ORDERING AND MARTENSITIC TRANSFORMATIONS
IN CU-ZN-MN SHAPE MEMORY ALLOYS
by
L. Chandrasekaran

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MARCH 1980
THIS WORK IS DEDICATED TO MY PARENTS, SARASU, BADRI AND SATYA.
ACKNOWLEDGEMENTS

I am particularly indebted to my supervisor, Dr. A.P. Miodownik, for his constant encouragement and advice throughout the course of this work. My thanks are also due to Prof. M.B. Waldron for allowing me to make use of the laboratory facilities, and to Mr. G.B. Brook (Fulmer Research Institute) for helpful suggestions.

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SYNOPSIS

Shape memory effect is a phenomenon in which a specimen, apparently plastically deformed at some low temperature, reverts to its undeformed original shape on heating to a somewhat higher temperature. A common property of all the systems that show this effect is that they all exhibit a thermo-elastic martensitic transformation, and the shape memory effect is observed when the alloy is deformed at a partly or wholly martensitic condition and then heated to the matrix phase. The matrix is usually highly ordered and the martensite invariably inherits the order of the matrix phase.

In the present investigations, an attempt has been made to study the effect of order on the martensitic transformation characteristics in the system Cu-Zn-Mn, showing the shape memory effect. Investigations have been directed towards determining the effect of manganese content and the effect of low temperature ageing and quenching on ordering, and thereby on martensitic transformations. Resistance measurement with temperature and tensile testing methods have been used to show that manganese up to 10 at.% acts almost like zinc in Cu-Zn-Mn alloys. Low temperature ageing and quenching of the matrix phase result in rises in $M_s$ temperature which are proportional to the manganese content and the temperature of ageing. The entropy change accompanying the martensitic transformation is independent of heat treatment and is almost the same as that found in Cu-Zn alloys, suggesting that the martensite inherits the order of the parent phase. The matrix phase undergoes
secondary ordering transition, $B2 \rightarrow DO_3/L2$, in addition to
the primary ordering transition $A2 \rightarrow B2$ at high temperatures.
Because of rapid diffusion, ageing above the $B2 \rightarrow DO_3/L2$ transition temperature does not produce markedly different
structures than ageing at lower temperatures. The effects
on $M_s$ due to ageing and quenching are essentially attributed
to disordering of the parent phase.

Starting with calculations based on an improved BWG model
to take into account the total ordering behaviour in the $\beta$-phase,
it is demonstrated that an explicit calculation of the $M_s$
temperature can be made by combining ordering data for both
the parent and product phases with a regular solution model
and phase stabilities. It is also shown that such a thermo-
dynamic analysis performed on binary Cu-Zn and ternary Cu-Zn-Mn
alloys satisfactorily accounts for both the retrograde solidus
that are so characteristic of these alloys, and the variation
of $M_s$ with composition. The rises in $M_s$ with low tempera-
ture ageing and quenching are shown to be due to the ordering
energy being higher in the $\beta$-phase than in the $\alpha$-phase. It is
suggested that in the system Cu-Zn-Al, where $M_s$ is depressed
on disordering, the reverse is the case.
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INTRODUCTION

Any alloy whose retained metastable high temperature phase undergoes extensive deformation below a critical temperature that is recoverable on heating is said to exhibit shape memory effect. The systems that exhibit this phenomenon, e.g. Ti-Ni\(^{(1)}\), Cu-Al-Ni\(^{(2)}\), Cu-Zn-Al\(^{(3)}\), Cu-Zn-Si\(^{(4)}\), Au-Cd\(^{(5)}\), Au-Cu-Zn\(^{(6)}\), etc., all undergo a partial or complete martensitic transformation on quenching from high temperature, and stressing accentuates this phenomenon. Much of this work has been reviewed quite recently\(^{(7)}\). Almost all the alloy systems that exhibit this effect seem to have the following common features:

1) The parent phase is highly ordered.
2) The martensitic transformation is thermo-elastic.
3) The transformation exhibits twinning or faulting mode.

These observations have led some pioneer workers in this field to propose that the high degree of order in the parent phase and the thermo-elastic nature of martensitic transformation are prerequisites for shape memory effect to exist\(^{(8)}\).

Theoretical considerations based on fault embryo models have led Cohen and Olson\(^{(9)}\) to conclude that there is only one single necessary and sufficient condition for thermo-elastic behaviour of martensitic transformation, namely the relative absence of plastic accommodation for the transformational shape change, and it has been shown theoretically that a high degree of order in the parent phase could result in greater
elastic accommodation of the transformational shape change, and thereby greater degree of thermo-elasticity. However, quantitative data regarding the effect of various degrees of order on martensitic transformation characteristics are not available for the systems showing shape memory effect. In view of the potential applications of the shape memory effect, it has become important to explore in detail the ordering phenomenon and its effect on martensitic characteristics so as to enable prediction of martensitic transformation behaviour under a given set of circumstances for a given system exhibiting the memory effect.

The present investigations were undertaken with this object in view. The ternary system Cu-Zn-Mn was chosen because it was expected that retention of various degrees of order by heat treatment alone would be feasible in this system, eliminating the necessity of having to change alloy composition to change the degree of order. Moreover, there is no data on martensitic transformations in this system, in spite of its suggested suitability as a good replacement for nickel in Cu-Zn-Ni alloys. The present study has been directed towards the determination of the effect of manganese on martensitic transformation behaviour and the effect of parent phase heat treatment on the subsequent martensitic transition. Attempts have been made to explain the results by relating the effects observed to free energy changes attendant on ordering.

This thesis is divided into four major parts. The first part deals with relevant literature on martensitic
transformation in noble metal based alloys and experimental observations relating to the effect of heat treatment on such transformations through changes in ordering characteristics in the parent phase. The second part deals with the formalism of the model adopted here for describing the ordering behaviour in BCC and FCC alloys. The various factors involved in the calculation of the free energies are also discussed. In the third part, the experimental techniques and results obtained for the system Cu-Zn-Mn are described. The final part consists of an analysis of the results on the basis of the model adopted and the conclusions drawn from the present study.
CHAPTER 2

LITERATURE REVIEW (EXPERIMENTAL)

2.1 GENERAL

The crystal structure and microstructure of the matrix β-phase depends sensitively on its exact composition, temperature, pressure, and thermal history, and these features in turn influence strongly the martensitic phase. In this chapter the characteristics of the β-phase and the product martensitic phase in the noble metal based systems will be reviewed. There already exist two excellent and exhaustive reviews, one on "Martensitic transformations in noble metal based alloys"(11), and the other on "Shape memory effect"(7). The present review is based on these to some extent, but is designed to focus more attention on information that has direct relevance to ordering in β-phase and its influence on martensitic transition.

2.2 ALLOY SYSTEMS WITH STABLE β-PHASE

It has been known for a long time that the crystal structure and the chemical composition of the phases occurring in noble metal based systems are related to a certain electron/atom ratio(12). Thus, when metals of higher valency are added to copper, silver, or gold, similar phases usually appear at similar electron concentrations; the α-(FCC) phase boundary is reached at an electron concentration of 1.4, a β-phase (often BCC) appears at 1.5, and so on. H.Jones proposed that these effects come from the Brillouin Zone.
Structure of the alloys $^{(13,14)}$. Brillouin zones are volumes in reciprocal vector space which enclose the allowed energy values for the free electrons in a crystal. It was shown by H. Jones that the number of electrons that can be accommodated in these zones is different for the two phases BCC and FCC and that their relative stabilities were a function of electron concentration. His estimate of the energy difference between the FCC and BCC phases as a function of $e/a$ is shown in Fig.2.1. However, other factors lead to considerable variations in the phase diagrams.

**FIG.2.1**: The difference between Fermi energies of FCC (\(\alpha\)) and BCC (\(\beta\)) structures as a function of $e/a$ (Ref.13).

Solute elements forming $\beta$-phase alloys with copper, silver, and gold are given in Fig.2.2$^{(11)}$. 
FIG. 2.2: The positions of the Solvent (A) and Solute (B and C) components in the periodic table. The small boxes indicate the solvent which forms a β-phase with the respective solute element (Ref.11).

In numerous binary and ternary systems the β-phase is stable over a large composition and temperature range (Fig.2.3).

FIG.2.3: Shape of β-phase fields in copper and silver alloys (Ref.125).
2.3 CRYSTAL STRUCTURES OF THE DISORDERED AND ORDERED \( \beta \)-PHASES

The Bravais lattice of the \( \beta \)-phase in nobel metal based alloys is BCC. In some systems it is ordered, and in some others it is disordered. The BCC superlattice structures are:

(a) The CsCl structure (Fig.2.4) (B\(_2\); phase symbol \( \beta_2 \)) where both the binary and ternary B\(_2\) structures have to be considered; stoichiometric composition A\( B \) for binary and A(B,C) or (A,C)B for ternary.

(b) The Fe\(_3\)Al structure (DO\(_3\); phase symbol \( \beta_1 \)), stoichiometric composition A\(_3\)B (Fig.2.5).

(c) The Cu\(_2\)MnAl structure (Fig.2.6) (L\(_2\); phase symbol \( \beta_3 \)), stoichiometric composition A\(_2\)BC. L\(_2\) structure is the same as DO\(_3\) except that the B atoms are substituted by C atoms in positions 2 and 4 of Fig.2.7.

The superlattices may all be described in terms of four interpenetrating FCC lattices corresponding to eight BCC unit cells with different occupation probabilities of sub-lattices by A, B, and C atoms. Both the B\(_2\) and DO\(_3\)/L\(_2\) structures may occur at different compositions and temperatures in binary and ternary alloys, e.g. FeAl\(^{(15)}\), Au-Cu-Zn\(^{(16,17)}\), theoretical predictions and experimental verification of the existence of two ordered phase fields have been carried out for some systems, e.g. Fe-Si\(^{(18)}\), Au-Cu-Zn\(^{(19)}\). Atomic ordering causes tetragonal or orthorhombic distortions.
The unit cells of the B2 (2.4), DO₃ (2.5) and L2₁ (2.6) structures and the generalised unit cell (2.7).
However, the ordered unit cell of the β-phase may be tetragonally distorted for reasons other than atomic ordering \(^{(20)}\).

2.4 STRUCTURAL INSTABILITY OF β-PHASES AT LOW TEMPERATURES

Varieties of anomalous effects termed 'premartensitic phenomena' occur in the parent β-phase as the temperature is lowered and is just above martensitic Start temperature, \(M_s\). These include softening of elastic constants \(^{(21)}\) (Fig.2.8), resistivity anomalies \(^{(22)}\), diffuse diffraction effects \(^{(23)}\), and calorimetric effects \(^{(24)}\).

\[ \frac{C_{11} - C_{12}}{2} \] in β-phase alloys (Ref.21).

Numerous BCC metals and alloy phases exhibit a decreasing magnitude of \(C' = \frac{(C_{11} - C_{12})}{2}\) elastic shear modulus with decreasing temperature, thus indicating a decrease in structural stability with respect to \{110\} <110> shears.
This was pointed out by Zener\(^{(25)}\) with regard to the \(\beta\)-Hume-Rothery phases, and has been investigated for several metals and alloy systems. From the experimental determination of the anisotropy ratio \(A = C_{44} / C'\) in the binary and ternary Au-Cd\(^{(26)}\) and the Au-Cu-Zn\(^{(21)}\) alloys and other BCC phases, the following features are noticeable:

1. 'A' increases with decreasing temperature as \(M_s\) is approached (Fig.2.9).

2. 'A' increases with changes in composition as the concentration range of instability to martensite transformation is approached (Fig.2.10).

3. Superlattice formation and other coherent precipitation reactions upon cooling \(\beta\) raise \(C'\) and lower \(M_s\) correspondingly\(^{(26,27)}\). However, it is worth noting from Table 2.1 that the 'A' values near the onset of martensitic transformations for different systems differ widely, whereas the shear modulus \(C'\) is more or less the same \((\approx 10^{11}\text{ dynes/cm}^2)\). This value of \(C'\) is also observed in some Cu-Zn-X systems undergoing martensitic transition\(^{(28)}\). However, there seems to be no significant change in the value of the shear modulus with composition or with temperature, even near \(M_s\), in these alloys.

Evidence has been put forward for the occurrence of '\(\omega\)' type phase forming by a displacive mechanism before martensitic transformation in systems Cu-Zn\(^{(29)}\) and Cu-Al-Mn\(^{(30)}\). The lowering of the \(C'\) occurs simultaneously with '\(\omega\)' precipitation in these systems. However, there is as yet no direct evidence to link '\(\omega\)' formation with subsequent martensitic transitions in these systems.
<table>
<thead>
<tr>
<th>System</th>
<th>Shear Modulus $C' = \frac{1}{2} (C_{11} - C_{12}) \times 10^{-11}$ Dynes/cm²</th>
<th>Anisotropy Ratio $A = \frac{C_{44}}{C'}$</th>
<th>Reference No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au-Cd 47.5</td>
<td>0.92</td>
<td>11.6</td>
<td>(26)</td>
</tr>
<tr>
<td>Au-Cd</td>
<td>0.86</td>
<td>14.1</td>
<td>(26)</td>
</tr>
<tr>
<td>Cu-Zn (45-48)</td>
<td>0.87</td>
<td>5-10</td>
<td>(127), (29)</td>
</tr>
<tr>
<td>Au-Zn</td>
<td>0.9</td>
<td>3.3</td>
<td>(127)</td>
</tr>
<tr>
<td>$Au_xCu_{55-x}Zn_{45}$</td>
<td>0.3</td>
<td>$&gt;16$</td>
<td>(21)</td>
</tr>
</tbody>
</table>
FIG. 2.9: Anisotropy ratio A for Au-Cd alloys as a function of temperature (Ref. 26).

FIG. 2.10: Compositional dependence of the $A_S$ temperature and the elastic anisotropy (Ref. 21).
2.5 MARTENSITIC TRANSFORMATION IN NOBLE-METAL BASED SYSTEMS

According to Meyrick and Powell\(^{(31)}\): "a martensitic transition is a structural change generated by atomic displacements and not achieved by diffusion, corresponding to a homogeneous deformation which may be different in small adjacent regions and which gives rise to an invariant plane strain through which the parent and product are related by a substitutional lattice correspondence, an irrational habit plane, and a precise orientation relationship". The features usually and not necessarily associated with martensitic transitions are that:

1. the transformation is diffusionless, i.e. the composition remains the same and ordered phases transform to ordered phases;
2. the starting temperature \(M_s\) varies with composition and alloying additions;
3. the transformation is athermal and reversible with a temperature hysteresis;
4. deformation above \(M_s\) (but close to \(M_s\)) causes transition into the martensitic phase consistent with the shear nature of the transformation.

The different types of martensites as characterised by their structures, microstructural features, and modes of formation, are systematically combined in Table 1 of Ref.(11) along with their phase symbols and the phase and structure symbols of the matrix phases, and is reproduced here as Table 2.2.
## Table 2.2

Structure and Phase Symbols of the Matrix and Martensite Phases.

<table>
<thead>
<tr>
<th>Matrix Phase</th>
<th>Structure after lattice strain</th>
<th>Martensite Phase</th>
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<tr>
<td>Phase Symbol</td>
<td>Structure</td>
<td>Structure after lattice invariant strain</td>
</tr>
<tr>
<td>$\beta$</td>
<td>bcc disordered $A_2$</td>
<td>$\beta$-type</td>
</tr>
<tr>
<td></td>
<td>fcc disordered $A_1$</td>
<td>Lattice invariant strain: stacking shifts (structural + random) (alternating structures, depending on composition) stacking sequences: 1R: $ABCBACABAB$ 11H: $ABCBACABAB$ 3R: $ABCACAB$ 6H: $ABCACABAB$ lamellar composites of 3R+2H 3R+1R 3R+3R twin</td>
</tr>
<tr>
<td>$\beta_1$</td>
<td>bcc ordered $DO_{19}$ (TiAl$_3$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>hcp ordered $DO_{19}$ (Cu$_2$Ti)</td>
<td></td>
</tr>
<tr>
<td>$\beta_2$</td>
<td>bcc ordered $B_2$ (CsCl)</td>
<td>$\gamma$-type</td>
</tr>
<tr>
<td></td>
<td>fcc ordered $L_1_2$ (CuAl)</td>
<td>Lattice invariant strain: stacking sequences: 2H: $AB$</td>
</tr>
<tr>
<td></td>
<td>hcp ordered $B19$ (MgCd)</td>
<td></td>
</tr>
<tr>
<td>$\beta_3$</td>
<td>bcc ordered $L_2_1$ (MnCu$_2$Al)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>fcc ordered $L_2_1$ (MnCu$_2$Al)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>hcp ordered $L_2_1$ (MnCu$_2$Al)</td>
<td></td>
</tr>
</tbody>
</table>

Notes:
- $\beta$-type indicates the stacking sequence of the martensite variant.
- $\gamma$-type indicates the stacking sequence of the martensite variant.
- $\epsilon$ and $\epsilon'$ symbols refer to the deformation and relaxation-induced martensite, respectively.

*Matrix and Martensite Phases* refers to the structure and phase symbols of the matrix and martensite phases, respectively.
The first main divisions of the martensitic phase is given by the modes of transformation. The group called 'quench induced martensite' comprises the phases formed by the commonly known martensitic transitions occurring in compact specimens upon quenching. The group called 'deformation and relaxation induced martensite' consists of martensites formed upon deformation of matrix phase and due to particular relaxation conditions prevailing in thin foils, respectively. A further sub-division of the transformation modes in quench induced martensite is based on kinetics. Depending on various factors, a single system may exhibit one particular mode or a combination of kinetic modes, sequentially or simultaneously. The various martensites classified according to the mode of transformation based on kinetics are:

(a) Quench induced burst martensite

This most common mode occurring at \( T \leq M_b \) \( \leq M_s \) where \( M_b \) denotes the upper temperature limit of the transformation by this mode consists of the formation of comparably large amounts of martensite (typically 10 to 30% volume) in 'bursts' which are caused by auto-catalytic nucleation and rapid growth of numerous plates. The reverse transformation requires super-heating. The hysteresis is due to the energy required for nucleation of the reverse transformation.

(b) Stress-induced burst martensite

This mode occurs upon stressing the metastable matrix space at \( M_s \geq T \leq T_o \). Nucleation is induced by the applied stress; the growth proceeds as in the case of quench induced burst martensite.
(c) **Thermo-elastic martensite**

This martensite transformation mode is observed upon cooling to $M_d \leq T \leq M_s$ and is characterised by the formation of thin parallel-sided single plates or wedge-shaped pairs of plates which form and grow progressively as the temperature is lowered below $M_s$ and which shrink and disappear on reversing the temperature change. This behaviour arises because the matrix accommodates the shape deformation of the martensite plate elastically, so that at a specified temperature, the plate and matrix are in equilibrium. Any change in temperature displaces the equilibrium; therefore the plate grows or shrinks. A typical resistance vs temperature plot obtained during a complete cooling and heating cycle for an alloy of Au-Cd undergoing a thermo-elastic martensitic transformation is shown in Fig.2.11. It can be seen that the hysteresis is very small in such transformations compared to the hysteresis involved in non-thermoelastic transitions, e.g. Fe-Ni.

![Resistance vs temperature plot](image)

**FIG.2.11** : Resistance -vs- temperature plots, typical of thermoelastic (Au-Cd) and non-thermoelastic (Fe-Ni) transformations (Ref.72).
(d) Stress-induced growth of martensite

This term refers to martensitic transformations induced by external stress at $T > T_o$ which are characterised by the growth rate of individual plates being a direct function of the rate at which the stress is increased. This transformation may be practically reversible, thus representing a complete mechanical analogue to thermo-elastic martensite (super-elastic behaviour). A typical super-elastic transformation curve obtained during a loading and unloading cycle is given in Fig.2.12\textsuperscript{(32)}.

![Superelastic stress-strain curve](image)

**FIG.2.12**: Superelastic stress-strain curve for a single crystal of Cu-Zn-Sn alloy at 24°C (76°C above $M_s$) (Ref.32).

The transformation starts at a critical stress $\sigma_A$ and continues at increasing stresses until it is completed at the strain $\varepsilon_M$ (point B) whereupon the stress rises sharply. On unloading, the retransformation starts at a lower stress (point C) and terminates at $\sigma_{A_f}$ (point D). The value of $\sigma_T$ depends
strongly on temperature. A plot of $\sigma_{T}^{P+M}$ vs $T$ for a Cu-Zn alloy (Fig.2.13) shows that the straight line plot extrapolates to the $M_s$ temperature at zero stress\(^{33}\).

**FIG.2.13:** Plots of stress for formation of martensite ($\sigma_{T}^{P+M}$) and stress for plastic deformation of the matrix phase ($\sigma_P$) as a function of temperature in Cu-Zn single crystals (Ref.33).

