td>2.861 (ordered)</td>
</tr>
<tr>
<td></td>
<td>48.3 cobalt</td>
<td>2.859 (disordered)</td>
</tr>
<tr>
<td></td>
<td>2.08 vanadium</td>
<td></td>
</tr>
<tr>
<td>Fe$_3$Al</td>
<td>23.5 aluminium</td>
<td></td>
</tr>
<tr>
<td>FeAl</td>
<td>49. aluminium</td>
<td>2.909</td>
</tr>
</tbody>
</table>
TABLE 9

The Orientation of Cracks in Fatigued $\beta'$-Copper-Zinc

<table>
<thead>
<tr>
<th>Composition and Temperature</th>
<th>Crystal Angle from [011] Zone (Degrees)</th>
<th>Crack Angle from [100] Zone (Degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>42.5 at.% zinc, room temp.</td>
<td>2/1</td>
<td>1$\frac{1}{2}$</td>
</tr>
<tr>
<td></td>
<td>3/1</td>
<td>1$\frac{1}{2}$</td>
</tr>
<tr>
<td></td>
<td>4/1</td>
<td>1$\frac{1}{2}$</td>
</tr>
<tr>
<td></td>
<td>5/1</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>6/1</td>
<td>1$\frac{1}{2}$</td>
</tr>
<tr>
<td></td>
<td>6/2</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>7/1</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>7/2</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>8/1</td>
<td>1$\frac{1}{2}$</td>
</tr>
<tr>
<td></td>
<td>9/1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>10/1</td>
<td>1$\frac{1}{2}$</td>
</tr>
</tbody>
</table>

| 48.25 at.% zinc, 77°K      | 1                                       | 2$\frac{1}{2}$                       |
|                            | 1$\frac{1}{2}$                         | 2                                    |
|                            | 3                                       | 2                                    |
|                            | 2                                       | 0                                    |
### TABLE 10

**Tensile Test Results for β¹-Copper-Zinc Alloys**

<table>
<thead>
<tr>
<th>Composition at.% zinc</th>
<th>Test Temp. °K</th>
<th>Elongation %</th>
<th>Mean Ultimate T. Strength kg./mm.²</th>
<th>Mean UTS. kg./mm.²</th>
</tr>
</thead>
<tbody>
<tr>
<td>48.25</td>
<td>77</td>
<td></td>
<td></td>
<td></td>
</tr>
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<td></td>
<td></td>
<td>10.5</td>
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<td>47.1</td>
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<td>13.5</td>
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<td>48.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.0</td>
<td>14</td>
<td>47.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>17.0</td>
<td></td>
<td>46.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18.5</td>
<td></td>
<td>33.4</td>
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<tr>
<td></td>
<td></td>
<td>19.5</td>
<td></td>
<td>39.8</td>
</tr>
<tr>
<td>48.25</td>
<td>293</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>23.5</td>
<td>21.5</td>
<td>30.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25.0</td>
<td></td>
<td>35.4</td>
</tr>
<tr>
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<td></td>
<td>8.5</td>
<td></td>
<td>30.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.5</td>
<td></td>
<td>29.1</td>
</tr>
<tr>
<td>39.8</td>
<td>293</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>13.0</td>
<td>12.5</td>
<td>31.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13.5</td>
<td></td>
<td>33.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.0</td>
<td></td>
<td>34.0</td>
</tr>
</tbody>
</table>

**Loading Rate** 1 kg./second
TABLE 11

The Orientation of Flat Fracture Facets
Determined from X-Ray Back Reflection Photographs

<table>
<thead>
<tr>
<th>Material</th>
<th>State</th>
<th>Plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta'$-Copper-zinc (42.5 at.% zinc)</td>
<td>ordered</td>
<td>${110}$</td>
</tr>
<tr>
<td>Iron-cobalt-vanadium</td>
<td>ordered</td>
<td>${100}$</td>
</tr>
<tr>
<td>Iron-aluminium (23.5 at.% aluminium)</td>
<td>disordered</td>
<td>${100}$</td>
</tr>
<tr>
<td>Iron-aluminium (49 at.% aluminium)</td>
<td>ordered</td>
<td>${111}$</td>
</tr>
</tbody>
</table>
TABLE 12