(e) Combination of stress-induced and thermally-induced growth and reverse transformation of martensite

The growth of martensite under reversible conditions depends on temperature and stress as state variables. Fig.2.14(a) shows a combination of stress-induced growth and a reverse transformation by heating; this is associated with the so-called 'shape memory effect'. The shape change of the specimen caused by the stress-induced transformation is reversed by the thermally-induced reverse transformation. Fig.2.14(b) shows the same case for the sequence; deformation of martensite, and reverse transformation by reheating. Although these growth processes are essentially reversible, irreversible processes cannot be entirely eliminated.
(a) Stress induced growth of martensite from a non-martensitic matrix and thermally induced reverse transformation. Shape memory effect.

(b) Stress induced reorientation of a martensite and thermally induced reverse transformation. Shape memory effect.

**FIG. 2.14:** Interrelations between temperature, $T$, macroscopic strain $\varepsilon_m$, and reversible martensitic growth. Full lines = growth of martensite. Broken lines = reverse transformation. Dotted lines = cooling without transformation. $\sigma$ = applied stress.
2.6 CRYSTAL STRUCTURES OF THE MARTENSITIC PHASES

It can be seen from Table 2.2 that the crystal structures of the final martensitic product are characterised by complicated stacking sequences which are a result of various distortions and deviations arising from atom size effects and inherited order. All these, however, can be referred to fundamental structures disregarding their superlattices and distortions. The three different types of fundamental structures that occur are: FCC, HCP, and close-packed orthorhombic with periodic stacking shifts. The fundamental structures of the \( \beta \)-type martensites which are derived from BCC \( \rightarrow \) FCC transition are either FCC or an orthorhombic close-packed structure which consists of an array of close-packed planes with a more or less well-defined complicated stacking sequence. The stacking sequence occurring most frequently is \( \text{ABC/BCA/CAB} \) designated as 3R. For the description of the atomic arrangements and the crystallographic details of the stacking variants one is referred to Ref.No.11. In general, the martensitic phase inherits the ordered state of the matrix, and the antiphase domain boundary of the ordered structure in the matrix phase, which is different for B2 and DO\(_3\)/L2\(_1\) ordered structures, is transferred to the martensite along with the superlattice. The relative positions of the different atom species in the \{110\} planes of the BCC matrix lattice remain unchanged as these planes become shear planes of the first strain during transformation and are converted into the basal planes of the martensite. The basal planes thus obtained from the different ordered structures of the matrix are shown in Fig.2.15.
The atomic order in the matrix not only determines the superlattice of the martensite structure but also by virtue of size effects and changes in bonding, the exact packing symmetry in the martensite. The deviations so caused in turn affect the strains associated with the martensitic transitions and the concentration dependence of $M_s$. These deviations are manifest as orthorhombic, triclinic, or monoclinic distortions and a modulation of inter-planar spacing between the basal planes. Orthorhombic distortions have been measured on Cu-Zn, Cu-Zn-Ga, Cu-Zn-Si, Cu-Zn-Al martensites and monoclinic distortions on Cu-Al, Au-Mn, and Cu-Zn martensites. Periodic modulation of the interplanar spacing between the basal planes have been observed in long-period superlattice structures of $\beta_1$ Cu-Al martensite. X-ray diffractograms show up these distortions as splitting up of certain peaks and have been utilised to investigate the composition dependence of martensite structures in Cu-Zn-Al, Cu-Zn-Si, Cu-Zn-Ga, and Cu-Al.
2.7 EXPERIMENTAL OBSERVATIONS IN SELECTED SYSTEMS

In this section a summary of the experimental observations regarding the matrix and product phases, their response to intermediate heat treatments insofar as changes in structural and transformational characteristics are concerned, will be reviewed. Only systems that show thermo-elastic transition will be considered.

2.7.1 Copper-Zinc

From Fig. 2.16 it can be seen that in this system the $\beta$-phase extends from ~36.3 to 55.3 at % Zn at temperatures close to the solidus. Alloys up to ~38 at % Zn generally undergo massive transformation to face centered cubic phase on quenching to room temperature. The other alloys may be quenched to R.T. without transforming, except for the ordering reaction leading to B2 structure. On further cooling, it has been established that the martensite obtained is of the $\beta_2''$ (3 R/1R) type\(^{36}\). All the different kinetic modes of martensitic transformation have been observed in this system\(^{28,40-41}\). Ahlers\(^{43}\) has shown that there exists a good correlation between $M_s$ and tetragonality in these alloys with zinc content in the range 38.2 to 40 (at. %).

An extensive study of the effect of tempering on martensites in Cu-Zn alloys (with impurities <1.5%) by Kaminsky\(^{44}\) showed that the room temperature retained martensite which had a high tetragonality in the as quenched state, became progressively cubic with ageing time at 125°C (Fig.2.17).
FIG. 2.16: Low temperature transformations of the $\beta$-phase in Cu-Zn systems (Ref. 128).

FIG. 2.17: Effect of tempering time at 125°C on the tetragonality of martensite formed by cooling a Cu-39.1% Zn alloy to -196°C (Ref. 44).
Low temperature ageing studies carried out by Hummel\(^{45}\) on \(\beta\)-Cu - 39.1% Zn alloy (Figs. 2.18 (i) & (ii)) showed that there was an increase in resistivity of 3% on ageing in the region 60° to 120°C, and that the increase in resistivity was very fast and reached 50% of the final value at any temperature in this temperature interval in a few minutes. Long-time anneal (16 hours) at a temperature of 135°C, even though registering an increase in resistivity of 3.5% in the parent phase, did not have any noticeable effect on the \(M_s\) temperature (Fig. 2.18 (iii)). On the other hand, an extended period of annealing for 50 hours at a higher temperature of 150°C resulted in a 12.4% increase in resistivity, signifying the onset of a different transformation which had already been identified as a bainitic reaction.

Earlier studies on tempering behaviour of Cu-Zn alloys have shown\(^{46-48}\) that an extensive phase reaction \(\beta_1 + \beta_1 + \beta^\text{I}\) is observed when \(\beta_1\) brass is isothermally annealed above 150°C, and this has been classified as a bainitic transition. These transitions are accompanied by a steep increase in resistance and hardness and lattice parameter. Optical and electron-microscopic observations have also confirmed the phase transition. These transitions have been observed when a specimen was quenched from 820°C to 225°C and kept at 225°C for an hour or more, or when a specimen quenched from 820°C to room temperature was annealed at 150°C for 70 hours. On annealing above 250°C, the transformation \(\beta_1 + \beta^\text{I} \rightarrow \beta_1 + \alpha\) ensues, which is accompanied by a fall in hardness value. The structure of the bainitic product is almost the same as that of the martensite.
(i) Resistance change with temperature.
Ageing time, 5 minutes.
Measurement temp., 20°C.

(ii) Resistance change with time at various ageing temperatures.
Measurement temp., 20°C.

(iii) Resistance change as a function of temperature:
(a) before heat treatment;
(b) after 16 hours at 134°C.

FIG. 2.18: Results of low temperature ageing studies in 8-brass (38.8 wt% Zn). (Ref. 45).
2.7.2 Copper-Aluminium

The copper-rich end of the phase diagram for this system, along with the $M_s$ temperatures and ordering temperatures, are shown in Fig.2.19.

FIG.2.19: Partial phase diagram for the Cu-Al system. (Ref.11).

All the basic variants of martensite phases have been found. Depending on composition, both the $\beta$-type and $\gamma$-type variants occur in this system (49). Tempering studies on martensitic Cu-Al alloys have shown that the $\beta$-phase formed by annealing in the $\beta$-phase field may be disordered ($A2$), or ordered ($D0_3$), depending on annealing temperature and composition (11). Growth of ordered regions in a disordered matrix without the introduction of internal domain boundaries have been observed in a Cu-25% Al alloy on isothermal annealing in the 400-535°C range (50). The domain boundaries are preserved through the subsequent martensitic transition.
2.7.3 Copper-Aluminium-Nickel

Copper-Aluminium-Nickel alloys which contain about 14 wt % Al and 4 wt % Ni have been known to transform thermoelastically for some time \(^{(51)}\). Suitable combinations that exhibit this effect have the approximate formula \((\text{Cu,Ni})_3\text{Al}\), and if the influence of nickel is neglected, they order with the \(\text{DO}_3\) structure. This ordered phase transforms to martensite \((\gamma_1)\) \((2\text{H}\) structure) at a transformation temperature \(M_s\) which is sensitively dependent on the Nickel and Aluminium concentrations. However, the type of quench employed affects the martensite formed profoundly \(^{(52,53)}\). Drastic quench results in a \(\beta_1'\) martensite with a \(18\text{R}\) structure. Drastic quench above \(M_s\) and ageing above \(M_s\) for a long time results in complete \(\gamma_1'\) formation. A mixture of \(\beta_1'\) and \(\gamma_1'\) martensites are observed in alloys aged after quench for shorter periods. The time required to condition the \(\beta\)-phase to give complete conversion to \(\gamma_1'\) martensite on cooling corresponds to the time taken for the resistivity to reach a minimum on tempering above \(M_s\) \((\text{Fig.2.20})\).

![Plot of resistance vs tempering time above \(M_s\), for a Cu-Al-Ni alloy \((\text{Ref.52})\).](image-url)
It has been shown that the structure is an incompletely ordered \( \text{Fe}_3\text{Al} \) structure on quenching, which changes to Heusler type superstructure on ageing in the range \(-10^\circ\) to \(260^\circ\) (54). This is presumably the first structural change that occurs on ageing. Results of specific heat measurements after ageing at different temperatures following quenching are given in Figs. 2.21 and 2.22).

**FIG. 2.21**: Specific heat of the aged Cu-Al-Ni alloy quenched from \(900^\circ\)C and aged at each temperature shown for 18 hours (Ref.54).

**FIG. 2.22**: Variation of \(A_s\) and \(A_f\) temperatures of Cu-Al-Ni alloy as a function of ageing temperature (Ref.54).
The reverse transformation temperatures $A_s$ and $A_f$ increase linearly up to an ageing temperature of 180°C, after which the increase is rather sharp. It has been suggested by Stobbs et al\(^5\) that the sharp increase in $A_s$ after ageing at 180°C and above is associated with segregational precipitation of a \('\omega\'-like\) phase.

2.7.4 Copper-Zinc-Manganese

A comprehensive phase diagram determination for this system was carried out by T.R.Graham et al\(^6\) in the 1940s. It was reinvestigated in 1972 by Gondo et al. The isothermal sections of the ternary phase diagrams at various temperatures are taken from the works of Graham et al and are given in Figs.2.23 (a) - (d)). Sections at 5, 10, and 15% Mn through the Cu-Zn-Mn system as derived from the diagram of Graham et al are given in Fig.2.24. The diagram proposed by Gondo et al, delineating the boundary of ordered phase fields in this system, are shown in Fig.2.25. A typical plot of specific heat vs temperature curve for a quenched and an annealed $\beta$-phase specimen taken from the results of Gondo et al\(^7\) is given in Fig.2.26. Figure 2.27 shows the effect of Mn on the ordering temperature $T_c$ of the $\beta$-phase, as determined by Gondo et al. Stoloff et al\(^8\) have also determined the variation of $T_c$ with Mn in $\beta$-phase alloys, which is in agreement with Fig.2.27.

From the ternary isothermal sections it is seen that a complete range of solid solubility exists for Mn in the $\beta$-phase alloys from 815°C to 650°C. The quasi-binary sections
FIG. 2.23: Cu-Zn-Mn ternary isothermal diagrams (Ref. 56).
FIG. 2.24: Quasi-binary Copper-Manganese-Zinc phase diagrams at manganese contents of 5%, 10%, and 15%. (Ref. 10)
FIG. 2.25: $\beta-\beta'$ order-disorder transformation boundary in the Cu-Zn-Mn system. 
'--' indicates alloys showing no transformation. (Ref. 58).
(a) Annealed

(b) As quenched

FIG. 2.26: Specific heat vs temperature curves for alloy Cu-43.9 Zn-5.9 Mn (at. %) (Ref. 58)

FIG. 2.27: Composition dependence of order-disorder transition temperature, $T_c$ (Ref. 58).
show that the ternary Cu-Zn-Mn exhibits similar characteristics to the binary Cu-Zn alloys. Both systems possess a high temperature $\beta$-phase region which transforms at lower temperatures to the $\alpha$-phase. The Cu-Zn-Mn system differs from the binary in that high manganese or high zinc promotes the formation of an FCC T-phase at low temperatures. The results of Gondo et al show that there is a well-defined area inside which ordering reactions are expected. It is possible that an alloy near the boundary could be chosen which would be amenable to heat treatment to give various degrees of order. It has been reported by Gondo et al that additions of manganese in excess of 4% facilitate such retentions of order by quenching.

There is no data regarding the martensitic transformations in this system.

2.7.5 Copper-Zinc-Aluminium

It has been found that in this system the martensitic structures that result on quenching exhibit various stacking sequences characterised by different stacking fault densities. It has also been established that the stacking fault density is directly related to the orthorhombic distortions due to ordering, and it varies as a function of composition and possibly as a function of prior heat treatment. Variations in super-elastic behaviour have been observed, depending on prior heat treatment. The stress necessary to induce martensitic transition ($\sigma_{T\rightarrow M}$) at any temperature in an alloy with $M_S = -90^\circ C$ has been measured after ageing at $100^\circ C$ for an hour.
and after flash heating at 300°C. It can be seen from Fig.2.28 that \( \sigma_{T}^{P+M} \) is increased in both cases, (i.e. \( M_s \) is decreased), the increase being very marked in the latter treatment. Ageing at room temperature after the latter treatment results in a faster decrease in the value of \( \sigma_{T}^{P+M} \) with time. From the plots of \( \sigma_{T}^{P+M} \) vs temperature (Fig.2.29) for the as-quenched (line (a)) and flash heated (line (b)) samples, it is seen that the line (b) has the same slope as line (a) but is shifted to the left. No structural changes have been detected after ageing at 100°C.

Schofield and Miodownik\(^{61}\) have reported similar observations in this system. Quenching and ageing treatments at intermediate temperature conducted by them show that \( M_s \) in the as-quenched condition is depressed, which then rises up to its equilibrium value on ageing at room temperature. Ageing at intermediate temperatures (275°K - 425°K) results in increased \( M_s \) until a limiting temperature characteristic of a particular composition is reached. Quenching from above this temperature after ageing results in a depressed \( M_s \), which is the same as that for a specimen quenched from higher temperature (870°C) initially. The kinetics of \( M_s \) recovery in the specimens quenched from higher temperature (870°C) is faster than the kinetics of \( M_s \) recovery in specimens quenched from intermediate temperatures above the limit mentioned. This has been attributed to the presence of quenched in vacancies in the former. It has also been proposed by them that a secondary ordering \( B2-L2_1 \) transition in the ageing temperature ranges employed may be the cause of \( M_s \) changes observed, and attempts have been
FIG.2.28: $\sigma_{T}^{P \rightarrow M}$ of a Cu-Zn-Al alloy after different thermal treatments and subsequent ageing at room temperature:
(a) 1 hour at 100°C, and then aged at room temperature;
(b) Flash-heated to 300°C and then aged at room temperature.

FIG.2.29: Effect of flash-heating on the $\sigma_{T}^{P \rightarrow M}$ -vs- temperature plot (Ref.3).
(a) As quenched;
(b) Flash-heated to 300°C and quenched.
made to define the secondary ordering phase field. Recently, Cook and Brown\(^{(62)}\) have also reported similar observations of \(M_s\) changes with long time ageing in a 70 Cu/26 Zn/4 Al alloy. Their results show that the \(M_s\) change is reversible as long as the ageing temperature is below 120°C. On ageing above 120°C, reversibility is lost. An activation energy value of 65 ± 5 kJ/mol has been estimated for this process, and it compares well with 58 kJ/mol for ordering processes in equi-atomic brass reported by Clark and Brown\(^{(63)}\). Ahlers and Rapacioli\(^{(64)}\) report direct observation of a B\(_2\) + L\(_2\) transition in Cu-Zn-Al alloys with \(a/b = 1.48\) by resistivity and electron microscopic techniques. S.C. Singh et al\(^{(65)}\) have proposed phase diagrams that define these ordered phase fields. However, they have not related the \(M_s\) variations to the secondary ordering process.

2.7.6 Gold-Zinc

The β-phase of the Au-Zn system is located about the equi-atomic composition and has the B\(_2\) structure and retains a considerable degree of long-range order up to the melting point\(^{(66)}\). Alloys containing greater than 48 at % Zn are unstable and undergo a martensitic transformation; the martensitic start temperature \(M_s\) increasing with increasing zinc concentration, in contrast to other systems where it decreases with zinc content\(^{(67)}\) (Fig. 2.30).
FIG. 2.30: The β and β' phase fields and the composition dependence of $M_S$ temperature in systems Cu-Zn and Au-Zn (Ref. 67).

Pops and Ridley (35) reported that quenching from high temperature lowered the $M_S$, i.e. stabilised the β-phase, but only in alloys which were located on the zinc-rich side of the equi-atomic composition. The effect of air-cooling and furnace-cooling on the $M_S$ temperature, along with the $M_S$ of the quenched alloys, is given in Fig. 2.31.

FIG. 2.31: Effects of cooling rate on $M_S$ temperature in Au-Zn alloys (Ref. 35).
Their conclusion, on the basis of their exhaustive experiments, was that no single factor could be singled out as responsible for the observed $M_S$ variations.

2.7.7 Gold-Copper-Zinc

In this system the quasi-binary section $\text{Au}_x\text{Cu}_{55-x}\text{Zn}_{45}$ is the one that has been investigated by various workers $^{(6,68,69)}$. The ordering characteristics and the martensitic transitions have been particularly well established. The following results are characteristic of this system, namely:

1. There exists a disordered BCC phase, $\beta$ (A2) at higher temperatures, followed by a $\text{CsCl}$ type ordered phase, $\beta_1$ (B2) and a Heusler type ordered phase ($L_2$); and, finally, at lower temperatures, a martensite phase holding the Heusler type arrangement (Fig.2.32)

![Phase diagram of the $\text{Au}_x\text{Cu}_{55-x}\text{Zn}_{45}$ alloy (Ref.21)](image)

FIG.2.32 : Phase diagram of the $\text{Au}_x\text{Cu}_{55-x}\text{Zn}_{45}$ alloy (Ref.21)

2. Both the transition temperatures of the Heusler phase ($T_C$) and of the martensitic phase ($A_S$) exhibit a maximum at the Heusler composition.
(3) As a premonitory feature, softening of the shear constant \( C' = (C_{11} - C_{12}) / 2 \) is observed in the region above \( M_s \).

The Heusler type ordered structure forms very quickly on cooling from high temperature and cannot be suppressed even by a drastic quench. However, on heating above the Heusler ordering temperature, the structure changes from \( L2_1 \) to \( A2 \) directly at the \( T_c(B2/L2_1) \) temperature, and it needs more than an hour of isothermal annealing in the \( B2 \) phase field to induce \( B2 \) order\(^{(69)} \).

The influence of intermediate heat treatments on martensitic transitions have not been reported so far in this system.

2.7.8 Gold-Silver-Cadmium

This system is similar to the system Au-Cu-Zn in the sense that there exist two ordered configurations, \( B2 \) and \( L2_{1} \), and there is a martensitic transition at lower temperatures\(^{(70)} \). It differs from the Au-Cu-Zn system in its response to quenching. A rapid quench can arrest the \( B2-L2_{1} \) transition from taking place and thus a martensite could be made to inherit the \( B2 \) ordered structure instead of the corresponding \( L2_{1} \) structure.

Studies on martensitic transformations in this system have been conducted\(^{(71)} \) and in the quasi-binary alloy system \( \text{Au}_{52.5-x}\text{Ag}_x\text{Cd}_{47.5} \) for quenched alloys, the \( M_s \) is lower than for the slowly cooled ones. As has been observed earlier, a rapid quench arrests the secondary ordering transition, so it seems reasonable to conclude that the \( M_s \) corresponding to the
B2 ordered structure is lower than the $M_s$ corresponding to L2$_1$ structure, even though the L2$_1$ structure is the more stable one.

2.8 CONCLUSIONS BASED ON EXPERIMENTAL OBSERVATIONS

From the experimental observations reviewed so far, it is quite obvious that ordering characteristics are likely to be different in different systems even though all of them possess the same Bravais lattice, namely, BCC, and undergo a thermo-elastic transition. It has been broadly pointed out that the kind of stacking shifts observed in Cu-Zn-Al, Cu-Zn-Si, Cu-Zn-Ga, and Cu-Al martensites is strongly dependent on the orthorhombic distortion which arises from ordering in the parent phase (36). A correlation between $M_s$ and the tetragonality of the faulted FCC lattice in binary Cu-Zn and the ternary alloys mentioned above has been shown to exist by Ahlers et al (43) (Fig. 2.33), which suggests that increasing order, i.e. tetragonality, should result in decreasing $M_s$.

**FIG.2.33**: $M_s$ temperature vs $c/a$ in Cu-Zn and Cu-Zn-X alloys (Ref. 43).
However, it is seen that in the systems Cu-Zn-Al, Cu-Al-Ni, Au-Ag-Cd, Au-Zn, and Au-Cd, the alloys quenched from higher temperatures with expected lower degrees of order have a lower $M_s$ as compared to the same alloys aged at lower temperatures after high temperature quenching (restoring higher order). This means that order affects the stabilities of these different systems in different ways, and/or that different types of ordering kinetics exist in different systems. Even though lattice softening may be expected to play an important role in these systems, it is to be noted that the onset of martensitic transformation is not associated with a vanishing value of $C'$, but rather with a finite, though small, value. This indicates that it is the relative stability of the two structures which determines the structure formed and the transformation temperatures.

However, no definite thermodynamic correlation between the ordered state of the parent phase and the resulting martensite structures has so far been established in Cu-Zn-based systems because of the experimental difficulties in arresting the ordering reaction. It was thought that such a correlation could be established in the Cu-Zn-Mn system for the following reasons:

1) Manganese replaces zinc without seriously changing the binary Cu-Zn phase diagram character up to about 10%.

2) Additions of manganese lower the ordering temperature, and quenching alloys containing more than 4.7% Mn results in retained disorder.
These facts should enable one to study the influence of varying degrees of order without changing composition in the ternary, and afford an insight into the behaviour of the binary Cu-Zn system as well. Once the correlation between order and transformation characteristics is established, it should be possible to analyse the thermodynamics of martensitic transition by adopting a suitable model to take into account the various contributions to free energy changes that decide the phase transition characteristics.
CHAPTER 3

LITERATURE SURVEY (THEORETICAL)

3.1 THERMODYNAMIC FORMULATION OF THE MARTENSITIC AND ORDERING TRANSITIONS

3.1.1 Introduction

Since the martensitic transformation is diffusionless and the alloy composition does not vary during the transformation, the system can be considered as a single component system. In Fig. 3.1 the variation of free energies of $\alpha'$ (Martensite) and $\gamma$ (Austenite) phases of an alloy Fe-29% Ni is shown (72). $G^{\alpha'}$ and $G^{\gamma}$ (the free energies of $\alpha'$ and $\gamma$ phases, respectively) intersect at $T_o$, which is the true transition temperature at which $G^{\alpha'} = G^{\gamma}$. $M_s$ and $A_s$ are, respectively, lower and greater than $T_o$ for non-thermoelastic transitions; for thermo-elastic transitions the relative position of the measured transition temperatures with respect to $T_o$ is more uncertain. However, the value of $T_o$ may be calculated theoretically by making some reasonable assumptions (33,71). In single component systems, all that one needs to know are the free energy functions for the two phases. In alloys and other multi-component systems, calculation of free energies usually requires at least a regular solution model. Even then account has to be taken of several non-chemical free energy contributions, since martensitic transitions involve strains and creation of defects. Johansson (73) was the first to attempt thermodynamic calculations of martensitic transitions.
Zener (74) and Cohen (75) improved upon this method, but by far the most successful approach has been due to Cohen and Paranjape (75) and Cohen and Kaufman (72). Cohen and Paranjape adopted the basic thermodynamic expression which treated the energy change accompanying the transition as made up of chemical, strain, and other non-chemical terms:

$$\Delta G^{\gamma \rightarrow \alpha'} = \Delta G^{\gamma \rightarrow \alpha} + \Delta G^{\alpha \rightarrow \alpha'} + \Delta G \text{ (non-chemical terms)}.$$  

$M_s$ predictions for the systems Fe-C (by Cohen and Paranjape) and Fe-Ni (Cohen and Kaufman) on the basis of this approach yielded satisfactory results. However, there has been no similar attempt to predict $M_s$ in $\beta$-brass type alloys. For such a calculation, account has to be taken of the contribution to free energy by ordering and electronic factors, in addition
to the other terms in the free energy expression.

3.1.2 Various aspects of free energy calculations

The regular solution model is based on the assumption that atoms interact through bonds of constant energy with their neighbours\(^{(76)}\). The free energy vs composition curve for a single-phase homogeneous random solution of a binary system \(AB\) is schematically illustrated in Fig.3.2(a). The free energy of the solution is referred to standard states of the components, which are usually the pure components. However, the pure components may or may not be of the same crystal structure as the phase under consideration. It has been postulated that all different structures are potentially possible for a given element or alloy, and whether or not a particular structure will be stable under a given set of conditions is dictated by the relative free energy value of all the possible structures under the same conditions\(^{(77,78)}\). This means that, for a true comparison of the free energies of different phases, the free energy of each phase with a particular structure (say FCC) should be referred to the same crystal structure of the components, i.e. FCC. To achieve this, a suitable conversion of the elemental standard states to a common crystal structure should be performed. The stability parameters which are needed for this conversion have been defined and numerically determined for a large number of elements\(^{(78)}\). Table 3.1 shows the values for some elements of interest\(^{(79)}\). Curve (b) in Fig.3.2 shows the altered free energy curve when the conversion is made.
FIG. 3.2: Free energy -vs- composition curves for a BCC phase in noble metal systems. Curves (a) to (d) show the progressive change in the nature of the curves as the various contributions are taken into account.
Absolutely random behaviour is possible only in ideal, dilute solutions. Strong deviations from randomness occur when the components are dissimilar and the concentrations of the solute are large. These lead to ordered phases and the ordered phase fields are confined to small regions around stoichiometric compositions in the phase diagram. Occurrence of an ordered phase alters the free energy of the phase, as shown in curve (c) of Fig.3.2.

We have already seen that in the noble metal-based systems there is a possibility of a significant contribution to phase stability arising purely from electronic factors. These contributions exhibit rapid increases in electron energy due to Fermi surface-Brillouin zone interactions, and can contribute energy of the order of $10^2$-10$^3$J/mol, depending on the systems in question. Curve (d) of Fig.3.2 illustrates the effect of this contribution. Other contributions arise from the presence of interfaces, strain and defects like stacking faults, twins, and dislocations. The total free energy function for a particular phase should really take into account all these faults and their possible variations with temperature. Accuracy of prediction will depend upon the availability of pertinent data. However, an attempt can still be made even in the absence of such data.

3.1.3 Choice of model for free energy calculations

The first step towards such an analysis necessitates the adoption of a model that will describe adequately the ordering behaviour in the parent and product phases. Phase
# TABLE 3.1

Lattice stability parameters for copper and zinc.

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\Delta G$ values from Ref. 79. J/mol.</th>
<th>$\Delta G$ values actually used in the present work. J/mol.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>$\Delta G_{\text{FCC} \rightarrow \text{BCC}} = 6270 - 3.34 T$</td>
<td>$6270 - 2.51 T$</td>
</tr>
<tr>
<td>Zinc</td>
<td>$\Delta G_{\text{HCP} \rightarrow \text{FCC}} = 1840 - 1.67 T$</td>
<td>Same as in Ref. 79.</td>
</tr>
<tr>
<td></td>
<td>$\Delta G_{\text{FCC} \rightarrow \text{BCC}} = 1045 - 0.84 T$</td>
<td>&quot; &quot; &quot;</td>
</tr>
</tbody>
</table>
FIG. 3.3: Free energy differences between the α (complex cubic), β (primitive cubic), γ (FCC), and δ (BCC) forms of manganese as a function of temperature (Ref. 79).
transitions in general have been studied making use of approximate solutions of the Ising model originally proposed to discuss transitions in magnetic systems. Several approximations of the Ising model have been proposed, the principal one among them being originally due to Bragg-Williams, Gorsky, Bethe, Guggenheim and Fowler, Kirkwood, and Kachaturyan. The BWG model is the simplest one, and it has been modified by Inden and others to take into account nearest, as well as next nearest neighbour interactions in the BCC and FCC phases. Agreement of the model predictions with the experimental data has been found to be sufficiently good, at least for a semiquantitative description of the experimental findings in Fe-Si, Fe-Al, Fe-Co systems, and in some paramagnetic alloy systems like Au-Cu-Zn and Au-Ag-Zn. In view of its promise, it has been adopted as the basis of our model calculations in the present study.

The salient features of the model as applied to the BCC and FCC cases are described in the next section. A more detailed description of how this has been applied to the present research problem will be found in Chapter 5.

3.2 BINARY BCC PHASE - BWG MODEL

3.2.1 Definition of order parameters

The main feature of the BWG model is the description of atomic distributions as random inside certain suitable sublattices. The choice of these sublattices follows from the kind of interaction between atoms. It has been theoretically shown by Richards and Cahn that both nearest neighbour and
FIG. 3.4: $\text{DO}_3$ Unit Cell.
next nearest neighbour interactions have to be taken into account in determining the nature of ordering in BCC or FCC alloys. The BCC lattice (Fig. 3.4) may be divided into four FCC sublattices, I, II, III, and IV, with the atomic configurations described by occupation probabilities \( p_i^L \) of sublattice site 'L' by the component 'i'. The atoms inside (I + II) are nearest neighbours with respect to the atoms inside (III + IV) and vice-versa; the atoms inside I or III are second nearest neighbours with respect to the atoms inside II or IV, respectively, and vice-versa.

Any atomic configuration in a binary alloy \( A_{1-B_{1-C}} \) can then be described with the aid of the following three suitable parameters, which are a combination of the independent occupation probabilities \( p_i^L \).

\[
\begin{align*}
    x &= \frac{1}{2} (p_A^I + p_A^{II} - p_A^{III} - p_A^{IV}) \quad \text{(3.1.a)} \\
    y &= \frac{1}{2} (p_A^{III} - p_A^{IV}) \quad \text{(3.1.b)} \\
    z &= \frac{1}{2} (p_A^I - p_A^{II}) \quad \text{(3.1.c)}
\end{align*}
\]

The probabilities in terms of these parameters are given by:

\[
\begin{align*}
    (a) \quad p_A^I &= C_A + x + z \\
    (b) \quad p_A^{II} &= C_A + x - z \\
    (c) \quad p_A^{III} &= C_A - x + y \\
    (d) \quad p_A^{IV} &= C_A - x - y \\
    (e) \quad p_B^I &= C_B - x - z \\
    (f) \quad p_B^{II} &= C_B - x + z \\
    (g) \quad p_B^{III} &= C_B + x - y \\
    (h) \quad p_B^{IV} &= C_B + x + y
\end{align*}
\]
where $C_A$ and $C_B$ are concentrations of A and B, respectively.

The limits of the parameters depend on the composition of the alloy, and are given by:

(a) $0 \leq x \leq C_B$ for $0 \leq C_B \leq 0.5$

(b) $0 \leq y \leq \min (C_A - x, C_B + x)$ ... (3.3)

(c) $0 \leq z \leq \min (C_A + x, C_B - x)$

The greatest value of these parameters corresponds to the highest degree of order.

An equal distribution of the atoms onto the four sub-lattices (random distribution corresponding to structure A2) is obtained when $x=y=z=0$.

The state $x \neq 0$, $y=z=0$ indicates 'A' preferentially occupying I and II ($x > 0$), or III and IV ($x < 0$). It follows that the number of AB neighbours in nearest neighbour (n.n) positions is increased, i.e. this corresponds to the $B_2$ structure.

From an equivalent standpoint, it follows that $y \neq 0$, or $z \neq 0$ describes a surplus of A atoms in next nearest neighbour (n.n.n) positions, which corresponds to the $D0_3$ structure.

3.2.2 Expression for configurational free energy

A binary BCC solid solution with a homogeneous distribution of solute may be taken as the first example.

To determine what atomic configuration in this solid solution
is most stable at a fixed temperature $T$, and for a fixed alloy composition, the free energy is calculated under the assumption that the configurational part can be separated from the other contributions. The most stable atomic configuration then follows from the minimum value of the configurational free energy/mole 'G' alone which is given by:

(b)

$$G_{\text{BCC}}^{(b)} = U^0 - N C_A C_B \left(4 W^{(1)} + 3 W^{(2)} \right) - \frac{N}{2} \left[ (8 W^{(1)} - 6 W^{(2)}) x^2 + 3 W^{(2)} (y^2 + z^2) \right] + \frac{N k T}{4} \sum L \left( p_A^L \ln p_A^L + p_B^L \ln p_B^L \right)$$

...(3.4)

The first term $U^0$ is the the internal energy of pure components; the second term is the energy of mixing; the third term gives the energy contribution due to ordering, and the fourth term is the entropy contribution of the configuration which may also be expressed in terms of $x, y, z$. $N$ is Avagadro's number, and $k$ the Boltzmann constant. The parameters $W^{(1)}$ and $W^{(2)}$ are the interchange energies of the process, $2 AB \neq AA + BB$ for n.n. and n.n.n., respectively, and for eqn.(3.4) to be valid, these are expressed in $k$ units:

$$1 k \text{unit} = 3.3 \times 10^{-24} \text{cal} = 13.8 \times 10^{-24} \text{J}.$$  

These are deduced from the nearest and next nearest neighbour bond energies, $V_{ij}^{(K)}$. Thus :

(a) $W^{(1)} = -2 V_{AB}^{(1)} + V_{AA}^{(1)} + V_{BB}^{(1)}$

(b) $W^{(2)} = -2 V_{AB}^{(2)} + V_{AA}^{(2)} + V_{BB}^{(2)}$
According to this definition, positive values for $W^{(1)}$ and $W^{(2)}$ correspond to greater affinity between unlike, than between like atoms. These energies are presumed to be independent of temperature and of environment of atom sites where the interchange process is considered. If the values of $W^{(1)}$ and $W^{(2)}$ are known, $G_{\text{BCC}}^{(b)}$ can be calculated with respect to $x,y,z$, treating the temperature and the alloy composition as fixed parameters. The most stable configurations are then deduced from:

1. the necessary equilibrium conditions:
\[
\frac{\partial^2 G_{(b)}}{\partial x \partial y} = \frac{\partial^2 G_{(b)}}{\partial y \partial z} = \frac{\partial^2 G_{(b)}}{\partial z \partial x} = 0
\]

and

2. the sufficient equilibrium conditions that all principal minors of the functional matrix:
\[
\left[ \frac{\partial^2 G_{(b)}}{\partial \varepsilon \partial \tau} \right] \quad \text{with} \quad \varepsilon, \tau = x,y,z \quad \text{are positive.}
\]

3.2.3 Expressions for critical ordering temperatures

From an analysis of the sufficient conditions, it can be deduced that there are three temperature intervals in which the minimum of $G$ corresponds to either $A_2$, $B_2$, or $D\text{O}_3$ type configurations. The critical temperatures $T_x(A_2/B_2)$, $T_y(B_2/D\text{O}_3)$, by which these intervals are marked, depend on the interchange energies and alloy composition, as seen from the following expressions:
\[ k T_x^{\text{BWG}} (A_2/B_2) = (8W^{(1)} - 6W^{(2)})_{\text{BWG}} C_A C_B \quad \ldots (3.7) \]

\[ k T_y^{\text{BWG}} (B_2/D_03) = 6W^{(2)}_{\text{BWG}} (C_A - x_{\min}(T_y))(C_B + x_{\min}(T_y)) \quad \ldots (3.8) \]

for \( W^{(1)} > 0 \) and \( 0 \leq W^{(2)} \leq \frac{2}{3} W^{(1)} \)

or \( W^{(1)} > 0 \) and \( W^{(2)} \leq 0 \).

So if \( W^{(1)} \) and \( W^{(2)} \) are known quantitatively, the critical temperature \( T_x^{\text{BWG}} (A_2/B_2) \) can be calculated directly from equation (3.7) with respect to the alloy composition. The critical temperature \( T_y^{\text{BWG}} (B_2/D_03) \) can be calculated from equation (3.8) using a numerical determination of \( x_{\min}(T_y) \) from equation (3.6). The significance of the superscript \( \text{BWG} \) is explained in section 3.5.2.

### 3.3 TERNARY BCC PHASE (BWG MODEL)

#### 3.3.1 Definition of order parameters

The extension of the binary BWG model to the ternary system is achieved by slight alterations to the definitions of the order parameters.

A ternary alloy with concentrations \( C_A, C_B, \) and \( C_C \) of the three components \( A, B, \) and \( C, \) is considered. The total number of atoms is \( N, \) distributed over \( 4N_0 \) lattice sites. The occupation probabilities \( p_i^L \) (\( i = A,B,C; L = I,II,III,IV \)) are combined to give the order parameters as follows:
(a) \( x_j = \frac{1}{2} (p_j^I + p_j^II - p_j^III - p_j^IV) \)

(b) \( y_j = \frac{1}{2} (p_j^III - p_j^IV) \)

(c) \( z_j = \frac{1}{2} (p_j^I - p_j^III) \)

\( j = A, B \)

The occupational probabilities \( p_i^{(L)} \) are obtained in terms of \( x_j \), \( y_j \), \( z_j \), as follows:

(a) \( p_A^I = C_A + x_A + z_A \); (b) \( p_A^II = C_A + x_A - z_A \)

(c) \( p_A^III = C_A - x_A + y_A \); (d) \( p_A^IV = C_A - x_A - y_A \)

(e) \( p_B^I = C_B + x_B + z_B \); (f) \( p_B^II = C_B + x_B - z_B \)

(g) \( p_B^III = C_B - x_B + y_B \); (h) \( p_B^IV = C_B - x_B - y_B \)

(k) \( p_C^I = C_C - (x_A + x_B) - (z_A + z_B) \);

(l) \( p_C^II = C_C - (x_A + x_B) + (z_A + z_B) \);

(m) \( p_C^III = C_C + (x_A + x_B) - (y_A + y_B) \);

(n) \( p_C^IV = C_C + (x_A + x_B) + (y_A + y_B) \)

The variation intervals for the order parameters, \( x_j \) and \( y_j \) obtained on imposing the conditions:

\[ 0 \leq p_i^{(L)} \leq 1 \quad \text{and} \quad C_A + C_B + C_C = 1 \]
3.3.2 Expression for configurational free energy

The configurational free energy/mole \( G(t) \) of the three-component solid solution is given by:

\[
\begin{align*}
G^{BCC} (t) &= U_0 - N \left[ 4 \left( C_A C_B W_{AB}^{(1)} + C_A C_C W_{AC}^{(1)} + C_B C_C W_{BC}^{(1)} \right) \right. \\
&\quad + 3 \left( C_A C_B W_{AB}^{(2)} + C_A C_C W_{AC}^{(2)} + C_B C_C W_{BC}^{(2)} \right) \left. \right] \\
&\quad - \frac{N}{2} \left[ \frac{E_{AB}^R}{E_{BC}^R} x_A^2 + \frac{E_{AC}^R}{E_{BC}^R} x_B^2 + (E_{AC}^R + E_{BC}^R - E_{AB}^R) x_A x_B \right. \\
&\quad + 3 W_{AC}^{(2)} \left( y_A^2 + z_A^2 \right) + 3 W_{BC}^{(2)} \left( y_B^2 + z_B^2 \right) + 3 (W_{AC}^{(2)} + W_{BC}^{(2)}) \right. \\
&\quad - W_{AB}^{(2)} \left( y_A y_B + z_A z_B \right) \right] - \frac{NkT}{4} \sum_i \sum_{L} \frac{P_i^{(L)}}{P_i^{(L)} \ln P_i^{(L)}} \\
\end{align*}
\]

where \( E_{ij}^R = \left[ 8 W_{ij}^{(1)} - 6 W_{ij}^{(2)} \right] \)

The first term is the internal energy of the pure components; the second is the energy of mixing; the third term, the energy
contribution due to ordering; and the fourth term, the entropy contribution due to ordering which can also be expressed in terms of \( x_j, y_j, z_j \) parameters. \( N \) is the Avagadro number, and \( k \) the Boltzmann constant.