The Relative Spacing of $\frac{1}{2}a_0 <111>$ Superpartials in B2 Alloys

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_c , ^\circ K$</th>
<th>$G_{111} \times 10^{12}$ dynes/cm$^2$</th>
<th>$S_{max}$</th>
<th>$\frac{G}{T_c \cdot S_{max}^2}$</th>
<th>Slip Direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta^t$-CuZn</td>
<td>740</td>
<td>0.112</td>
<td>1</td>
<td>1.51 $\times 10^8$</td>
<td>$&lt;111&gt;$</td>
</tr>
<tr>
<td>$\beta^t$-AuZn</td>
<td>~1100</td>
<td>0.123</td>
<td>1</td>
<td>1.12 $\times 10^8$</td>
<td>$&lt;100&gt;$</td>
</tr>
<tr>
<td>Fe-50%Co</td>
<td>993</td>
<td>~0.6</td>
<td>1</td>
<td>6.05 $\times 10^8$</td>
<td>$&lt;111&gt;$</td>
</tr>
<tr>
<td>Fe$_3$Al</td>
<td>1073</td>
<td>~0.6</td>
<td>0.5</td>
<td>22.4 $\times 10^8$</td>
<td>$&lt;111&gt;$</td>
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</tbody>
</table>
### TABLE 13

Relative Values of Applied Stress in a Given Crystallographic Direction to Produce Slip on the System \{110\} <111>

<table>
<thead>
<tr>
<th>Direction</th>
<th>$\alpha$</th>
<th>$\cos \alpha$</th>
<th>$\beta$</th>
<th>$\cos \beta$</th>
<th>$\cos \alpha \cdot \cos \beta$</th>
<th>$1/\cos \alpha \cdot \cos \beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;100&gt;</td>
<td>45°</td>
<td>0.707</td>
<td>54°44'</td>
<td>0.578</td>
<td>0.408</td>
<td>2.45</td>
</tr>
<tr>
<td>&lt;110&gt;</td>
<td>60°</td>
<td>0.500</td>
<td>35°16'</td>
<td>0.816</td>
<td>0.408</td>
<td>2.45</td>
</tr>
<tr>
<td>&lt;111&gt;</td>
<td>35°16'</td>
<td>0.816</td>
<td>70°32'</td>
<td>0.334</td>
<td>0.273</td>
<td>3.66</td>
</tr>
<tr>
<td>&lt;210&gt;</td>
<td>50°46'</td>
<td>0.632</td>
<td>39°14'</td>
<td>0.775</td>
<td>0.490</td>
<td>2.04</td>
</tr>
<tr>
<td>&lt;211&gt;</td>
<td>30°</td>
<td>0.578</td>
<td>61°52'</td>
<td>0.471</td>
<td>0.408</td>
<td>2.45</td>
</tr>
<tr>
<td>&lt;221&gt;</td>
<td>45°</td>
<td>0.707</td>
<td>54°44'</td>
<td>0.578</td>
<td>0.408</td>
<td>2.45</td>
</tr>
<tr>
<td>&lt;310&gt;</td>
<td>47°52'</td>
<td>0.670</td>
<td>43°06'</td>
<td>0.730</td>
<td>0.490</td>
<td>2.04</td>
</tr>
<tr>
<td>&lt;311&gt;</td>
<td>31°29'</td>
<td>0.853</td>
<td>58°31'</td>
<td>0.523</td>
<td>0.446</td>
<td>2.24</td>
</tr>
<tr>
<td>&lt;320&gt;</td>
<td>53°58'</td>
<td>0.588</td>
<td>36°49'</td>
<td>0.801</td>
<td>0.470</td>
<td>2.13</td>
</tr>
<tr>
<td>&lt;321&gt;</td>
<td>40°54'</td>
<td>0.756</td>
<td>51°53'</td>
<td>0.617</td>
<td>0.466</td>
<td>2.15</td>
</tr>
</tbody>
</table>
### TABLE 14

Values of the Orientation Function $F(y)$ for Crystal Pairs of 46.95 at.% Zinc $\beta'$-Copper-Zinc