### 3.3.3 Expressions for critical ordering temperatures

The necessary conditions for a minimum in \( G \) at \( T \) for a composition, are:

\[
\frac{\partial G}{\partial x_i} = \frac{\partial G}{\partial y_i} = \frac{\partial G}{\partial z_i} = 0 \quad i = A, B \quad \ldots \quad (3.15)
\]

The sufficient conditions are that the principal minors of the matrix:

\[
\left[ \frac{\partial^2 G}{\partial e \partial \tau} \right] \quad \text{with} \quad e, \tau = x_i, y_i, z_i, \text{ are positive.}
\]

The analysis of these conditions leads to the same conclusions as in the binary case, and the corresponding expressions for \( T_x(A2/B2) \) and \( T_y(B2/L2_1) \) are obtained as below:

\[
k_{T_x}^{BWG} = \frac{0.5 \left( \sum_{i,j} C_i C_j E_{ij} + \sqrt{\sum_{i,j} C_i C_j E_{ij}} \right)^2 - 4 C_A C_B C_C (E_{AC} E_{BC})}{\ldots} \]

\[
\ldots - \frac{1}{4} \left[ E_{AC} + E_{BC} - E_{AB} \right]^2 \right) \} \quad \ldots \quad (3.16)
\]

where \( ij = AB, AC, BC, \text{ and } E_{ij} = \left( 8 W_{ij}^{(1)} - 6 W_{ij}^{(2)} \right)_{BWG} \)

\[
k_{T_y}^{BWG} = 3 \left\{ \Omega + \sqrt{\Omega^2 - \left[ 4 W_{AC}^{(2)} W_{BC}^{(2)} - \left[ W_{AC}^{(2)} + W_{BC}^{(2)} \right. \right. \right. \right. \]

\[
\ldots - \left. \left. \left. \left. W_{AB}^{(2)} \right]_{BWG} (C_A - x_A) (C_B - x_B) (C_C + x_A + x_B) \right\} \right\} \quad \ldots \quad (3.17)
\]
where
\[ \Omega = (W^{(2)}_{AC})_{BWG} (C_B + C_C + x_A) (C_A - x_A) \]
\[ + (W^{(2)}_{BC})_{BWG} (C_A + C_C + x_B) (C_B - x_B) \]
\[ - \left[ W^{(2)}_{AC} + W^{(2)}_{BC} - W^{(2)}_{AB} \right]_{BWG} (C_B - x_B)(C_A - x_A) ; \]

\( x_A \) and \( x_B \) are the values of the order parameter in nearest neighbour positions at \( T = T_Y \).

3.4 BWG MODEL AS APPLIED TO BINARY AND TERNARY FCC ALLOYS

3.4.1 Definition of order parameters

In the FCC alloys, eight sublattices have to be considered for a rigorous analysis\(^{(98)}\). However, such a treatment is too complicated and, for the sake of simplicity, usually only the ordered atomic configurations in nearest positions are considered, i.e. only four sublattices are taken. However, this does not mean that \( W^{(2)} \) can be ignored\(^{(94)}\) as it has been shown that ordered atomic configuration in nearest neighbours may be strengthened by energies of the second shell.

Since only four sublattices are considered, the order parameters are defined exactly as in the BCC case, and the various relations between occupational probabilities and the composition are the same as for the BCC alloys, both binary and ternary. It follows that the same should be true for the entropy expressions as well.
3.4.2 Expressions for free energy

The configurational free energy for the binary FCC alloy is given by the expression:

\[ G_{(b)}^{\text{FCC}} = U^O - 6N \left[ C_A C_B \left( W^{(1)} + \frac{W^{(2)}}{2} \right) \right] - N \left( 2x^2 + y^2 + z^2 \right) \]

\[ \left[ W^{(1)} - \frac{3}{2}W^{(2)} \right] + \frac{NKT}{4} \sum_{L=1}^{4} p_A^L \ln p_A^L + p_B^L \ln p_B^L \]

where all the terms have the same significance as in equation (3.4).

For the ternary alloys, the configurational free energy is:

\[ G_{(t)}^{\text{FCC}} = U^O - 6N \left[ C_A C_B \left( W^{(1)}_{AB} + \frac{W^{(2)}}{2}_{AB} \right) + C_A C_C \left( W^{(1)}_{AC} + \frac{W^{(2)}}{2}_{AC} \right) \right] \]

\[ + C_B C_C \left( W^{(1)}_{BC} + \frac{W^{(2)}}{2}_{BC} \right) \]

\[ - N \left[ \left( 2x_A^2 + y_A^2 + z_A^2 \right) \left( W^{(1)}_{AC} - \frac{3}{2}W^{(2)}_{AC} \right) + \left( 2x_B^2 + y_B^2 + z_B^2 \right) \left( W^{(1)}_{BC} - \frac{3}{2}W^{(2)}_{BC} \right) \right] \]

\[ + \left( W^{(1)}_{AC} - \frac{3}{2}W^{(2)}_{AC} + W^{(1)}_{BC} - \frac{3}{2}W^{(2)}_{BC} - W^{(1)}_{AB} + \frac{3}{2}W^{(2)}_{AB} \right) \]

\[ \left\{ \left( W^{(1)}_{AC} - \frac{3}{2}W^{(2)}_{AC} + W^{(1)}_{BC} - \frac{3}{2}W^{(2)}_{BC} - W^{(1)}_{AB} + \frac{3}{2}W^{(2)}_{AB} \right) \right\} \]

\[ + \frac{NKT}{4} \sum_{L=1}^{4} p_A^L \ln p_A^L + p_B^L \ln p_B^L + p_C^L \ln p_C^L \ldots (3.19) \]

where the different terms have the same significances as in equation (3.14).
3.4.3 Expressions for critical temperatures

Since ordering in nearest neighbour only is considered, the range of possible values for the interchange energies is \( W^{(1)} > 0 \), \( W^{(2)} \leq 0 \) (94). Then the uppermost chemical order/disorder transition is \( Ll_2 \leftrightarrow Al \), which, at \( C_B = 0.5 \), coincides with \( Ll_0 \leftrightarrow Al \). These transitions are predicted to occur discontinuously (91). For paramagnetic and diamagnetic binary alloys, the critical temperature of the transition is given by:

\[
k_T = \frac{Ll_2 + Al}{W^{(1)} - \frac{1}{2} W^{(2)}} = 4 C_B (1 - C_B) \left[ W^{(1)} - \frac{1}{2} W^{(2)} \right]_{BWG} \quad \cdots (3.20)
\]

For ternary alloys, the critical temperature is given by:

\[
k_T = \frac{Ll_2 + Al}{BWG} = \theta + \left\{ \theta^2 - C_A C_B C_C \left[ 16 \left( W^{(1)}_{AC} - \frac{1}{2} W^{(2)}_{AC} \right)_{BWG} \right] \right. \\
\left. + \left[ W^{(1)}_{BC} - \frac{3}{2} W^{(2)}_{BC} \right]_{BWG} + 4 \left[ W^{(1)}_{AC} - \frac{3}{2} W^{(2)}_{AC} \right]_{BWG} \right\}^{\frac{1}{2}} \quad \cdots (3.21)
\]

where \( \theta = \left[ 2 C_A C_C \left( W^{(1)}_{AC} - \frac{3}{2} W^{(2)}_{AC} \right) + 2 C_B C_C \left( W^{(1)}_{BC} - \frac{3}{2} W^{(2)}_{BC} \right) \right. \\
\left. + 2 C_A C_B \left( W^{(1)}_{AB} - \frac{3}{2} W^{(2)}_{AB} \right) \right]_{BWG} \)
3.5 DETERMINATION OF ENERGY PARAMETERS $W^{(K)}$

3.5.1 Determination of $W^{(K)}$ from energy measurements

Since $W^{(K)}$ are energy parameters, they are most easily determined from energy measurements like enthalpies of mixing of random alloys, or enthalpies of formation $G_H(C,T)$ of alloys with given atomic configurations. These entities can immediately be expressed by means of $W^{(K)}$ for a binary alloy $A_1-C_B$ with reference to the pure components in the same crystal structure as the alloy formed, e.g. BCC:

(a) $G_H^{A_2} = -NC(1-C) \left[ 4W^{(1)} + 3W^{(2)} \right]$

(b) $G_H^{B_2} = -N \left[ C(4W^{(1)} + 3W^{(2)} - 6C^2W^{(2)}) \right]$ for $C < 0.5$

(c) $G_H^{D_03} = -NC(4W^{(1)} + 3W^{(2)})$ for $0 \leq C \leq 0.25$

(d) $= -N \left[ 1.5W^{(2)} + C(4W^{(1)} - 3W^{(2)}) \right]$ for $0.25 \leq C \leq 0.5$

(e) $G_H^{B_32} = -N \left[ C(4W^{(1)} + 3W^{(2)}) - 4C^2W^{(1)} \right]$ for $C \leq 0.5$

Similarly, for FCC solid solutions, one gets:

(f) $G_H^{A_1} = -NC(1-C) \left( 6W^{(1)} + 3W^{(2)} \right)$

(g) $G_H^{L_10} = -N \left[ C(6W^{(1)} + 3W^{(2)}) - C^2(4W^{(1)} + 6W^{(2)}) \right]$ for $C \leq 0.5$

(h) $G_H^{L_12} = -N \left[ C(6W^{(1)} + 3W^{(2)}) - 12C^2W^{(2)} \right]$ for $0 \leq C \leq 0.25$

(k) $G_H^{P_{mmm}} = -N \left[ W^{(1)} - 1.5W^{(2)} + C(2W^{(1)} + 9W^{(2)}) - 12C^2W^{(2)} \right]$ for $0.25 \leq C \leq 0.5$

...Eqn.3.22

...Eqn.3.23
Here, \( N \) is the total number of atoms, and the label \( T = 0^\circ\text{K} \) indicates that these expressions hold for completely long-range ordered alloys.

If the experimental enthalpies of formation refer to the standard states of pure components with crystal structures differing from that of the alloy formed, these data must be converted, as described in Section 3.1.2.

3.5.2 Determination of \( W^{(K)} \) from critical temperatures

The critical temperature of long-range order can be connected, with the interchange energies \( W^{(K)} \), only by means of statistical models. Due to the various approximations in the various models, the interchange energies \( W^{(K)} \) as determined from energy measurements, yield different critical temperatures, \( T_{\text{critical}} \) (89).

The simplest approximation (BWG) yields analytical expressions for the uppermost critical temperatures \( T_{\text{crit}} \) in terms of \( C \) and \( W^{(K)} \). Its advantage is the minor numerical work, as compared to the actually more sophisticated cluster variation (CV) method. It has been shown for BCC alloys that, as far as a determination of \( W^{(K)} \) from critical temperatures is concerned, the BWG results can be used if \( T_{\text{crit}} \) is corrected by a temperature scale factor, \( \chi \), whose numerical value depends on the ratio \( W^{(2)}/W^{(1)} \); \( \chi \) is determined from the CV result \( T_{\text{crit}}(0.5) \) for BCC alloys (Fig.3.5) (89). Thereby, it turned out that, fortunately, the experimental temperatures follow the temperature-scaled BWG results \( T_{\text{crit}} = \chi T_{\text{crit}} \) more closely than...
FIG. 3.5: Temperature scale factor $\chi$ in dependence on the ratio of the interchange energies in 'nnn' and in 'nn' with $W^{(1)} > 0$ (Ref. 19).
the original CV results. For FCC alloys, the CV calculations have been done with $W^{(2)} = 0$. The correction factor in such cases is estimated to be in the range $0.5 \leq \chi \leq 0.9$ in the absence of precise information (94).

It is thus possible to determine $W^{(K)}$ using the SRO corrected BWG formulae for the uppermost critical temperatures.

\[
\begin{align*}
\text{BCC :} & \quad B_2 + A_2 \\
K T^{(C)} & = \chi C(1-C)(8 W^{(1)} - 6 W^{(2)}) \quad \ldots 3.24(a) \\
D O_3 + A_2 \\
K T^{(C)} & = \chi C(1-C) 6 W^{(2)} \quad \ldots 3.24(b) \\
B 32 + A_2 \\
K T^{(C)} & = \chi C(1-C) 6 W^{(2)} \quad \ldots 3.24(c)
\end{align*}
\]

It depends on the ratio $W^{(2)}/W^{(1)}$ which transition exhibits the highest critical temperature for a given composition.

\[
FCC: \quad Ll_2 + Al \\
K T^{(C)} = \chi C(1-C)(4 W^{(1)} - 5 W^{(2)}) \quad \ldots 3.25
\]

For BCC alloys the value of $\chi$ must be taken from Fig. 3.5. For FCC alloys, as no such $\chi$ vs. $W^{(2)}/W^{(1)}$ plot exists the value has to be chosen depending on the accuracy of information regarding ordering temperature and enthalpy of formation (See Section 5.6.4).

3.5.3 Determination of $W^{(K)}$ by extrapolation from ternary data (BCC)

Sometimes critical temperature data for a binary system may be unobtainable from considerations of binary
phase diagrams alone, either because of the non-occurrence of the phase in question or because of non-detectability of critical temperature, e.g. Au-Cu and Au-Zn.

In such cases, an extrapolation from ternary to binary is sometimes possible, depending on the availability of the following data\(^{19}\):

1. Ternary ordering temperatures \( T_x(A_2/B_2) \) of any relevant quasi-binary section of the system \( ABC \).

2. \( W^{(1)} \) and \( W^{(2)} \) parameters of at least one of the binaries constituting the ternary, (say) \( AB \).

3. Enthalpies of formation of the relevant structure for the binaries \( AC \) and \( BC \), or \( T_y(B_2/L_2) \) data for any ternary composition.

The critical ordering temperature \( T_x(A_2/B_2) \) for ternary alloys depends, as can be seen from equation (3.16), on the quantities:

\[
E_{ij} = \left[ 8 W^{(1)}_{ij} - 6 W^{(2)}_{ij} \right]_{\text{BWG}} \quad \text{with} \quad ij = AB, BC, CA.
\]

If, say, \( E_{AB} \) is known, then \( E_{BC} \) and \( E_{AC} \) can be varied until the best fit of the experimental data for \( T_x(A_2/B_2) \) is obtained. From these expressions, the temperature \( T_x(C=0.5) \)
for the binary alloys AC and BC are obtained since

\( T_x(C=0.5) \) is directly proportional to them (see equation (3.24)).

With this, a first piece of information for \( W^{(1)} \) and \( W^{(2)} \)
is obtained, as shown by equation (3.26). If the enthalpy of

formation \( \Delta H^f(A2)_{(C=0.5)} \) is known, then a second piece
of information is as shown by equation (3.27), obtained
by substituting \( C=0.5 \) in equation (3.22):

\[
X \left[ 2 \frac{W^{(1)}}{k} - 1.5 \frac{W^{(2)}}{k} \right] = T_x(C=0.5) \quad \ldots (3.26)
\]

\[
kN \left[ \frac{2 W^{(1)}}{k} + 1.5 \frac{W^{(2)}}{k} \right] = -\Delta H^f(C=0.5) \quad \ldots (3.27)
\]

Solution of (3.26) and (3.27) with reference to the plot of \( X \) vs \( \frac{W^{(2)}}{W^{(1)}} \) (Fig.3.5), yields the separate values of the parameters \( W^{(1)} \) and \( W^{(2)} \) for the binary AC or BC, as the case may be.

In the case where enthalpy of formation is not available
but critical temperature \( T_y(B2/L21) \) for any particular
ternary combination is available, then the following procedure
can be adopted to get the second information needed to solve
for \( W^{(1)} \) and \( W^{(2)} \). The critical temperature \( T_y \) for
ternary alloys (see equation (3.17)) depends on the degree of order in nearest neighbour established at \( T_y' \), and on the
interchange energies \( W^{(2)}_{ij} \). In order to get the values of these order parameters, the transcendental equations of the
equilibrium conditions in the ternary alloys (equation (3.17))
have to be solved numerically. This calculation, together
with \( T_x(0.5) \), can yield the values of \( W^{(1)} \) and \( W^{(2)} \) (see
Section 5.5).
3.6 COMPUTER CALCULATION OF THE FREE ENERGIES OF BCC AND FCC PHASES

It is possible, in principle, to calculate the free energies of the ordered phases as a function of temperature once the interchange energy parameters $W^{(1)}$ and $W^{(2)}$ are known for the particular phases. The actual method is rather time-consuming and tedious because of the necessity for a trial and error method to be employed for determining the minimum free energy value at every temperature.

It has been shown by Inden\(^{(98)}\) that a polynomial representation of the order contribution to the free energies, using $W^{(K)}$ parameters, yields free energy values not far from the ones obtained by more rigorous methods. Such a polynomial representation has been adopted here to calculate the ordering contribution to the free energies of the BCC and FCC phases. A brief description of the polynomial representation of the order contribution to the free energy is given first. Suitable modifications, needed to account for the contributions arising from difference in crystal structure of the various components at $0^\circ\text{K}$, are pointed out.

3.6.1 Formulation of the free energy of ordering by a polynomial in temperature

In this section only the ordering portion of the free energy is of interest, and the random solid solution is chosen as the reference state and the free energy difference

$$
\Delta G^{\text{ord}}(C,T) = G^{\text{ord}}(C,T) - G^{\text{dis}}(C,T)
$$

is considered.
In Fig. (3.6) this free energy difference is schematically shown for one particular case of one continuous ordering transformation at the critical ordering temperature $T_{\text{ord} \rightarrow \text{dis}}$. If several ordering transformations occur, the corresponding free energies must be superimposed.

### 3.6.2 One second-order transition

Four conditions are fulfilled by the free energy if a single second-order transition is presumed to occur at $T_{C} = T_{\text{ord} \rightarrow \text{dis}}$.

\begin{align*}
\Delta G(C,0^\circ K) &= H(C,0^\circ K) - H(C,0^\circ K) = \Delta H(C,0^\circ K) \\
\left. \frac{d}{dT} \left( \Delta G(C,T) \right) \right|_{T=0^\circ K} &= S(C,0^\circ K) - S(C,0^\circ K) = \Delta S(C,0^\circ K) \\
\Delta G(C,T_C) &= 0 \\
\left. \frac{d}{dT} \left( \Delta G(C,T_C) \right) \right|_{T=T_C} &= 0
\end{align*}

With these four conditions, a polynomial of the third-order can be formulated:

\[ \Delta G = \varepsilon + (\theta \cdot T_C) - (3\varepsilon + 2\theta \cdot T_C) \tau^2 + (2\varepsilon + \theta \cdot T_C) \tau^3 \]

\[ \tau = \frac{T}{T_C}; \quad \varepsilon = \Delta H(C,0^\circ K) \quad \text{and} \quad \theta = S(C,0^\circ K) - S(C,0^\circ K) \]

The parameters $T_C$, $\varepsilon$, and $\theta$ are the input data of the present polynomial.
3.6.3 Two or more continuous order-disorder transformations

The case of several order-disorder transformations can also be treated with the polynomials if these are evaluated separately for any of the transformations. Assuming the sequence of transformations \( \text{dis} \leftrightarrow \alpha \leftrightarrow \beta \leftrightarrow \gamma \), etc., one has to evaluate:

\[
\begin{align*}
(1) \quad & \Delta G(C,T) \text{ with } T_C = T \\
& \varepsilon = \Delta H(C,O_{0K}) \\
& \theta = S(C,O_{0K}) - S^\alpha \\
(2) \quad & \Delta G(C,T) \text{ with } T_C = T \\
& \varepsilon = \Delta H(C,O_{0K}) \\
& \theta = S(C,O_{0K}) - S^\beta \\
(3) \quad & \text{As in (2), with } \beta, \gamma \text{ replacing } \alpha, \beta \\
\end{align*}
\]

The total free energy of ordering is then the sum of various contributions.

3.6.4 Discontinuous transformation

At the critical temperature of discontinuous transition \( \text{dis} \leftrightarrow \text{ord} \) the free energy of ordering \( \Delta G(C,T) \) goes to zero with non-zero slope. Strictly speaking, the value of this slope must be introduced into the R.H.S. of the expression

\[
\frac{d}{dT} \left( \Delta F(C,T_C) \right) \bigg|_{T = T_C} = 0.
\]
FIG. 3.6: Variation of free energy of ordering with temperature with reference to the random solution.
Absolute values can only be obtained from numerical analysis. However, this case can still be treated by the polynomial method, provided it is realised that this must lead to a less good approximation than for the previous case.

3.6.5 Polynomial input data in terms of model parameters

In Section 3.6.2 it was seen that the input data for the polynomial consisted of the critical temperature of ordering $T_C$, $\varepsilon = \Delta H_{\text{dis} \rightarrow \text{ord}}^{(C,O^0K)}$, and $\theta = S_{\text{dis}}^{(C,O^0K)} - S_{\text{ord}}^{(C,O^0K)}$. These can be obtained from the energy parameters $W(K)$ as described below:

(i) $T_C$

In BCC alloys, both continuous and discontinuous transitions occur, depending on $W(1)/W(2)$ ratios. The critical temperatures are easily obtained, as described in Section 3.5, once the $W(K)$ values are known.

In FCC alloys, as long as ordering only in nearest neighbourhood is considered, the uppermost order-disorder transition is discontinuous at all compositions, and the temperatures of these transitions can be obtained by proper substitutions in equation (3.21).