<table>
<thead>
<tr>
<th>Crystal Pair</th>
<th>axis 1</th>
<th>axis 2</th>
<th>axis 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 1</td>
<td>0.29</td>
<td>0.29</td>
<td>0.21</td>
</tr>
<tr>
<td>A 2</td>
<td>0.32</td>
<td>0.21</td>
<td>0.27</td>
</tr>
<tr>
<td>B 1</td>
<td>0.29</td>
<td>0.11</td>
<td>0.23</td>
</tr>
<tr>
<td>B 2</td>
<td>0.13</td>
<td>0.14</td>
<td>0.09</td>
</tr>
<tr>
<td>C 1</td>
<td>0.32</td>
<td>0.21</td>
<td>0.22</td>
</tr>
<tr>
<td>C 2</td>
<td>0.20</td>
<td>0.21</td>
<td>0.15</td>
</tr>
<tr>
<td>D 1</td>
<td>0.16</td>
<td>0.20</td>
<td>0.24</td>
</tr>
<tr>
<td>D 2</td>
<td>0.33</td>
<td>0.25</td>
<td>0.28</td>
</tr>
<tr>
<td>E 1</td>
<td>0.12</td>
<td>0.15</td>
<td>0.09</td>
</tr>
<tr>
<td>E 2</td>
<td>0.31</td>
<td>0.23</td>
<td>0.05</td>
</tr>
<tr>
<td>F 1</td>
<td>0.31</td>
<td>0.18</td>
<td>0.25</td>
</tr>
<tr>
<td>F 2</td>
<td>0.03</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td>G 1</td>
<td>0.25</td>
<td>0.12</td>
<td>0.24</td>
</tr>
<tr>
<td>G 2</td>
<td>0.15</td>
<td>0.31</td>
<td>0.26</td>
</tr>
<tr>
<td>H 1</td>
<td>0.32</td>
<td>0.21</td>
<td>0.22</td>
</tr>
<tr>
<td>H 2</td>
<td>0.32</td>
<td>0.19</td>
<td>0.24</td>
</tr>
<tr>
<td>Direction</td>
<td>α</td>
<td>cos α</td>
<td>β</td>
</tr>
<tr>
<td>-----------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>&lt;100&gt;</td>
<td>45°</td>
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<td>90°</td>
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Fig. 251 Fe$_3$Al, disordered. Fatigued 1.0 \times 10^6$ cycles. Detail of Fig. 250.

Fig. 252 Fe$_3$Al, ordered. Fatigued 9.0 \times 10^6$ cycles at 293°K. Grain boundary at (A), Fig. 253.
Fig. 253 $\text{Fe}_3\text{Al}$, ordered. Fatigued $9.0 \cdot 10^6$ cycles at $293^\circ\text{K}$.

Fig. 254 $\text{Fe}_3\text{Al}$, disordered. Fatigued $1.0 \cdot 10^6$ cycles at $293^\circ\text{K}$.
Fig. 255 Fe₃Al, disordered. Detail of crack tip at left Fig. 254.

Fig. 256 Fe₃Al, ordered. Fatigued 1.26 \times 10^6 cycles.
Fig. 257. \( \text{Fe}_2\text{Al} \), disordered. Fatigue 0.59 \( \times \) \( 10^6 \) cycles at 293°K.
Figs. 258 and 259 Fe$_3$Al, ordered. After $9.0 \times 10^6$ cycles, at 293 K, (above), and $12.6 \times 10^6$ cycles, (below).
Fig. 260 Fe$_3$Al, disordered. Fracture face, produced by Fatiguing 0.59 x $10^6$ cycles at 293°K.

Fig. 261 Fe$_3$Al, ordered. Fatigued 70 x $10^6$ cycles at 77°K.
Fig. 262 Fe₃Al, disordered. Fatigued $14 \cdot 10^6$ cycles at $77^°K$.

Fig. 263 Fe₃Al, ordered. Fatigued $70 \cdot 10^6$ cycles at $77^°K$. 
Fig. 264 Fe$_3$Al, disordered. Fatigued $14 \cdot 10^6$ cycles at 77$^\circ$K.

Fig. 265 Fe$_3$Al, ordered. Fatigued $70 \cdot 10^6$ cycles at 77$^\circ$K. The left-hand crack is intercrystalline, the right-hand, transcrystalline.
Figs. 266 and 267 42.5 at.% zinc $\beta'$-copper-zinc. Fatigue fracture surfaces.
Fig. 268 Laue back-reflection photograph from the face in Fig. 266. Orientation (110).
Figs. 269 and 270 46.95 at.% zinc $\beta'$-copper-zinc.

Fatigue fracture surfaces from the same specimen.
Figs. 271 and 272. 48.25 at.% zinc $\beta'$-copper-zinc. Fracture surfaces produced during fatigue at 293°K.
Figs. 273 and 274 48.25 at.% zinc $\beta^\prime$-copper-zinc. Fracture surfaces produced during fatigue at 77°K.
Figs. 275 and 276 $\beta'$-gold-zinc. Fracture surfaces produced by fatigue at 293°K.
Figs. 277 and 278 $\beta'$-gold-zinc. Fracture surfaces produced by fatigue at 77°K. Direction of crack propagation in Fig. 278, bottom right to top left.
Fig. 279 $\beta'$-gold-zinc. Fracture surface produced by fatigue at 77°K. White line shows specimen surface.
Figs. 280 and 281 FeCo-V, disordered. Fatigued 12.3 \times 10^6 cycles. White line shows specimen edge, Fig. 280.
Figs. 282 and 283 reCo-V, ordered. Fatigued $17.6 \times 10^6$ cycles. Fig. 282, fracture surface of grain B; Fig. 283. See also Fig. 246 for grain A.
Fig. 284 FeCo-V, ordered. Laue back-reflection x-ray photograph from the surface of grain A. Orientation nearly \( \{100\} \).
Figs. 285 and 286 FeCo-V, ordered. Grain B in the specimen surface, Fig. 285, and in the specimen edge, Fig. 286.
Figs. 287 and 288 $\text{Fe}_3\text{Al}$, disordered. Fracture surfaces formed during fatigue at 293°K.
Fig. 289  Laue back-reflection x-ray photograph taken from the face in Fig. 288. Orientation \{100\}.

Fig. 290  Fe$_3$Al, ordered. Specimen fatigued 9.0 $\times$ 10$^6$ cycles at 293$^\circ$K.
Fig. 291 FeAl Single crystal cleavage fracture face. Lines indicate $<110>$ traces.

Fig. 292 FeAl. Laue back-reflection x-ray photograph taken from a fracture surface. Orientation $\{111\}$.
Fig. 293 The variation in the spacing of $\frac{1}{2}a_o<111>$ super-partial in $\beta'$-copper-zinc, as a result of the change in $T_c$ and $S$ with changing zinc content. Values are expressed as a function of the spacing at 50 at.% zinc.
Fig. 294 Simple model to show the origin of elastic stress concentration at a grain boundary in an elastically anisotropic solid.

Fig. 295 Slip plane in a crystal. The angle between slip direction and stress axis, $\beta$, and between slip plane normal and stress axis, $\alpha$. Applied stress, $P$. 
GRAIN BOUNDARY

E₁  E₂

COMPRESSION

DATUM (UNSTRESSED)

TENSION

\[ \frac{E_1}{E_2} \propto \frac{E_2}{E_1} \]

p

α β
Fig. 296  Plot of the reciprocal of the shear modulus, $G$, and the reciprocal of Young's modulus, $E$, for $\beta'$-copper-zinc, against the orientation function $F(\gamma)$, after Artman and Thompson, 1952 (87).

Fig. 297  Plot of the applied stress to cause slip, (expressed as $1/\cos\alpha \cdot \cos\beta$, Fig. 295) against the orientation function, $F(\gamma)$, for slip on the system $\{110\} <111>$. 
Fig. 298 Elastic stress/strain curves for $\beta'$-copper-zinc for various orientations of the applied stress.
Fig. 299  Graphical method to determine the elastic stress interaction at the grain boundary of a bicrystal composed of crystals of differing orientation. A, <111>/<100> pair, B, <221>/<100> pair, C, <321>/<100> pair.
\[ E = 1.82 \quad E = 0.245 \]

\[ E = 1.11 \quad E = 0.245 \]

\[ E = 0.695 \quad E = 0.245 \]

\( [11] \)

\( [22] \)

\( [32] \)

FLOW STRESS

\begin{align*}
\text{STRESS} & \quad \text{STRAIN} \\
0 & \quad 0 \\
1 & \quad 1 \\
2 & \quad 2 \\
3 & \quad 3 \\
4 & \quad 4 \\
5 & \quad 5 \\
6 & \quad 6 \\
7 & \quad 7 \\
8 & \quad 8 \\
9 & \quad 9 \\
10 & \quad 10 \\
11 & \quad 11 \\
12 & \quad 12 \\
\end{align*}

\begin{align*}
\text{STRESS} & \quad \text{STRAIN} \\
0 & \quad 0 \\
1 & \quad 1 \\
2 & \quad 2 \\
3 & \quad 3 \\
4 & \quad 4 \\
5 & \quad 5 \\
6 & \quad 6 \\
7 & \quad 7 \\
8 & \quad 8 \\
9 & \quad 9 \\
10 & \quad 10 \\
11 & \quad 11 \\
12 & \quad 12 \\
\end{align*}