(ii) $H_{(C,O^0K)}$

In the case of both binary and ternary systems, the value of $H_{(C,O^0K)}$ can be obtained from the expressions for the total free energy for a given composition. The maximum value of
the relevant order parameter (or parameters) for the particular
ordered configuration is substituted in the appropriate
dis$^+\text{ord}$ expressions, and the value $H_{\text{C},0^\circ\text{K}}$ obtained. Equation (3.4)
is used for binary BCC alloys, and equation (3.14) for ternary
BCC alloys. Equations (3.18) and (3.19) are used for binary
and ternary FCC alloys, respectively;

$$\text{dis} \quad \text{ord}$$

(iii) $S_{\text{C},0^\circ\text{K}} - S_{\text{C},0^\circ\text{K}}$

As a result of the adoption of the BWG formalism and
the same number of lattice site occupation probabilities, the
entropy expressions for BCC and FCC turn out to be identical.
The values of the entropies at $0^\circ\text{K}$ for any ordered structure
is then obtained by first assigning the maximum value to the
relevant order parameter or parameters, as the case may be.
This will enable calculation of the individual probabilities,
which can then be substituted in the entropy equation

$$S = -\frac{N}{4} \sum_{L} \sum_{i} p_{i}(L) \ln p_{i}(L)$$

$i = A, B \quad L = I, II, III, IV$ for binary,

and $i = A, B, C, \quad L = I, II, III, IV$ for ternary,
to yield the entropies of the desired ordered structure.

3.6.6 Total free energy of the BCC and FCC phases

From the expressions for free energy, it can be seen
that the total configurational free energies of the BCC and
FCC phases consist of four terms, namely, the energy of the
pure components, the energy of mixing, ordering energy, and
the entropy contribution. The latter three terms can be
estimated at any temperature by the methods described. The
energy of the pure components in the BCC and FCC phases
is estimated by taking into account the stability parameters
given in Table 3.1.

The other contributions, namely the electronic, the
strain energy, and the defect contributions, will have to be
considered as and when a particular alloy is examined.
As there is no information on how Mn affects martensite transformation temperatures, the first series of experiments were performed to determine the martensitic transformation temperature as a function of Mn content, by two different methods. Low temperature ageing effects on martensitic transformation in some alloys was also investigated.

A second series of experiments were performed on a different group of alloys to detect the influence of various quenching rates on retaining disorder. Based on the observations of these experiments and theoretical predictions, some selected compositions were made which were then analysed to yield thermo-dynamic data pertaining to martensitic transitions and order transitions. In this Chapter, the experimental methods are described and the results obtained are recorded.

4.1 PREPARATION OF ALLOYS

Alloys listed in Table 4.1 were all made from 99.9% pure copper, 99.9% pure zinc, and 99.9% pure electrolytic manganese in 10 or 20 gms quantities by melting weighed quantities together in evacuated quartz tubes at sufficiently high temperatures.
<table>
<thead>
<tr>
<th>Alloy No.</th>
<th>Composition in at.%</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>Zn</td>
</tr>
<tr>
<td>A 1</td>
<td>60.7</td>
<td>39.3</td>
</tr>
<tr>
<td>A 2</td>
<td>61.7</td>
<td>38.3</td>
</tr>
<tr>
<td>A 3</td>
<td>61.5</td>
<td>38.0</td>
</tr>
<tr>
<td>A 4</td>
<td>61.5</td>
<td>37.5</td>
</tr>
<tr>
<td>A 5</td>
<td>61.6</td>
<td>37.3</td>
</tr>
<tr>
<td>A 6</td>
<td>61.4</td>
<td>36.2</td>
</tr>
<tr>
<td>A 7</td>
<td>61.3</td>
<td>35.2</td>
</tr>
<tr>
<td>A 8</td>
<td>60.0</td>
<td>34.0</td>
</tr>
<tr>
<td>A 9</td>
<td>60.8</td>
<td>30.0</td>
</tr>
<tr>
<td>A 10</td>
<td>60.0</td>
<td>30.0</td>
</tr>
<tr>
<td>A 11</td>
<td>60.2</td>
<td>25.0</td>
</tr>
<tr>
<td>A 12</td>
<td>59.6</td>
<td>23.6</td>
</tr>
<tr>
<td>B 1</td>
<td>50.1</td>
<td>42.4</td>
</tr>
<tr>
<td>B 2</td>
<td>55.0</td>
<td>25.7</td>
</tr>
<tr>
<td>B 3</td>
<td>50.2</td>
<td>30.5</td>
</tr>
<tr>
<td>B 4</td>
<td>48.9</td>
<td>28.5</td>
</tr>
<tr>
<td>B 5</td>
<td>53.2</td>
<td>21.4</td>
</tr>
<tr>
<td>B 6</td>
<td>46.3</td>
<td>22.5</td>
</tr>
</tbody>
</table>
They were mixed thoroughly in the molten condition, and then allowed to solidify outside the furnace. The cast pellets were homogenised in the same quartz tubes for three days in the β-phase condition, and then water-quenched. The weight losses observed were never more than 0.2%, and so it was assumed that the compositions were not significantly different from the intended ones. Micro-probe analysis showed that there was no silicon pick-up at all. The pellets were then hot forged to a rectangular shape, then cold-rolled and cold-swaged with intermediate stress-relieving anneals, to give thin strips or wires, as desired. The wires used for resistance and stress-strain measurements were 0.93 mm in diameter, and 75 mm long.

4.2 MEASUREMENTS OF MARTENSITIC TRANSFORMATION TEMPERATURE

4.2.1 Resistance measurements

One of the standard methods of martensitic transformation temperature measurement is the four-probe resistance measurement method. The specimen in the form of a wire or thin strip is spot-welded to four copper wires and a thermocouple, as shown schematically in Fig.4.1(a). The wires (1) and (2) on the two extreme sides of the specimen act as current leads through which a constant current is made to pass. The potential drop across the wires (3) and (4) is measured as a function of temperature as the temperature of the specimen is varied by suitable means. Since martensitic transformation is always
FIG. 4.1: Schematic diagram of:

(a) the resistance measurement setup;
(b) a typical record of a martensitic transformation cycle.
accompanied by a sharp resistivity change, a plot of resistance vs temperature should yield the transformation temperature. By making use of a proper device for continuous cooling and heating, and an x-y recorder for continuous measurement of the potential drop (y axis) and the temperature (x axis), a complete record of the transformation cycle can be obtained. In Fig. 4.1(b) a typical plot is shown.

In the present experiments, as the martensitic transition temperatures were expected to be below room temperature, the wires were cooled at a constant rate by immersing into cold gaseous nitrogen above liquid nitrogen, contained in a deep, wide-mouthed dewar. A similar heating rate was obtained by withdrawing the wire from the bath at the same rate. The transition temperatures were taken at the points at which the resistance curve started to deviate from linearity. The accuracy of such measurements was ±2°C. The wire specimens for such measurements were initially quenched from the appropriate β-tising temperatures into iced brine. To avoid zinc loss, the specimens were chromium-plated prior to homogenising in the β-phase, and kept at the homogenising temperature for only 2 to 3 minutes. Metallographic examination showed that they were completely β-phase alloys after such quenching treatments. Plating was removed by acid leaching before spot welding the copper wires and the thermocouple.

Such resistance vs temperature measurements to obtain the martensitic transformation temperatures were conducted on alloys (A2, A5, A6, A7, A9, A10, A11, and A12) to establish how $M_s$ etc. varied with Mn content. Low temperature ageing treatments and their effect on transformation temperatures
FIG. 4.2: Effect of low temperature ageing on the nature of the transformation curve of alloy A7.
FIG. 4.3: Effect of low temperature ageing on the nature of the transformation curve of alloy A9.

(A9) Alloy 60-8Cu/300Zn/92Mn

Relative resistance change

Temperature

as quenched

after 20 hrs. at 70°C
Effect of flash-heating and subsequent ageing at room temperature on the martensitic transition temperature in alloy A10 (Resistance method).
FIG. 4.5: \( M_s \) temperature variation with ageing time at low temperatures. (Resistance method).
### TABLE 4.2

Martensitic Transformation Temperatures of Cu-Zn-Mn Alloys (Resistance Method)

<table>
<thead>
<tr>
<th>Alloy No.</th>
<th>$M_s$</th>
<th>$M_f$</th>
<th>$A_s$</th>
<th>$A_f$</th>
<th>Hysteresis</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 2</td>
<td>219</td>
<td>189</td>
<td>205</td>
<td>233</td>
<td>15</td>
</tr>
<tr>
<td>A 5</td>
<td>198</td>
<td>164</td>
<td>174</td>
<td>207</td>
<td>12</td>
</tr>
<tr>
<td>A 6</td>
<td>183</td>
<td>136</td>
<td>161</td>
<td>195</td>
<td>12</td>
</tr>
<tr>
<td>A 7</td>
<td>179</td>
<td>140</td>
<td>158</td>
<td>191</td>
<td>13</td>
</tr>
<tr>
<td>A 9</td>
<td>125</td>
<td>110</td>
<td>121</td>
<td>136</td>
<td>12</td>
</tr>
<tr>
<td>A 10</td>
<td>112</td>
<td>≈ 90</td>
<td>94</td>
<td>123</td>
<td>14</td>
</tr>
<tr>
<td>A 11</td>
<td>105</td>
<td></td>
<td>108</td>
<td>112</td>
<td></td>
</tr>
<tr>
<td>A 12</td>
<td>No transformation observed above 80 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
were carried out on alloys (A7, A9, A10). The results of the martensitic transformation investigations are listed in Table 4.2. Figures 4.2 and 4.3 show the result of low temperature ageing on the nature of the transformation curve. Figure 4.4 shows the decay of $M_s$ temperature with time in the alloy A10; flash-heated to 200°C, and subsequently aged at room temperature. Figure 4.5 shows the $M_s$ variation with ageing time in alloys A7, A9, and A10 at low temperature.

4.2.2 Stress-strain measurements at various temperatures

As stated earlier, martensitic transformation can be induced by external stress at $T > T_o$, which is characterised by pseudo-elastic behaviour. The plot of $\sigma T$ vs $T$ for a Cu-Zn alloy (Fig. 2.13) shows that the straight line plot extrapolates to the $M_s$ temperature at zero stress. This makes it possible to use the stress-strain measurements at various temperatures above $M_s$, to yield the $M_s$ temperatures for the various alloys. Most of the alloys previously subjected to resistance measurements were subjected to this mode of $M_s$ determination as well. Stress-strain curves at various temperatures were obtained on wire samples that had been quenched from the $\beta$-phase field. The strain rate employed was $5 \times 10^{-4}$/sec. Tensile tests were carried out in a Hounsfield E tensile testing machine. The specimen temperature was controlled by immersing it in a wide-mouthed dewar containing methanol at the appropriate temperatures. The maximum recoverable strain in polycrystalline specimens was of the order of $\approx 5\%$, and pseudo-elastic behaviour persisted up to $80^oK$ above $A_f$, after
FIG. 4.6: Typical stress-strain curve of a pseudo-elastic Cu-Zn-Mn alloy.
FIG. 4.7: $\sigma_p \rightarrow M$ vs. temperature curves for Cu-Zn-Mn alloys. The temperatures at which the extrapolated lines intersect the X-axis correspond to the $M_s$ temperatures.
FIG. 4.8: Effect of ageing on $\sigma_p - \nu P_M$ -vs- temperature plots of alloy A 6.
FIG. 4.9: Effect of low temperature ageing on $\sigma_{pl} - M$ -vs- temperature plots of alloy A10.
FIG. 4.10: Effect of flash-heating and subsequent low temperature ageing on the $\sigma_p - M$ vs. temperature plots of alloy A10.
<table>
<thead>
<tr>
<th>Composition in At. %</th>
<th>Mn</th>
<th>From Resistance vs. T Data</th>
<th>Extrapolation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>Zn</td>
<td></td>
<td></td>
</tr>
<tr>
<td>61.6</td>
<td>37.3</td>
<td>1.1</td>
<td>198</td>
</tr>
<tr>
<td>61.4</td>
<td>36.2</td>
<td>2.4</td>
<td>190</td>
</tr>
<tr>
<td>61.3</td>
<td>35.5</td>
<td>3.5</td>
<td>179</td>
</tr>
<tr>
<td>60.8</td>
<td>30.0</td>
<td>9.2</td>
<td>125</td>
</tr>
<tr>
<td>60.0</td>
<td>30.0</td>
<td>10.0</td>
<td>114</td>
</tr>
</tbody>
</table>
which plastic deformation tended to occur. In the present work, the specimens were strained only up to 2%, and the stresses attained were always below the stress necessary to start 'memory type plastic deformation' (99).

A stress-strain curve typical of the ones obtained at different temperatures for the polycrystalline wire specimens of alloys A5, A6, A7, A9, is shown in Fig.4.6. \( \sigma_{p-M} \), the stress necessary to induce martensite at any temperature, is taken as the value at which the stress-strain curve departs from linearity. The variation of \( \sigma_{p-M} \) vs. temperature for the alloys quenched and aged at room temperature are plotted in Fig.4.7. The effect of ageing at intermediate ageing temperatures on the \( \sigma_{p-M} \) vs. T plots were obtained on alloy Nos. A6 and A10, and are shown in Figs.4.8 to 4.10. The results of \( M_s \) determination obtained by extrapolation to zero stress for the alloys mentioned are shown in Table 4.3.

4.3 X-RAY MEASUREMENTS : DETECTION OF CHANGES IN ORDER PARAMETER

4.3.1 Superlattice lines

Detection of various degrees of order by measurement of superlattice line intensities is a standard method of investigation employed in ordering studies in alloys (100). The principle involved and the limitations of the method are described briefly.

Let us consider the case of a BCC alloy made up of components A and B. The Bravais lattice positions for the BCC are given by \([000]\) and \([\frac{1}{2} \frac{1}{2} \frac{1}{2}]\). The intensities
of the diffraction lines are proportional to the square of the structure factor $F$, which is given by:

$$F = \sum_j \sum_k f_j e^{2\pi i(hu_k + kv_k + \lambda w_k)}$$

...(4.1)

where $f_j =$ atomic scattering factor of component $j$ equal to its atomic number in the first approximation.

$[u_k \ v_k \ w_k]$ are the position vectors of species $j$.

$[h \ k \ l]$ are Miller indices of the diffracting plane.

The intensity of the diffracted line from plane $(hkl)$ is given by $I_{hkl} = A |F|^2$ where $A$ is a constant made up of different factors.

**Case I**: Random distribution of species $A$ and $B$

The components $A$ and $B$ are randomly distributed among the lattice sites in the case of a disordered alloy and the occupation of any particular site by either component $A$ or $B$ is proportional to the concentration. In such a situation, the value of $f_j = f = (c_A f_A + c_B f_B)$ where $c_A$ and $c_B$ are the mole fractions of $A$ and $B$, respectively. The intensity $I_{hkl}$ from any plane $(hkl)$ then is given by:

$$I_{hkl} \propto \left[ f \left[ 1 + e^{2\pi i (h+k+l)} \right] \right]^2$$

If the value of $(h+k+l)$ is even, then:

$$I_{hkl} \propto 4 f^2$$

and if it is odd, then:

$$I_{hkl} = 0.$$
For a random distribution of the components A and B in a BCC alloy, then, we can observe only the lines corresponding to planes 110, 200, 112, and so on.

Case II

In the ordered state, A and B atoms preferentially occupy certain positions. In a perfectly ordered structure in a stoichiometric BCC alloy, the \([000]\) positions are occupied by one type of atom (say A), and the \([\frac{1}{2} \frac{1}{2} \frac{1}{2}]\) positions are occupied by the other type of atoms (say B). Then the equation for diffracted intensity \(I_{hkl}\) is given by:

\[
I_{hkl} \propto |F|^2 = \left( f_A + f_B e^{\pi i (h+k+l)} \right)^2
\]

If \((h+k+l)\) is even, then \(I_{hkl} \propto (f_A + f_B)^2\)

If \((h+k+l)\) is odd, then \(I_{hkl} \propto (f_A - f_B)^2\)

Or, in other words, for an ordered alloy 'superlattice' reflexions corresponding to the planes 100, 111, etc. can exist, in contrast to Case I. It should theoretically be possible to detect such superlattice lines in any ordered alloy; however, they are detected easily only when \((f_A - f_B)^2 > 4\). Sometimes, by a suitable choice of X-ray tube, this factor can be made to increase even if the atomic numbers are very close to each other. In Cu-Zn alloys, superlattice lines have been detected by such methods, making use of X-ray tubes with zinc targets\(^{(100)}\). In Mn-Zn alloys, it has been possible to detect superlattice lines using X-ray
### Table 4.4
Lattice Parameters and Hardness Values of Cu-Zn-Mn Alloys as a Function of Cooling Rate.

<table>
<thead>
<tr>
<th>Homogenising Temperature (°C)</th>
<th>Alloy No.</th>
<th>Microhardness Values (VPN) of Specimens quenched into:</th>
<th>Lattice Parameter (Å) of Specimens quenched in:</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Iced Brine</td>
<td>Water at 150°C</td>
<td>100°C</td>
<td>Iced Brine</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600°C</td>
<td>B1</td>
<td>156</td>
<td>150</td>
<td>147</td>
</tr>
<tr>
<td>750°C</td>
<td>B2</td>
<td>180</td>
<td>179</td>
<td>179</td>
</tr>
<tr>
<td>750°C</td>
<td>B3</td>
<td>205</td>
<td>188</td>
<td>188</td>
</tr>
<tr>
<td>750°C</td>
<td>B4</td>
<td>188</td>
<td>187</td>
<td>187</td>
</tr>
<tr>
<td>750°C</td>
<td>B5</td>
<td>198</td>
<td>185</td>
<td>185</td>
</tr>
<tr>
<td>750°C</td>
<td>B6</td>
<td>223</td>
<td>206</td>
<td>206</td>
</tr>
</tbody>
</table>

- No superlattice lines detected.
- Wire Specimen: 2.977 2.980
- Powder specimen: 2.985
- On quenching into water at 100°C massive precipitation occurs.
tubes with Fe targets. It was therefore considered possible that a ternary Cu-Zn-Mn alloy with high manganese content would enable the superlattice lines to be detected with an Fe-target X-ray tube. The alloys used in such tests were alloys No. B2, B2, B5. Debye-Sherrer (114.7 mm) powder cameras were used to take the X-ray patterns in all cases. The specimens were in either wire or powder form. However, no superlattice lines were observed in any of the samples tested. This means that, even up to a 25% substitution of zinc by manganese, there is insufficient enhancement in the X-ray intensities of the superlattice line in a Cu-Zn system using the D.S. method.

4.3.2 Lattice parameter measurements

Ordering in alloys has been known to result in lattice parameter changes, and lattice parameter measurements have been utilised in a number of cases to detect ordering transitions. In the present investigations, lattice parameters were measured, using the powder diffraction technique mentioned in the previous section, after suitable heat treatments on high manganese alloys Nos. B2, B3, and B5. Extrapolation functions were used to measure the lattice parameter values to the accuracy of ± 0.002 Å. These values are listed in Table 4.4. No significant changes that could be attributed to ordering are observed.

4.4 INVESTIGATIONS USING THE DIFFERENTIAL SCANNING CALORIMETER

The design of the differential scanning calorimeter is based on the principle of differential thermal analysis.
The apparatus consists of a suitably designed holder (DSC cell) with provisions for measuring temperatures of a test specimen and a standard separately. The holder can be sealed and operated such that the standard and test specimens are heated or cooled at a desired rate inside the cell. As long as there is no transformation taking place in the test specimen, say during a heating run, the temperatures of the test and standard specimens increase at the same rate, and are equal at any instant of time. However, if at any temperature the test specimen undergoes a transformation involving absorption or evolution of heat, then the temperature of the test specimen lags or leads the temperature of the standard, as long as the transformation is taking place. Once it is complete, the temperature of the test specimen once again equals the temperature of the standard. This difference in temperatures of the test and standard specimens arising out of a phase transition can be amplified and plotted automatically as a function of temperature, using an x-y recorder and quantitative data like the transformation temperature, heat of formation etc. can be obtained once the operational instrumental variables of the DSC and x-y recorders are standardised to enable direct interpretation from such plots.

The Du Pont DSC incorporates the facilities desired for obtaining such data. It has been possible to operate from -160°C to 200°C at a desired heating rate, using a special cooling attachment. Heating and cooling runs in the
FIG. 4.11: Typical DSC trace corresponding to a martensite to parent transition in a Cu-Zn-Mn alloy.

(A3) Alloy 61.5Cu/38Zn/0.5Mn

as quenched from 870°C
Heating rate 10°C/min

FIG. 4.12: DSC trace corresponding to a second-order transition (Schematic).
FIG.4.13: DSC traces showing arrests associated with $L_2 \rightarrow B_2$ in Cu-Zn-Mn alloys.
<table>
<thead>
<tr>
<th>Alloy No.</th>
<th>Composition (in at.%)</th>
<th>( T_y (B_2 \ L_{21}) ) (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B 3</td>
<td>50.2 / 30.5 / 19.3</td>
<td>367</td>
</tr>
<tr>
<td>B 2</td>
<td>55.0 / 25.7 / 19.3</td>
<td>417</td>
</tr>
<tr>
<td>A 1</td>
<td>60.7 / 39.3 / 1</td>
<td>355</td>
</tr>
<tr>
<td>A 3</td>
<td>61.5 / 37.5 / 0.5</td>
<td>360</td>
</tr>
<tr>
<td>A 4</td>
<td>61.5 / 37.5 / 1.0</td>
<td>369</td>
</tr>
<tr>
<td>A 8</td>
<td>60.0 / 34.0 / 6.0</td>
<td>389</td>
</tr>
<tr>
<td>A10</td>
<td>60.0 / 30.0 / 10.0</td>
<td>375</td>
</tr>
</tbody>
</table>
range 20°C to 600°C have also been possible at desired rates.