\begin{align*}
\text{STRESS} & \quad \text{STRAIN} \\
0 & \quad 0 \\
1 & \quad 1 \\
2 & \quad 2 \\
3 & \quad 3 \\
4 & \quad 4 \\
5 & \quad 5 \\
6 & \quad 6 \\
7 & \quad 7 \\
8 & \quad 8 \\
9 & \quad 9 \\
10 & \quad 10 \\
11 & \quad 11 \\
12 & \quad 12 \\
\end{align*}
Fig. 300  Plot of the applied stress to cause slip on the system \{110\} <100>, (expressed as \(1/\cos\alpha \cdot \cos\beta\), Fig. 295) against the orientation function, \(F(\gamma)\).
SLIP on SYSTEM \{110\}<100>
Fig. 301 Nearest neighbour broken bond configuration on the (111) plane of the A2 or B2 structure.

Fig. 302 Plot of the function $D$, Table 16, against direction of bonding (type I, II or III bonds, Fig. 1) for the A2 or B2 structure.
Fig. 303 Ternary diagram to show favoured fracture planes for combinations of bonding in the I, II or III directions, Fig. 1.

Fig. 304 Plan view of the surface shown in Fig. 303.
Fig. 305 Surface traces of the markings in Figs. 169 and 170 relative to the axes in the specimen N - S and E - W.

Fig. 306 Laue back-reflection x-ray photograph of the grain containing the markings shown in Fig. 170, taken from the section surface.
Fig. 307 Stereographic projection of the orientation of the grain showing surface markings, Figs. 169 and 170, to obtain the habit plane of the markings, marked ⊙.
Fig. 308 Pole traces of cracks formed next to boundaries in 46.95 at.% zinc $\beta'$-copper-zinc, plotted on the standard 001 stereographic projection.

Fig. 309 Standard 001 stereographic projection divided into standard triangles.
Crack Initiation during the Fatigue of \( \beta \)-Brass

Metallographic observations on the fatigue damage of \( \beta \)-brass in reversed bending have been reported. A characteristic type of damage was observed in which short markings appeared, normal to, and sometimes on both sides of, some grain boundaries. These markings did not have the same traces as slip within the grain and formed adjacent to, but not in, the grain boundaries.

Further work has been performed on 48.25 at. per cent zinc \( \beta \)-brass fatigued in reversed bending both at room and liquid nitrogen temperatures. A sheet was hot-rolled to about 1.2 mm and specimens cut out in a jig. These were then recrystallized by a short anneal at 830° C and quenched into iced 10 per cent caustic soda. Surface layers were ground off, and specimens electropolished for 6 h in orthophosphoric acid. This ensured an unworked surface, as shown by the etch-pit distribution. A soft-iron pole-piece was attached to the free end of the specimen, which vibrated at resonant frequency under the influence of an alternating magnetic field. The specimen geometry resulted in a frequency from 100 to 300 c/s. The applied stress could not be measured using this arrangement, but after an initial period of work-hardening, a constant frequency was maintained, until fatigue-cracking started.

Cross-slip was frequently observed at room temperature, together with some curved and intersecting slip traces. At \(-196° C\) cross-slip was much less frequent, and slip traces tended to be straight.

Fig. 1. Electron micrograph of region of short slip markings and cracks next to a grain boundary in \( \beta \)-brass (46.95 at. per cent zinc) fatigued at room temperature. C/Pt replica
At room temperature the more frequent mode of crack initiation was intergranular, either from triple points or along grain boundaries ending at the edge of the specimen. Short markings next to grain boundaries were seen as a second mode of crack initiation. These consisted of very fine markings of the type shown in Fig. 1, extending about 10µ from the grain boundary, but not necessarily on the active slip plane remote from the boundary, interspersed with 'persistent' markings or cracks often at regular intervals. Two surface analyses of these markings showed that they were incipient cracks lying on or close to {110} planes. Both slip and short markings were observed either on one side only or on both sides of the boundary. Cracks longer than others on one side of the boundary were always associated with longer cracks in the second grain. The occurrence of matching cracks across a boundary seemed to be determined by the correspondence of {110} planes in the two crystals. If {110} planes correspond, cracks may easily propagate across the boundary; if not, propagation will be difficult despite stress concentration at the crack tip. These cracks appeared to form in succession, probably by a process producing slip intensification and a crack by the classical mode of fatigue-crack formation, in which cross-slip is known to be important.

The regularity of spacing of short cracks next to the boundary in β-brass seems to indicate that they are formed by the progressive relief of stresses in the grain boundary region. Occasionally one of these cracks propagated, in which case its direction changed a short distance from the boundary in the manner observed by Forsyth, such that the direction was influenced by the normal applied stress. Even if a crack had been initiated in the grain boundary,

Fig. 2. β-brass (48·25 at. per cent zinc) fatigued 7·5 × 10⁶ cycles at −196°C showing cleavage-type cracks on {110} planes
it was frequently found to propagate in a transcrystalline manner.

Specimens were fatigued at $-196^\circ$ C by standing the specimen clamping block in liquid nitrogen inside a Dewar flask. Failure always occurred by the propagation of a cleavage-type crack on $\{110\}$ planes through the specimen. Again these planes did not always correspond with the active slip planes, which are variously reported as exclusively $\{110\}$ (ref. 4), and almost exclusively $\{211\}$ (ref. 5) at $-196^\circ$ C. Intergranular crack initiation was absent. A series of parallel cracks was observed from some grain boundaries (Fig. 2). These cracks had a spacing of about 10$\mu$ or more and the longer ones propagated a considerable distance into the grain. Shorter markings were also observed and, on sectioning on a second surface, no cracks were observed, but regions of transformation product were seen to correspond with the markings on the specimen surface (Fig. 3). It has been shown$^6$ that martensite may be induced in stable $\beta$-brass by deformation, so that the occurrence of transformation product indicates an increase in the stress in this region. No martensite was found associated with cleavage-type cracks.

It is proposed that stress concentrations of a sufficient magnitude to produce slip and cracks can arise at a grain boundary if the crystals composing it have a 'soft' and a 'hard' orientation to the applied stress. McManus$^7$ has investigated the change in the elastic moduli of $\beta$-brass with temperature and composition. For a 48.25 at. per cent zinc alloy his results give values of $0.249 \times 10^{11}$ and $1.94 \times 10^{12}$ dynes/cm$^2$ for Young's modulus measured in the $<100>$ and $<111>$ directions, respectively. The low value of $E_{[100]}$ implies weakness to $\{110\} [\overline{1}0\overline{1}]$ shear, as pointed out by Zener$^8$. The details of the stress

Fig. 3. Same specimen as in Fig. 2. Section through a boundary showing short markings. Transformation product, presumably martensite. Electron micrograph, C/Pt replica
distribution in the neighbourhood of the boundary between two anisotropic crystals will be complex, but a simple model may be postulated which can approximate to these conditions.

Fig. 4 shows the edge of a bicrystal composed of one 'soft' and one 'hard' crystal. On compression the two crystals deform elastically to differing extents, but to maintain coherency across the boundary the soft crystal will deform less in this region and the hard crystal more than in regions remote from the boundary. The magnitude of the lateral deformation in the grain boundary region will be inversely proportional to the ratio of the moduli in that direction. In tension the sign of the stresses will be reversed, but their magnitude will be the same as in compression. Such a stress concentration may be relieved in two ways. Either a crack can be initiated in the grain boundary between the two crystals, or a series of parallel cracks can form normal to the boundary. A grain boundary crack will be a more efficient means of stress relief, and its initiation will be particularly favoured if the boundary terminates in the edge of the specimen. Once the crack has formed, propagation criteria become important and the crack may spread on a transcrystalline path. Short cracks normal to the boundary can be formed when the boundary is limited by triple points. Once such a crack has formed, the stress distribution near it will be changed, and the stress concentration moved along the boundary, allowing more slip to occur and new cracks to form. Short slip markings are sometimes found associated with cracks along the grain boundary. It is possible that an intergranular crack may produce a stress concentration favouring the formation of short slip markings, or that fracture may be completed in a region of short cracks next to the grain boundary by the propagation of an intergranular
crack. Short slip markings will be most pronounced a short distance from the boundary because coherency constraints between the two grains will limit the formation of large slip steps at the grain boundary itself. The occurrence of cleavage-type cracks at low temperatures in β-brass is consistent with the increase in brittleness of body-centred cubic metals with falling temperature.

In order to test the importance of elastic stress concentrations at grain boundaries in β-brass during fatigue, the orientation of a number of crystal pairs the mutual boundary of which shows fatigue damage is being determined and examined, with the view of differentiating between the conditions necessary to initiate a crack in an intergranular manner, or to initiate short cracks next to grain boundaries.

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