In all the present investigations copper was used as the standard, and the weight of the standard was kept the same as that of the test specimen.

A typical DSC trace obtained for alloy undergoing martensite to parent phase transition is shown in Fig.4.11. Such a plot is typical of any first-order transition that involves a discontinuity in the free energy vs temperature curve. The transition temperatures are marked on the plot and are measured to the accuracy of ± 1 to 2°C.

In the case of a second-order transition, a discontinuity is observed only in the specific heat vs temperature curve i.e., \( \frac{d(\Delta H)}{dT} \) vs T curve. The corresponding free energy vs temperature curve shows only a slope change. A DSC trace corresponding to a second-order transition is schematically shown in Fig.4.12. The point (A) corresponds to the start of the transition, and the point (B) to the completion of the transition. All the alloys listed in Table 4.5 exhibited such a second-order transition, and the DSC traces obtained for them are shown in Figs.4.13.

The reverse martensitic transition temperatures \( A_s \) and \( A_f \), and the enthalpies of formation \( \Delta H_{M \rightarrow P} \) have been measured as a function of ageing treatment in the alloys Cu 61.5/Zn 38/Mn 0.5 as Cu 61.5/Zn 37.5/Mn 1.0, and the results are shown in Figs. 4.14 and 4.15. The ageing treatments were done at the appropriate temperatures for five
FIG. 4.15: $\Delta H_{M \rightarrow P}$ and quenched in excess heat as a function of ageing temperature (DSC).
minutes, since previous experiments showed that the results of longer ageing at temperatures lower than 140°C (2 hours) resulted essentially in the same sort of changes taking place. In the range 180 to 200°C, ageing for more than 30 minutes resulted in a gradual decrease in the $\Delta H$ values with increasing times, signifying bainitic transformation. Both the alloys showed an evolution of excess heat in the temperature range $20^\circ - 60^\circ$C when they were reheated in the DSC after ageing and quenching from temperatures above $80^\circ$C.

4.5 MICROHARDNESS MEASUREMENTS

Usually, ordering reactions are accompanied by a change in hardness value. Microhardness measurements to detect such changes in hardness as a function of cooling rate have been employed in establishing changes in degrees of order in Cu-Al alloys. In the present investigations, three different cooling rates were obtained by quenching in iced brine, quenching in water at $20^\circ$C, and quenching in water at $100^\circ$C. Microhardness measurements after such treatments were carried out on alloys Nos. Bl to B5. The average of several hardness values at different parts of a specimen was taken as the representative value of hardness. The specimens were completely in the $\beta$-phase conditions for all such measurements. The values of microhardness are given in Table 4.4. Like lattice parameter measurements, these measurements also do not show any variation that can be attributed to different rates of ordering depending on cooling rate. It is quite likely that the changes in degree or order are too small to be detected by this method.
CHAPTER 5

CALCULATIONS

5.1 GENERAL

As pointed out previously, formulation of an adequate free energy function for the parent and product phases is the primary requirement in a thermodynamic analysis of a phase transition. The free energy expressions based on the BWG model can be utilised for such a formulation if the nearest and next nearest neighbour interaction energy parameters are known for the binary system AB (or binaries AB, BC, CA in a ternary system ABC).

In the first part of this Chapter attention will be given to the calculation and deduction of the energy parameters for the various binaries Cu-Zn, Cu-Mn, and Zn-Mn in the BCC and FCC phases. In the next part, the stress-strain and calorimetric data are utilised to calculate the entropy variation accompanying martensitic transition, and the stored elastic energy, respectively. Finally, the free energy plots for various compositions are obtained.

5.2 PRELIMINARY CALCULATIONS OF ENERGY PARAMETERS FOR BCC Cu-Zn, Mn-Zn, and Cu-Mn PHASES

As previously described in Section 3.5, the energy parameter calculations require two pieces of information, namely the enthalpy of formation of the BCC phase, and the ordering temperature at any given composition. Energy parameters
<table>
<thead>
<tr>
<th>Composition (at.%)</th>
<th>Experimental $T_x(A_2/B_2) \degree K$</th>
<th>Calculated $T_x(A_2/B_2) \degree K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>Zn</td>
<td>Mn</td>
</tr>
<tr>
<td>50.3</td>
<td>49.3</td>
<td>0.4</td>
</tr>
<tr>
<td>50.6</td>
<td>47.8</td>
<td>1.6</td>
</tr>
<tr>
<td>50.9</td>
<td>46.7</td>
<td>2.4</td>
</tr>
<tr>
<td>50.6</td>
<td>46.8</td>
<td>2.6</td>
</tr>
<tr>
<td>50.8</td>
<td>45.6</td>
<td>3.6</td>
</tr>
<tr>
<td>51.0</td>
<td>44.5</td>
<td>4.5</td>
</tr>
<tr>
<td>51.0</td>
<td>43.5</td>
<td>5.5</td>
</tr>
<tr>
<td>50.1</td>
<td>43.5</td>
<td>5.5</td>
</tr>
</tbody>
</table>

* The best combination of $E_{ij}$ that yield the listed calculated ordering temperatures are given in Table 5.2.

** Ref. 59.
<table>
<thead>
<tr>
<th>Binary System</th>
<th>( \Delta H^f ) (C=0.5) kJ/mol</th>
<th>( ^*E_{ij} ) in K units</th>
<th>( T^o ) (C=0.5) K</th>
<th>( W(1) ) in K units</th>
<th>( W(2) ) in K units</th>
<th>( \chi )</th>
<th>( W(1)_{BWG} ) in K units</th>
<th>( W(2)_{BWG} ) in K units</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Zn</td>
<td>-11.35</td>
<td>2968</td>
<td>741</td>
<td>955</td>
<td>535</td>
<td>0.67</td>
<td>640</td>
<td>360</td>
<td>From Reference 19.</td>
</tr>
<tr>
<td>Mn-Zn</td>
<td>-15.00</td>
<td>3350</td>
<td>838</td>
<td>1240</td>
<td>770</td>
<td>0.63</td>
<td>780</td>
<td>485</td>
<td>( \Delta H^f ) taken from Table 5.3</td>
</tr>
<tr>
<td>Cu-Mn</td>
<td>+3.80</td>
<td>1750</td>
<td>438</td>
<td>-97</td>
<td>-476</td>
<td>0.84</td>
<td>-82</td>
<td>-400</td>
<td>( \Delta H^f ) taken from Reference 107.</td>
</tr>
</tbody>
</table>

\* 1 K unit = 13.8 \times 10^{-24} J.
utilising such data have been fairly accurately determined by Inden\(^{(19)}\) for the Cu-Zn system, and are given in Table 5.2. For the systems Mn-Zn and Cu-Mn, such data are not explicitly available. Fortunately, information on ordering temperatures in ternary Cu-Zn-Mn systems are available\(^{\text{(58,59)}}\), and are given in Table 5.1. These can be utilised to obtain the first information regarding the ordering temperature for the systems Mn-Zn, and Cu-Mn, as explained in Section 3.5.3. As regards the second piece of information, namely the enthalpy of formation of BCC Mn-Zn and BCC Zn-Mn, no experimental value is available. There are now two ways in which to proceed: firstly, to use empirical predictions of the Miedema type\(^{(103)}\) and check the calculated results by experiment; or to make experimental determinations of \(T_y\) or \(T_x\), thereby deducing the energy parameters, and then check if the associated heats of formation are consistent with Miedema type predictions. The first method to be adopted used the \(\Delta H^f\) values listed in Table 5.3 for which Miedema tives an error bar of \(\pm 4.0\) to \(6.0\) kJ/mol, which is taken to encompass the difference between various crystal structures and their modifications. Although this is a very crude approximation, there is a considerable body of experimental evidence\(^{(104)}\) which supports this contention. This means that such predicted values can at least provide a starting point for calculations for the two systems Mn-Zn and Cu-Mn. The energy parameter values so obtained are listed in Table 5.2.
### TABLE 5.3

Comparison of Experimental and Predicted Values for Heat of Formation

<table>
<thead>
<tr>
<th>System</th>
<th>Phase</th>
<th>* $\Delta H^f$ (C=0.5) KJ/mol</th>
<th>** $\Delta H^f$ (C=0.5) KJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu - Mn</td>
<td>Sol(Y) (1100°K)</td>
<td>$+3.3 \pm 4.6$</td>
<td>$+4.4$</td>
</tr>
<tr>
<td>Cu - Zn</td>
<td>Sol(\beta) (973°K)</td>
<td>$-11.3$</td>
<td>$-8.4$</td>
</tr>
<tr>
<td>Mn - Zn</td>
<td>No values available</td>
<td></td>
<td>$-15.0$</td>
</tr>
<tr>
<td>Ni - Zn</td>
<td>$\beta$ (1100°K)</td>
<td>$-19.0$</td>
<td>$-18.0$</td>
</tr>
<tr>
<td>Cu - Pd</td>
<td>(1350°K)</td>
<td>$-13.8$</td>
<td>$-10.9$</td>
</tr>
<tr>
<td>Cu - Pt</td>
<td>(1350°K)</td>
<td>$-10.5$</td>
<td>$-7.5$</td>
</tr>
</tbody>
</table>

* From Reference 107.

** From Reference 103.
5.3 **CALCULATION OF CRITICAL BCC ORDERING TEMPERATURES**

**ONCE THE ENERGY PARAMETERS ARE KNOWN**

Once the parameters are known, the ordering temperatures $T_x$ and $T_y$ are obtained by substituting for $W^{(k)}$ in the appropriate expressions. For $T_x$, direct substitution of the $W^{(k)}$ values is all that is required. However, for obtaining $T_y$ it is necessary to know the value of the order parameter/parameters at $T_y$. This has to be obtained by numerical methods.

5.3.1 **Method of obtaining $T_y$ (B2/D03) for binary BCC phase**

At $T_y$, only the order parameter $x \neq 0$ and the others, 'y' and 'z', are zero. The value of $x$ being in the range $0 \leq x \leq C_B$, the procedure described below can be adopted for getting $T_y$ and $x_{\text{min}}(T_y)$ simultaneously:

(a) A value of $x$ is chosen within the limits $0 \leq x \leq C_B$.

(b) Equation (3.8) is used to obtain an equivalent $T_y$ value.

(c) This value of $T_y$ is substituted in the expression for $\frac{\partial G}{\partial x}$, taking into account the fact that $y = z = 0$ at $T_y$. The expanded expression for $\frac{\partial G}{\partial x}$ after due simplification is:

$$\frac{\partial G}{\partial x} = k T_y \ln \left\{ \frac{(C_A + x)^2 (C_B + x)^2}{(C_A - x)^2 (C_B - x)^2} \right\} - 8 \left(4 W^{(1)} - 3 W^{(2)}\right)$$

......(5.1)

(d) $\frac{\partial G}{\partial x}$ is examined to see whether $\frac{\partial G}{\partial x} = 0$. If this is not the case, a different value of $x$ is taken, and
steps (b) to (d) are repeated until \( \frac{\partial G}{\partial x} = 0 \).

A computer program to calculate \( T_Y \) by this method for the binary alloys is given in Appendix I, along with an example.

5.3.2 Method of obtaining \( T_Y(B_2/L_2) \) for ternary BCC phases

In the case of ternary alloys, the calculation of \( T_Y \) requires two order parameters, \( x_{A_{\min}}(T_Y) \) and \( x_{B_{\min}}(T_Y) \). The calculation is performed as follows:

(a) \( x_A \) is chosen within the limits given by equation (3.13).

(b) Limits on \( x_B \) are automatically obtained from equation (3.13). For any chosen value of \( x_A \), \( x_B \) is varied within these limits.

(c) Equation (3.17) is used to obtain an equivalent \( T_Y \).

(d) This value of \( T_Y \) is substituted in the expressions for \( \frac{\partial G}{\partial x_A} \) and \( \frac{\partial G}{\partial x_B} \) taking into account the fact that \( y_i = z_i = 0 \), where:

\[
\frac{\partial G}{\partial x_A} = -\frac{4x_A}{kT_Y} (E_{AC}) - \frac{2x_B}{kT_Y} (E_{AC} + E_{BC} - E_{AB})
\]

\[
+ \ln \left[ \frac{(C_A + x_A)^2 (C_C + x_A + x_B)^2}{(C_A - x_A)^2 (C_C - x_A - x_B)^2} \right]
\]

\[\cdots (5.2)\]
\[
\frac{\partial G}{\partial x_B} = -\frac{4x_B}{kT_y}E_{BC} - \frac{2x_A}{kT_y}(E_{AC} + E_{BC} - E_{AB}) + \ln \left\{ \frac{(C_B + x_B)^2 (C_C + x_A + x_B)^2}{(C_B - x_B)^2 (C_C - x_A - x_B)^2} \right\} \quad \ldots (5.3)
\]

(e) \( \frac{\partial G}{\partial x_A} \) and \( \frac{\partial G}{\partial x_B} \) are then inspected for the condition that they are equal to zero simultaneously.

(f) If this is not the case, a different value of \( x_B \) is chosen, and steps (c) to (e) are repeated.

If \( \frac{\partial G}{\partial x_A} = \frac{\partial G}{\partial x_B} = 0 \), then the values of \( T_y, x_{A_{\text{min}}}(T_y) \) and \( x_{B_{\text{min}}}(T_y) \) are noted. If not, all the values of \( x_B \) within the limits imposed by equation (3.13) are tried.

(g) If the condition \( \frac{\partial G}{\partial x_A} = \frac{\partial G}{\partial x_B} = 0 \) is still not achieved, a new combination of \( x_A \) and \( x_B \) is introduced, and steps (b) to (f) are repeated until \( \frac{\partial G}{\partial x_A} = \frac{\partial G}{\partial x_B} = 0 \) is satisfied.

A computer program to carry out this procedure is given in Appendix 2, along with an example.

5.3.3 Comments regarding the applicability of the methods

Since it is an inherent assumption in the derivation of the expression for \( T_y \) that the transition proceeds along the route \( A_2 + B_2 + DO_3 \) (or \( L_{2_1} \)), a definite value for \( T_y \) and the order parameters at \( T_y \) are obtainable by this method only
when such a transition can exist for a given composition. If, however, there exists a possibility that the transition is discontinuous, i.e., it transforms directly from $A_2 \rightarrow DO_3/L2_1$, then these methods do not yield the correct results.

In such a case, $T_y$ can only be obtained by more rigorous methods that involve the standard methods of search for minimum free energy for the structures concerned. However, it is still possible to locate the composition at which the character of the ordering transition changes from the continuous type to the discontinuous type. Proceeding from the side of compositions that have a definite $T_y$, it will be the first composition for which the condition $\frac{\partial G}{\partial x_A} = \frac{\partial G}{\partial x_B} = 0$ will not be satisfied below $T_x$.

5.4  **PRELIMINARY PREDICTION OF ORDERING REACTIONS IN THE QUASI-BINARY SECTION $Cu_{60}/Zn_{40-x}/Mn_x$**

With the interaction parameters obtained for the various binaries of the ternary system Cu-Zn-Mn, it is now possible to obtain the boundaries of the ordered phase fields in the system using these values. This has been carried out for the specific quasi-binary section $Cu_{60} Zn_{40-x} Mn_x$ using the computing procedure described in the previous sections. The plot of the calculated critical temperatures vs Mn content (Fig.5.1), curve (a), shows that the $T_y$ temperature rises steeply from 350°K for a 60/40 alloy to ≈ 620°K for a 60/35/5 alloy. The transition then becomes discontinuous at about 8% Mn. Plots of $T_x$ and $T_y$ obtained for the same section by Inden, who has used the same energy parameters and the more rigorous
Fig. 5.1: Variation of $T_x$ ($A_2/B_2$) and $T_y$ ($B_2/L_2$) temperatures with Mn content in the quasi-binary system $Cu_{60}Zn_{40-x}Mn_x$ (Preliminary calculation).
### TABLE 5.4
Data Pertaining to the Calculations Leading to the Modified Parameters for BCC

<table>
<thead>
<tr>
<th>Binary System</th>
<th>$\Delta H^f_\text{C=0.5}$ (kJ/mol)</th>
<th>*$E_{ij}$ (in K units)</th>
<th>$T_x$ (C=0.5) (°K)</th>
<th>$W(1)$ (K units)</th>
<th>$W(2)$ (K units)</th>
<th>$X$</th>
<th>(1) $W_{BWG}$ (K units)</th>
<th>(2) $W_{BWG}$ (K units)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu - Zn</td>
<td>-10.45</td>
<td>2968</td>
<td>741</td>
<td>904</td>
<td>478</td>
<td>0.68</td>
<td>615</td>
<td>325</td>
<td>$\Delta H^f_\text{C=0.5}$ modified to fit experimentally determined $T_x$ (B2/L2₁) of Cu-Zn-Mn alloys</td>
</tr>
<tr>
<td>Mn - Zn</td>
<td>-6.3</td>
<td>3350</td>
<td>838</td>
<td>647</td>
<td>147</td>
<td>0.78</td>
<td>505</td>
<td>115</td>
<td></td>
</tr>
<tr>
<td>Cu - Mn</td>
<td>-4.2</td>
<td>1750</td>
<td>438</td>
<td>398</td>
<td>142</td>
<td>0.75</td>
<td>300</td>
<td>107</td>
<td></td>
</tr>
</tbody>
</table>

* 1 K unit = 13.8 x 10^{-24} J
method of analysis, showed that there was a point-to-point agreement between the two predictions in the composition region $x = 0$ to $\sim 8\%$. After that limit, the $T_x(A_2/B_2)$ temperatures are a better approximation for $T_C$ of discontinuous transition.

5.5 MODIFICATION OF THE PARAMETERS ON THE BASIS OF D S C RESULTS

From the $T_Y$ plot calculated for the quasi-binary section $\text{Cu}_{60}\text{Zn}_{40-x}\text{Mn}_x$, it is seen that, for manganese contents above $\sim 8\%$, the $L_2 + A_2$ discontinuous transition should take place on heating. However, from the DSC traces (Fig.4.13) obtained for alloys with 6\% and 10\% Mn, it is seen that the transition character is more likely to be second-order than first-order. This means that these alloys undergo a $L_2 \rightarrow B_2$ transition on heating from room temperature. The DSC traces for other alloys (Fig.4.13) of different compositions with Mn contents varying up to $\sim 19\%$ also show similar second-order characteristics. Taking this as definite evidence for a continuous $L_2 \rightarrow B_2$ transition and utilising the critical temperatures determined for some of these alloys, a different set of modified values of enthalpies of formation for the three binaries Cu-Zn, Mn-Zn, and Cu-Mn was obtained. They were then utilised in calculating the modified set of $W^{(K)}$ parameters for the three binaries. They are given in Table 5.4. The $T_Y$ plots for the alloys given in Fig.5.2 show that the agreement between the experimentally
Comparison of experimentally determined and back calculated values of ordering temperature $T_y(B_2/L_2)$ in Cu-Zn-Mn alloys.

**FIG.5.2:**
obtained and back calculated values of $T_y$, for all the alloys investigated using the modified $W^{(K)}$ values is quite good, justifying the modifications made to the $W^{(K)}$ values.

5.6 DETERMINATION OF $W^{(K)}$ PARAMETERS FOR FCC Cu-Zn, FCC Mn-Zn, AND FCC Cu-Mn SYSTEMS

5.6.1 System Cu-Zn

The relevant $W^{(K)}$ parameters for the system Cu-Zn in its FCC form have not been obtained so far, presumably because of lack of unambiguous experimental data regarding the ordering temperature in this system. Many investigations regarding the ordering behaviour of $\alpha$-brass in the composition region around Cu$_3$Zn have been conducted, and it has been shown that there is a considerable amount of short-range ordering below $= 525^\circ$K without any concrete evidence of long-range ordering, even at $= 350^\circ$K$^{(105)}$. This has been corroborated by $\gamma$-irradiation studies on $\alpha$-brass$^{(106)}$.

In the absence of a definite experimental value for $T_c$, it is assumed that $T_c(70 \text{ Cu}/30 \text{ Zn}) = 275^\circ$K. Taking the experimental heat of formation value from Ref.107 and substituting these values in equations (3.25) and (3.23), respectively, $W^{(1)}$ and $W^{(2)}$ values for the system $\alpha$-Cu/Zn are obtained, as given in Table 5.5. Value of $\chi$ is taken as 0.82 (See Section 5.6.4).

5.6.2 System Mn-Zn

It has been established that Mn Zn$_3$ alloy exhibits a perfect L1$_2$ structure ($\alpha'$) on annealing at 525$^\circ$K, and this is ferromagnetic below 140$^\circ$K$^{(108)}$. From the phase diagram
FIG. 5.3: Phase diagram of the system Zn-Mn (Ref. 109).
<table>
<thead>
<tr>
<th>Binary System</th>
<th>$\Delta H^f_{C=0.25}$ KJ/mol</th>
<th>$T_C(C=0.25)$ (°K)</th>
<th>$W^{(1)}$ (K units)</th>
<th>$W^{(2)}$ (K units)</th>
<th>X</th>
<th>$W^{(1)}_{BWG}$</th>
<th>$W^{(2)}_{BWG}$</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu - Zn</td>
<td>- 6.5</td>
<td>246</td>
<td>625</td>
<td>150</td>
<td>0.82</td>
<td>513</td>
<td>123</td>
<td>$\Delta H^f$ taken from Reference 107.</td>
</tr>
<tr>
<td>Zn - Mn</td>
<td>-11.3</td>
<td>575</td>
<td>1136</td>
<td>-140</td>
<td>0.82</td>
<td>932</td>
<td>-115</td>
<td>$\Delta H^f$ calculated from Miedema's estimate given in Table 5.3.</td>
</tr>
<tr>
<td>Cu - Mn</td>
<td>+ 2.2</td>
<td>0</td>
<td>-180</td>
<td>-120</td>
<td>0.82</td>
<td>-148</td>
<td>-98</td>
<td>$\Delta H^f$ taken from Reference 107</td>
</tr>
</tbody>
</table>
proposed by Nakagawa et al.\(^{(109)}\) (Fig. 5.3), it is seen that the \(\alpha'\) phase extends up to 600°K. Since no ordering transition temperatures have been given, and it is certain that it is above 525°K, it is tentatively taken to be 570°K. From the Medleja estimate of enthalpy of formation available for stoichiometric Mn-Zn alloy, from Table 5.3, an estimate of the enthalpy of formation for the 75 Mn/25 Zn alloy is obtained, as given in Table 5.5. Substituting these values in equations (3.23) and (3.25), the \(W^k\) parameters for Mn-Zn systems are obtained, as shown in Table 5.5. Value of \(\chi\) is taken as 0.82 (See Section 5.6.4).

5.6.3 System Cu-Mn

For the FCC Cu\(_3\)Mn alloy, the critical temperature of ordering is reported to be 450°C, i.e. 723°K\(^{(110)}\). However, an ordering temperature is difficult to establish unambiguously because of a miscibility gap at about that temperature\(^{(111)}\). As in the case of Cu\(_3\)Zn, it has been observed that there exists only short-range ordering below 400°C, i.e. 675°K, and annealing at lower temperatures indicates only attainment of equilibrium SRO\(^{(112, 113)}\). The existence of a positive heat of formation indicates the possibility that the parameters \(W^{(1)}\) and \(W^{(2)}\) may both be negative. Even though this does not preclude the fact that there could be an ordering reaction with a positive value of \(T_c\)\(^{(92)}\) as it is likely to be very low, it is assumed to be equal to 0°K for the alloy Cu\(_3\)Mn. Now utilizing the enthalpy of formation value from Ref.No.107, we get the values of \(W^{(1)}\) and \(W^{(2)}\) for Cu-Mn system as shown in Table 5.5. Value of \(\chi\) is taken as 0.82 (See following section).
5.6.4 Correction Factor $\chi$ for FCC Cu-Zn, Mn-Zn and Cu-Mn Alloys

As already mentioned in section 3.5.2 the correction factor $\chi$ for FCC alloys lies in the interval $0.5 \leq \chi \leq 0.9$ and a precise value cannot be ascribed to it even if both the informations concerning enthalpy of formation and the critical ordering temperature are known accurately because of the absence of CV results that have used both $W^{(2)}$ and $W^{(1)}$ parameters in their calculation. Unless a plot of $\chi$ vs. $W^{(2)}/W^{(1)}$. Similar to the one obtained for the BCC phase (Fig. 3.5) is available it is very difficult to get an accurate value of $W^{(2)}$ and $W^{(1)}$ for the FCC alloys. Taking into account the approximations involved in arriving at the enthalpy of formation and ordering temperature estimates in the Cu-Zn, Mn-Zn and Cu-Mn systems, the only way left open is to use the criterion that the free energy vs. temperature curves obtained using a particular set of $W^{(1)}$, $W^{(2)}$ values should reflect the expected smooth transition from ordered to disordered state in these alloys. Several values of $\chi$ were chosen in the interval $0.5 \leq \chi \leq 0.9$ and the resulting sets of $W^{(1)}$ and $W^{(2)}$ values were used to obtain the different free energy vs. temperature plots for each system. It was found that only the value $\chi = 0.82$ yielded $W^{(1)}$ and $W^{(2)}$ values that satisfied the requirement that the transition from ordered to disordered state be a smooth one. Consequently, a value of $\chi = 0.82$ was chosen for the FCC alloys of Cu-Zn, Mn-Zn and Cu-Mn systems.
5.7 ENTROPY CHANGE AND ELASTIC STORED ENERGY CALCULATIONS FROM STRESS-STRAIN AND CALORIMETRIC DATA

5.7.1 $\Delta S$ Calculation from stress-strain data

It is generally assumed that the entropy change $\Delta S$ accompanying a martensitic transition can be measured from the stress dependence of the transformation temperature, and investigations with Au-Cd\(^{(114)}\) and In-Tl\(^{(115)}\) systems, indeed, have shown that the critical shear stress $\sigma_M$ to induce the martensite is linearly dependent on $M_B(\sigma_M)$, and that the heat of formation calculated from $\Delta S$ agrees well with the value obtained by calorimetry. Ahlers and Arnedo have shown that in single crystals of Cu-Zn alloys, with Zn concentration in the range 39.2 to 40.4, the principal habit variant that is induced by stresses is the one with the highest shear component\(^{(33)}\). The shear stress component is $\tau_M = \sigma_M \mu_M$

where $\mu_M$ is the Schmidt factor. Within experimental error, $\frac{d\tau_M}{dM_S}$ has been shown to be independent of crystal orientation and concentration. The entropy change, then, is calculated from $\frac{d\tau_M}{dM_S}$ using the Clausius-Clapeyron equation $\Delta S = \gamma \frac{d\tau_M}{dM_S}$ where $'\gamma'$ is the amount of martensite shear. $\gamma$ is obtained from theory. It depends very little on zinc concentration, and is $\gamma = 0.17$ for 40\% - zinc - Cu alloy\(^{(33)}\).

Assuming the same value of $\gamma = 0.17$ and a Schmidt factor of 0.5 for polycrystalline specimens, the entropy change has been calculated for the Cu-Zn-Mn, as shown in Table 5.6.
<table>
<thead>
<tr>
<th>Alloy No.</th>
<th>( \frac{d\Phi_m}{d T_m} ) kg/mm(^2) (\Delta S^P + M) J/mole K</th>
<th>( \Delta S^P + M) kg/mm(^2) (\Delta T_m ) K</th>
<th>( \Delta S^P + M) kg/mm(^2) (\Delta T_m ) K</th>
<th>( \Delta S^P + M) kg/mm(^2) (\Delta T_m ) K</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.096 ± 0.004</td>
<td>1.30</td>
<td>1.02</td>
<td>&quot;</td>
</tr>
<tr>
<td>A5</td>
<td>0.096 ± 0.004</td>
<td>1.30</td>
<td>1.02</td>
<td>&quot;</td>
</tr>
<tr>
<td>A6</td>
<td>0.190</td>
<td>0.016</td>
<td>0.013</td>
<td>&quot;</td>
</tr>
<tr>
<td>A7</td>
<td>0.133</td>
<td>0.004</td>
<td>0.001</td>
<td>&quot;</td>
</tr>
<tr>
<td>A9</td>
<td>0.137</td>
<td>0.089</td>
<td>0.047</td>
<td>&quot;</td>
</tr>
<tr>
<td>A10</td>
<td>0.139</td>
<td>0.086</td>
<td>0.047</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

Data from Reference 33.

As quenched.

Given flash-heating at 200°C and quenched at 200°C flash-heating.

Aged at 100°C after 200°C flash-heating.
5.7.2 Stored energy calculation from calorimetric data

It has been shown theoretically by Cohen and Olson (9) that in thermo-elastic martensitic transitions the equilibrium situation is well described by the following equation:

\[ \Delta G_{ch} + 2 \Delta g_{el} = 0 \]  \( \ldots (5.4) \)

where \( \Delta G_{ch} \) = chemical free energy difference between martensite and parent phase;

\( \Delta g_{el} \) = elastic strain energy.

\( \Delta G_{ch} \) is negative below \( T_o \), the theoretical transition temperature. Assuming this relationship to be valid, Nakanishi et al (71) have calculated the stored strain energy in the following manner: Since the above balance exists at \( M_f \), the following conditions may be allowed:

\[ \Delta G_{ch} = 0 \]  at \( T_o \)

\[ \Delta G_{ch} = \Delta S_o (T_o - M_s) \]  at \( M_s \)

\[ \Delta G_{ch} = \Delta S_o (T_o - M_f) \]  at \( M_f \)

Here, \( \Delta S_o \) signifies the entropy change at \( T_o \) and is equal to \( \Delta H_o / T_o \). The enthalpy \( \Delta H_o \) may be assumed to be of the form:

\[ \Delta H_o = | \Delta H_{cooling} | + \Delta g_{el} \]

where \( | \Delta H_{cooling} | \) + real heat dissipated in the region

\( M_s \) to \( M_f \) = heat absorbed in the region

\( A_s \) to \( A_f \).
TABLE 5.7

$\Delta H^{M\rightarrow P}$ and $\Delta S^{M\rightarrow P}$ Values from DSC Experiments

<table>
<thead>
<tr>
<th>Alloy Composition (in at.%)</th>
<th>$\Delta H^{M\rightarrow P}$ J/mol</th>
<th>$\Delta G_{el}$ J/mol</th>
<th>$\Delta S^{M\rightarrow P}$ J/mol K</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu 38.5 Mn 0</td>
<td>250</td>
<td>24</td>
<td>1.18</td>
<td>From Reference 33.</td>
</tr>
<tr>
<td>Cu 38.0 Mn 0.5</td>
<td>160 -190</td>
<td>19 -21</td>
<td>0.86-0.96</td>
<td>As quenched and given requenching treatment from 200°C.</td>
</tr>
<tr>
<td>Cu 37.5 Mn 1.0</td>
<td>142 -159</td>
<td>17 -18</td>
<td>0.77-0.82</td>
<td>As quenched and given requenching treatment from 200°C.</td>
</tr>
</tbody>
</table>
82

\[ \text{At } M_f \frac{[ \Delta H_{\text{cooling}} + \Delta g_{el} ]}{T_o} (T_o - M_f) = 2 \Delta g_{el} \]

\[ \therefore \Delta g_{el} = \frac{[ \Delta H_{\text{cooling}} ]}{2 T_o - \Delta T} \times \Delta T \]

\[ \text{...(5.5)} \]

where \( \Delta T = T_o - M_f \)

As regards assigning the value of \( T_o \), the choice is between \( M_s \) and \( A_f \) since the hysteresis is quite small. Cohen and Olson \(^{(9)}\) have again indicated that \( T_o \) is likely to be nearer to \( A_f \) than to \( M_s \). Assuming \( T_o \) to be equal to \( A_f \), the values of stored energy and the entropy of transformation for the alloys calorimetrically examined are calculated and given in Table 5.7.

5.8 FREE ENERGY CALCULATIONS

The various chemical contributions to the free energy expression are the pure element energy, the mixing energy, the order energy, and the entropy terms. Each of these terms is calculated for each alloy, as described below.

5.8.1 Pure element and mixing energy terms

The stable crystal structure at \( ^0K \) of the elements copper, zinc, and manganese are FCC, HCP, and complex cubic, respectively. When considering the BCC or FCC phases, the appropriate conversion of the elements to the phase in question is performed first. The pure element contribution to the alloy is then obtained by multiplying each element contribution
by their respective concentrations and summing up. As regards the mixing energy term, it can be seen from the free energy expressions that this term is calculated easily once the values of $W^{(1)}$ and $W^{(2)}$ and the concentration of the different elements in the alloy is known.

5.8.2 Ordering energy and entropy terms

These terms are calculated when $W^{(1)}$ and $W^{(2)}$ values, along with the equilibrium order parameters at every temperature considered, are known. Theoretically, it is possible to calculate the equilibrium order parameters at every temperature for binary and ternary alloys by solving the transcendental equations resulting from the minimum free energy requirements. This is comparatively easier in binary alloys than in ternary alloys. For the ternaries, the polynomial approximation method discussed in Chapter 3 is more suitable, and much simpler.

5.8.3 Electronic, defect and stored energy terms

Apart from the chemical contributions to the free energies there are other terms arising from electronic origins, defects and stored lattice energies. In the ensuing calculations the electronic contributions have been taken into account as 'additional term' and its significance is discussed in Chapter 6. The stored energy term comprises mainly of stored elastic energy because of the thermoelastic nature of the martensite and is of the order of $\approx 20$J/mol in Cu-Zn based alloys (see Section 5.7.2). The defect contribution is mainly from stacking faults and is not likely to exceed $\approx 20$J/mol$^{(33)}$. Since the stored energy and the defect terms
together account for only a minor part of the total free energy change involved; these have not been taken into account explicitly in arriving at the free energy curves.

5.8.4 Free energy calculations for Cu-Zn binary and Cu-Zn-Mn ternary alloys

The free energy variation with temperature for the two crystal structures BCC and FCC for three alloy compositions 60 at.% Cu/40 at.% Zn, 61.5 at.% Cu/38.5 at.% Zn, and 63 at.% Cu/37 at.% Zn are calculated by the rigorous and polynomial approximation methods. Tables 5.8 to 5.13 list the pertinent details of the two types of calculations for the three alloys. The free energy plots for all the three alloys obtained by both the methods are given in Figs. 5.4 to 5.9. The free energy vs temperature plots for the BCC and FCC structures of the ternary alloys 61.5 Cu/37.5 Zn/1.0 Mn (at. %), 60.0 Cu/35.0 Zn/5.0 Mn (at. %) and 60.0 Cu/30.0 Zn/10.0 Mn (at. %) obtained by making use of the polynomial approach are given in Figs. 5.10 to 5.12. The pertinent details of the calculations are given in Tables 5.14 to 5.16. The lattice stability values for Mn have been estimated from Fig. 3.3.
<table>
<thead>
<tr>
<th>$T$ (°K)</th>
<th>$0$</th>
<th>$100$</th>
<th>$200$</th>
<th>$300$</th>
<th>$400$</th>
<th>$500$</th>
<th>$600$</th>
<th>$700$</th>
<th>$800$</th>
<th>$900$</th>
<th>$1000$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$u_0$</td>
<td>$736 - 0.876T$</td>
<td>$736 - 0.876T$</td>
<td>$736 - 0.876T$</td>
<td>$736 - 0.876T$</td>
<td>$736 - 0.876T$</td>
<td>$736 - 0.876T$</td>
<td>$736 - 0.876T$</td>
<td>$736 - 0.876T$</td>
<td>$736 - 0.876T$</td>
<td>$736 - 0.876T$</td>
<td>$736 - 0.876T$</td>
</tr>
<tr>
<td>$\Delta G_{\text{ord}}$</td>
<td>$-16646 x^2 + 3323 y^2 - T S_{\text{ord}}$ BCC J/mol</td>
<td>$-16646 x^2 + 3323 y^2 - T S_{\text{ord}}$ BCC J/mol</td>
<td>$-16646 x^2 + 3323 y^2 - T S_{\text{ord}}$ BCC J/mol</td>
<td>$-16646 x^2 + 3323 y^2 - T S_{\text{ord}}$ BCC J/mol</td>
<td>$-16646 x^2 + 3323 y^2 - T S_{\text{ord}}$ BCC J/mol</td>
<td>$-16646 x^2 + 3323 y^2 - T S_{\text{ord}}$ BCC J/mol</td>
<td>$-16646 x^2 + 3323 y^2 - T S_{\text{ord}}$ BCC J/mol</td>
<td>$-16646 x^2 + 3323 y^2 - T S_{\text{ord}}$ BCC J/mol</td>
<td>$-16646 x^2 + 3323 y^2 - T S_{\text{ord}}$ BCC J/mol</td>
<td>$-16646 x^2 + 3323 y^2 - T S_{\text{ord}}$ BCC J/mol</td>
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</tr>
<tr>
<td>$\Delta G_{\text{mix}}$</td>
<td>$-8338$</td>
<td>$-8338$</td>
<td>$-8338$</td>
<td>$-8338$</td>
<td>$-8338$</td>
<td>$-8338$</td>
<td>$-8338$</td>
<td>$-8338$</td>
<td>$-8338$</td>
<td>$-8338$</td>
<td>$-8338$</td>
</tr>
</tbody>
</table>
TABLE 5.9

VARIATIONS OF ORDERING PARAMETERS AND THE TOTAL FREE ENERGY WITH T IN 61.5/38.5 BRASS
(RIGOROUS METHOD) (FIG.5.5)

<table>
<thead>
<tr>
<th>B C C</th>
<th>FCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U_0 = 4966-2.51 T \text{ J/mol} ; \Delta G_{\text{mix}}^{\text{ord}} = -9934 \text{ J/mol}$; $\Delta G_{\text{BCC}}^{\text{ord}} = -(18127 x^2 + 5957 y^2) - TS_{\text{BCC}}^{\text{ord}} \text{ J/mol}$</td>
<td>$U_0 = 708 - 0.64 T \text{ J/mol} ; \Delta G_{\text{mix}}^{\text{ord}} = -8226 \text{ J/mol};$ $\Delta G_{\text{FCC}}^{\text{ord}} = -(6646 x^2 + 3323 y^2) - TS_{\text{FCC}}^{\text{ord}} \text{ J/mol}$ Additional term = + 440 J/mol.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>Ordering parameters</th>
<th>$S_{\text{BCC}}^{\text{ord}} \text{ J/mol/K}$</th>
<th>Ordering enthalpy</th>
<th>Total $\Delta G_{\text{BCC}} \text{ J/mol}$</th>
<th>T (°K)</th>
<th>Ordering parameters</th>
<th>$S_{\text{FCC}}^{\text{ord}} \text{ J/mol/K}$</th>
<th>Ordering enthalpy</th>
<th>Total $\Delta G_{\text{FCC}} \text{ J/mol}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.385 0.230</td>
<td>1.43</td>
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<td>-7970</td>
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<td>0.385 0.230</td>
<td>1.43</td>
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<td>T (°K)</td>
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<td>Ordering enthalpy</td>
<td>Total ΔG^BCC</td>
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<td>-11940</td>
<td>900</td>
<td>0 0</td>
<td>5.47</td>
<td>0</td>
<td>-12450</td>
</tr>
<tr>
<td>1000</td>
<td>0 0</td>
<td>5.47</td>
<td>0</td>
<td>-12800</td>
<td>1000</td>
<td>0 0</td>
<td>5.47</td>
<td>0</td>
<td>-13100</td>
</tr>
<tr>
<td>Structure</td>
<td>Order parameters</td>
<td>(S_{(0K)}) J/mol/K</td>
<td>(\Delta H_{(0K)}) J/mol</td>
<td>Input data to polynomial</td>
<td>Structure</td>
<td>Order parameters</td>
<td>(S_{(0K)}) J/mol/K</td>
<td>(\Delta H_{(0K)}) J/mol</td>
<td>Input data to polynomial</td>
</tr>
<tr>
<td>-----------</td>
<td>------------------</td>
<td>-----------------------</td>
<td>--------------------------</td>
<td>--------------------------</td>
<td>-----------</td>
<td>------------------</td>
<td>-----------------------</td>
<td>--------------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>A2</td>
<td>0 0</td>
<td>5.59</td>
<td>(\Delta H^{A2+B2} = -2900) J/mol</td>
<td>A1</td>
<td>0 0</td>
<td>5.59</td>
<td>(\Delta H^{Al+Ll_2} = 1196) J/mol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B2</td>
<td>0.4 0</td>
<td>2.08</td>
<td>(A2 + B2) (S - S) = 3.51 J/mol</td>
<td></td>
<td>(Ll_2)</td>
<td>0.4 0.2</td>
<td>1.4</td>
<td>(\Delta H^{Al+Ll_2} = 1196) J/mol</td>
<td></td>
</tr>
<tr>
<td>DO_3</td>
<td>0.4 0.2</td>
<td>1.4</td>
<td>(B2 + DO_3) = 238 J/mol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(U_0 = (4916 - 2.51T)\) J/mole; \(\Delta g^{mix} = -10070\) J/mol.

\(U_0 = (736 - 0.67T)\) J/mol; \(\Delta g^{mix} = -8338\) J/mol; Additional term = +400 J/mol.
<table>
<thead>
<tr>
<th>Structure</th>
<th>Order parameters</th>
<th>S ((0^\circ K)) J/mol/k</th>
<th>(\Delta H) ((0^\circ K)) J/mol</th>
<th>Input data to polynomial</th>
<th>Structure</th>
<th>Order parameters</th>
<th>S ((0^\circ K)) J/mol/k</th>
<th>(\Delta H) ((0^\circ K)) J/mol</th>
<th>Input data to polynomial</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2</td>
<td>0 0</td>
<td>5.54</td>
<td>0</td>
<td>(\Delta H^{A2+B2} = -2683) J/mol ((0^\circ K))</td>
<td>A1</td>
<td>0 0</td>
<td>5.54</td>
<td>0</td>
<td>(\Delta H^{A1+L1_2} = -1161) J/mol ((0^\circ K))</td>
</tr>
<tr>
<td>B2</td>
<td>0.385 0</td>
<td>2.24</td>
<td>A2 + B2 -2683</td>
<td>(S-S) = 3.3 ((0^\circ K)) J/mol/k (T_x(A2/B2) = 703^\circ K)</td>
<td>L1_2</td>
<td>0.385 0.23</td>
<td>1.43</td>
<td>(\Delta H^{B2+DO_3} = -316) J/mol ((0^\circ K))</td>
<td>(\Delta H^{Al+L1_2} = -1161) J/mol ((0^\circ K)) (T_x(B2/DO_3) = 341^\circ K)</td>
</tr>
</tbody>
</table>

\(U_o = (4966 - 2.51T)\) J/mole; \(\Delta G^{mix} = -9933\) J/mol.

\(U_o = (708 - 0.64T)\) J/mole; \(\Delta G^{mix} = -8226\) J/mol; Additional term = +500 J/mol.
**TABLE 5.13**  
**VARIATION OF TOTAL FREE ENERGY WITH T IN 63/37 BRASS (POLYNOMIAL APPROXIMATION METHOD)**  
*(FIG. 5.9)*

<table>
<thead>
<tr>
<th>BCC</th>
<th>FCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>( U_0 = (5018 - 2.51T) \text{ J/mole} )</td>
<td>( U_0 = (681 - 0.62T) \text{ J/mol} )</td>
</tr>
<tr>
<td>( \Delta G_{\text{mix}} = -9779 \text{ J/mol} )</td>
<td>( \Delta G_{\text{mix}} = -8098 \text{ J/mol}; ) Additional term = +700 J/mol</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Structure</th>
<th>Order parameters</th>
<th>( S ) (( ^O\text{K} ))</th>
<th>( \Delta H ) (( ^O\text{K} ))</th>
<th>Input data to polynomial</th>
<th>Structure</th>
<th>Order parameters</th>
<th>( S ) (( ^O\text{K} ))</th>
<th>( \Delta H ) (( ^O\text{K} ))</th>
<th>Input data to polynomial</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2</td>
<td>0 0</td>
<td>5.47</td>
<td>0</td>
<td>( \Delta H^{A2\rightarrow B2} = -2482 \text{ J/mol} ) (( ^O\text{K} ))</td>
<td>A1</td>
<td>0 0</td>
<td>5.47</td>
<td>0</td>
<td>( \Delta H^{Al\rightarrow Ll_2} = -1135 \text{ J/mol} ) (( ^O\text{K} ))</td>
</tr>
<tr>
<td>B2</td>
<td>0.37 0</td>
<td>2.38</td>
<td>A2 ( \rightarrow ) B2</td>
<td>( \Delta H^{B2\rightarrow DO_3} = -403 \text{ J/mol} ) (( ^O\text{K} ))</td>
<td>Ll_2</td>
<td>0.37 0.26</td>
<td>1.44</td>
<td>T_c (Al/Ll_2) = 306 ( ^O\text{K} )</td>
<td></td>
</tr>
<tr>
<td>D0_3</td>
<td>0.37 0.26</td>
<td>1.44</td>
<td>B2 ( \rightarrow ) DO_3</td>
<td>( \Delta H^{B2\rightarrow DO_3} = -403 \text{ J/mol} ) (( ^O\text{K} ))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**TABLE 5.14**

VARIATION OF TOTAL FREE ENERGY WITH $T$ IN 61.5 Cu/37.5 Zn/1.0 Mn ALLOY

(POLYNOMIAL APPROXIMATION METHOD) (FIG. 5.10)

<table>
<thead>
<tr>
<th>Structure</th>
<th>Order parameters</th>
<th>$S$ (K) J/mol</th>
<th>$\Delta H$ (K) J/mol</th>
<th>Input data to polynomial</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2</td>
<td>0.385 0.230 -0.375 -0.250</td>
<td>0.173</td>
<td>-349</td>
<td></td>
</tr>
<tr>
<td>B2</td>
<td>0.385 0.230 -0.375 -0.250</td>
<td>0.173</td>
<td>-349</td>
<td></td>
</tr>
<tr>
<td>L2</td>
<td>0.385 0.230 -0.375 -0.250</td>
<td>0.173</td>
<td>-349</td>
<td></td>
</tr>
</tbody>
</table>

**BCC**

$U_0 = (4971 - 2.49 T)$ J/mol

$\Delta G_{mix} = -9870$ J/mol

**FCC**

$U_0 = (735 - 0.63T)$ J/mol

$\Delta G_{mix} = -8199$ J/mol

Additional term = + 600 J/mol.
<table>
<thead>
<tr>
<th>Structure</th>
<th>Order parameters</th>
<th>$S$</th>
<th>$\Delta H$</th>
<th>$\Delta G_{\text{mix}}$</th>
<th>Input data to polynomial</th>
<th>Structure</th>
<th>Order parameters</th>
<th>$S$</th>
<th>$\Delta H$</th>
<th>Input data to polynomial</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2</td>
<td>0 0 0 0</td>
<td>6.84</td>
<td>$\Delta H = -2419$</td>
<td>$\Delta G_{\text{mix}} = -9753$</td>
<td></td>
<td>A1</td>
<td>0 0 0 0</td>
<td>6.84</td>
<td>$\Delta H = -1091$</td>
<td></td>
</tr>
<tr>
<td>B2</td>
<td>0.40 0 -0.35 0</td>
<td>3.33</td>
<td>$\Delta H = 3.51$</td>
<td>$T_A^{A2/B2} = 638^\circ$K</td>
<td></td>
<td>L1</td>
<td>0.40 0.20 -0.35 -0.30</td>
<td>2.19</td>
<td>$\Delta H = 377$</td>
<td>$T_c^{(Al/Li_2)} = 350^\circ$K</td>
</tr>
<tr>
<td>L1$_2$</td>
<td>0.40 0.20 -0.35 -0.30</td>
<td>2.19</td>
<td>$\Delta H = 377$</td>
<td>$T_c^{(B2/L1_2)} = 376^\circ$K</td>
<td></td>
<td>L1$_2$</td>
<td>0.40 0.20 -0.35 -0.30</td>
<td>2.19</td>
<td>$\Delta H = 377$</td>
<td>$T_c^{(B2/L1_2)} = 376^\circ$K</td>
</tr>
</tbody>
</table>
### Table 5.16

**VARIATION OF TOTAL FREE ENERGY WITH T IN 60 Cu/30 Zn/10 Mn ALLOY**

(POLYNOMIAL APPROXIMATION METHOD) (FIG. 5.12)

<table>
<thead>
<tr>
<th>Structure</th>
<th>Order parameters</th>
<th>S (o°C) J/mol/K</th>
<th>ΔH (o°C) J/mol</th>
<th>Input data to polynomial</th>
<th>Structure</th>
<th>Order parameters</th>
<th>S (o°C) J/mol/K</th>
<th>ΔH (o°C) J/mol</th>
<th>Input data to polynomial</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>FCC</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>A2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>7.46</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td>7.46</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B2</td>
<td>0.40</td>
<td>0</td>
<td>-0.30</td>
<td>0</td>
<td>B2</td>
<td>0.40</td>
<td>0</td>
<td>-0.30</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>3.95</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td>3.95</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>L2₁</td>
<td>0.40</td>
<td>0.20</td>
<td>-0.30</td>
<td>-0.40</td>
<td>L2₁</td>
<td>0.40</td>
<td>0.20</td>
<td>-0.30</td>
<td>-0.40</td>
</tr>
<tr>
<td></td>
<td>2.19</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td>2.19</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Additional terms:**
- B2 + L2₁: \( \Delta H = -557 \text{ J/mol} \)
- \( T_y(B2/L2₁) = 416^0 \text{ K} \)
- A1 + L2₂: \( \Delta H = -1217 \text{ J/mol} \)
- \( T_c(A1/L2₂) = 365^0 \text{ K} \)

**Equations:**
- \( U_o = (4966 - 2.25T) \text{ J/mol} \)
- \( \Delta G^{\text{mix}} = -9313 \text{ J/mol} \)
- \( U_o = (1002 - 0.5T) \text{ J/mol} \)
- \( \Delta G^{\text{mix}} = -7366 \text{ J/mol} \)
- Additional term = + 600 J/mol.
FIG. 5.4: FCC and BCC free energy curves for composition 60 Cu/40 Zn (at.%) (Rigorous method).
FIG. 5.5: FCC and BCC free energy curves for composition 61.5 Cu/38.5 Zn (at.%) (Rigorous method).
FIG. 5.6: FCC and BCC free energy curves for composition 63 Cu/37 Zn (at.%) (Rigorous method).
FIG. 5.7: FCC and BCC free energy curves for composition 60 Cu/40 Zn (at.%) (Polynomial approximation).
FIG. 5.8: FCC and BCC free energy curves for composition 61.5 Cu/38.5 Zn (at.%) (Polynomial approximation).
FIG. 5.9: FCC and BCC free energy curves for composition 63 Cu/37 Zn (at.%) (Polynomial approximation method).
FIG. 5.10: FCC and BCC free energy curves for composition 61.5 Cu/37.5 Zn/1.0 Mn (at.%) (polynomial approximation method).
FIG. 5.11: FCC and BCC free energy curves for composition 60 Cu/35 Zn/5 Mn (at.%) (polynomial approximation method).
FIG. 5.12: FCC and BCC free energy curves for composition 60 Cu/30 Zn/10 Mn (at.%) (polynomial approximation method).
DISCUSSION

6.1 INTRODUCTION

In this Chapter the experimental results and the calculations presented in the last two chapters will be discussed. The martensitic transformation characteristics for quenched and aged Cu-Zn-Mn alloys are analysed with respect to the known behaviour of Cu-Zn and Cu-Zn-X systems in the first three sections, highlighting the role of order. In the next section, the ordering characteristics of the $\beta$-phase are discussed, which is followed by an analysis of the free energy curves obtained on the basis of BWG formalism. It will then be shown that there exists a good correlation between theoretical prediction and experimental results.

6.2 EFFECT OF MANGANESE ON $M_s$ TEMPERATURE

The ternary isothermal phase diagrams for the system Cu-Zn-Mn (Fig.2.23) and the quasi-binary sections presented in (Fig.2.24) indicate the possibility that $\beta$-phase could be quenched at room temperature in Cu-Zn-Mn alloys with a copper content of 60%, and manganese up to 15%. However, in the present investigations, it was noticed that in the 60% copper alloys, once the Mn content exceeded 10%, the tendency for massive transformation was very pronounced, and a brine quench was not enough to arrest this transformation in 1 mm thick specimens. Such a tendency for massive transformation, which
is enhanced on replacing zinc with Mn in 60% copper alloys, has already been reported\(^{(56)}\) and is confirmed here. All the alloys designated by 'A' in Table 4.1 retain the \(\beta\)-phase on quenching from high temperature, and undergo a martensitic transformation on cooling. As can be seen from Table 4.2, the effect of manganese is to decrease the \(M_s\) temperature. Pops\(^{(116)}\) has shown that the \(M_s\) temperature in Cu-Zn-X alloys can be expressed as an additive function of various third element contributions. Using this formulation, the \(M_s\) for Cu-Zn-Mn alloys is given by:

\[
M_s(\circ K) = 3280 - 80x_{Zn} - (80 \pm 2)x_{Mn} \quad \text{...(6.1)}
\]

where \(x_{Zn}\) and \(x_{Mn}\) refer to atomic percentages of zinc and manganese, respectively. This seems to fit the experimental results up to about \(\approx 8\) at.\%. Above this value, the effect of manganese in lowering the \(M_s\) is less than that of zinc. Hume, Rothery and Haworth\(^{(117)}\) have suggested that the effect of manganese on the stability of the \(\alpha\) and \(\beta\) phases is the same as that of zinc, and have assigned the same electron contribution from manganese in Cu-Zn-Mn alloys. Assuming such an equivalence, the experimental \(M_s\) values and the calculated \(M_s\) values (using Pop's formula) can also be plotted on an \(\epsilon/a\) basis (Fig.6.1). It can be seen that the \(M_s\) values of Cu-Zn-Mn alloys appear to be consistently lower than those of Cu-Zn up to an \(\epsilon/a\) value of 1.496.

The results of the tensile tests show that Cu-Zn-Mn alloys exhibit pseudo-elastic behaviour similar to Cu-Zn, Cu-Zn-Si, and Cu-Zn-Sn alloys above \(M_s\), and a shape memory
FIG. 6.1: Variation of $M_s$ with Manganese content and comparison with the effect of Zinc on an electron concentration basis.
effect below $M_s$. The maximum recoverable strain in poly-crystalline specimens is $\approx 5\%$. This is lower than the 15\% recovery observed in Cu-Zn-Si and Cu-Zn-Sn alloys, but is of the same order of magnitude as in Ag-Cd alloys$^{118}$. The $M_s$ values obtained by extrapolation to zero stress are quite close to the values obtained by resistance measurement methods.

Arnedo and Ahlers$^{33}$ report that the $M_s$ values obtained by such extrapolation procedure in Cu-Zn alloys corresponded to burst-type martensite, which has a lower $M_s$ value than the corresponding thermo-elastic martensite. From the agreement between the $M_s$ values obtained by resistance methods and tensile test methods in the Cu-Zn-Mn system, it appears that the stress induced martensite in the Cu-Zn-Mn system corresponds to the thermo-elastic martensite.

6.3 ENTROPY CHANGE $\Delta S^{P+M}$ OF THE MARTENSITIC TRANSFORMATION IN Cu-Zn-Mn ALLOYS

The entropy changes attendant on martensitic transformation in Cu-Zn-Mn alloys deduced from tensile test and calorimetric data are listed in Tables 5.6 and 5.7, and are compared with the $\Delta S^{P+M}$ values obtained for the systems Cu-Zn, Cu-Zn-Al, and Ag-Cu-Cd in Table 6.1.

Ahlers and Arnedo$^{33}$ report that the value of $\Delta S^{P+M}$ is independent of composition in Cu-Zn alloys. The range of values observed by them occurred even in single crystals of the same composition, and they attribute the scatter to experimental error, because there was no evidence to account for any
**TABLE 6.1**

Comparison of $\Delta S^{P+M}$ values in various systems showing thermo-elastic martensitic transformation.

<table>
<thead>
<tr>
<th>System</th>
<th>Range of $\Delta S$ J/mol/K</th>
<th>Remarks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Zn</td>
<td>1.04 - 1.33</td>
<td>Alloys in the range 38.2% to 40.7% Zn.</td>
<td>(33)</td>
</tr>
<tr>
<td>Au-Ag-Cd</td>
<td>0.8 - 1.33</td>
<td>For alloys in the range $x_{Ag} = 0 - 40$. As quenched and aged.</td>
<td>(71)</td>
</tr>
<tr>
<td>Cu-Zn-Mn</td>
<td>0.86 - 1.33</td>
<td>For alloys with Mn = 0.5 - 10%. As quenched and aged.</td>
<td>Present work</td>
</tr>
<tr>
<td>Cu-Zn-Al</td>
<td>1.49</td>
<td>For alloys with 63:6 Cu/27.4 Zn/9.0 Al.</td>
<td>Calculated from data (130)</td>
</tr>
<tr>
<td>Au-Cd&lt;sub&gt;47.5&lt;/sub&gt;</td>
<td>2.26</td>
<td>-</td>
<td>(122)</td>
</tr>
</tbody>
</table>
difference in the structure of martensite, whether thermally induced or stress induced. It has been established that the thermal martensite, the stress induced martensite, and the stabilised martensite all have the same 3R structure, and the entropy change $\Delta S^{P+M}$ is independent of heat treatment in Cu-Zn-Al alloys. Nakanishi et al.\(^{(7)}\) have reported that the range of $\Delta S^{P+M}$ values for the system Ag-Au-Cd is unaffected by composition and heat treatment. In the present work, it has now been demonstrated that the system Cu-Zn-Mn also exhibits a range of $\Delta S^{P+M}$ values which are unaffected by composition and heat treatment. The fact that the entropy change is independent of the ageing treatment confirms that in all these systems the martensite inherits the order of the $\beta$-phase.

6.4 EFFECT OF LOW TEMPERATURE AGEING

6.4.1 Changes in transformation temperatures

The transformation temperatures are increasingly affected by low temperature ageing treatments as the manganese content is raised. However, these changes are not permanent as long as the temperature-time combination excludes the bainitic transition. From Figs.4.2 to 4.5, 4.8 to 4.10, and 4.14, it can be seen that all the transformation temperatures $(M_s, A_s, A_f)$ increase with the temperature of heat treatment. The results of low temperature ageing treatment shown in Figs.4.2 and 4.8 to 4.10 are typical of the kind of changes produced. Attention will therefore be focused on the results obtained on alloys 60.8 Cu/30.0 Zn/9.2 Mn (at.%) (A9), and
60.0 Cu/30.0 Zn/10.0 Mn (at.%) (A10) which have near about the same manganese content. The resistance vs temperature traces after various periods of time at 70°C for the 60.8 Cu/30.0 Zn/9.2 Mn alloy (A9) show that the area enclosed by the transformation curve becomes progressively smaller with time of ageing. The transformation temperatures increase up to a limit and stay constant with further ageing. Long time room temperature ageing (three weeks) after such a treatment restores the original as quenched value of the transformation temperatures. When such a well annealed specimen is given a flash-heating treatment at 200°C, the Ms temperature rises considerably, and on ageing at room temperature approaches the initial value with ageing time (Fig. 4.4).

$\sigma_{T \rightarrow M}^P$ vs $T$ plots obtained from tensile tests at various temperatures on such well annealed specimens point to the same trend in Ms changes. From Fig. 4.10 it can be seen that when a specimen is given a flash-heating treatment at $\approx 200^\circ$C, a straight line plot results which, on extrapolation to zero stress, shows that the flash-heated specimen has a higher Ms value as compared to the as quenched specimen, even though it is not as high as the Ms measured with the resistance technique for a similarly treated specimen. Subsequent ageing at 100°C shifts the line upward without changing the slope. Extrapolation to zero stress gives an Ms value which is slightly lower than the as quenched value. The differences in Ms values by the two techniques is mainly due to the fact that the time elapsed between quenching and subsequent testing was much shorter ($< 1$ minute) in the resistance method, as compared to the tensile test method ($< 10$ minutes). Bearing
FIG. 6.2: Variation of $\Delta M_s$ with Manganese and Aluminium
in mind this difference in testing conditions, it is concluded that the two testing methods confirm the same trend in $M_s$ changes with low temperature ageing, namely that $M_s$ increases with temperature of ageing.

6.4.2 Role of ordering

The effect of low temperature ageing of well annealed specimens on the transformation temperature can be discussed in the light of observed structural changes in Cu-Zn $\beta$-phase alloys reported by S.G.Cupshalk and N.Brown (119) which essentially reflect disordering. They have shown that specimens quenched from below the ordering temperature $T_c$ have no antiphase domains, and subsequent reheating of the specimens to a temperature below $T_c$ appears to result in no other change except a change in the degree of long-range order. A similar situation can now be invoked to explain the observed results of low temperature ageing in the Cu-Zn-Mn alloys.

Thermodynamically the $M_s$ changes can be attributed to changes in $\Delta G_{M_s}$ and $T_o$. An $M_s$ change can result when any one of the following conditions are satisfied, namely:

a) $\Delta G_{M_s}$ and $T_o$ both change; b) $T_o$ is constant and $\Delta G_{M_s}$ changes, or c) $\Delta G_{M_s}$ is constant and $T_o$ changes. If conditions (a) or (b) are assumed to operate then an $M_s$ change should be accompanied by a change in $\Delta S^{P\rightarrow M}$ (i.e.) a change in the slope of the $\sigma^P_{T\rightarrow M}$ vs $T$ curves.

From Fig. 4.10 it can be seen that well annealed specimens do not show a slope change on flash heating to a temperature below $T_c$ (A2/B2) and subsequent low temperature ageing. This added to the fact that all the transformation temperatures shift in the same direction to the same degree leads to the conclusion that low temperature ageing shifts only $T_o$ and does not affect $\Delta G_{M_s}$. This shift in $T_o$
after different ageing treatments is now directly attributable to disordering effects. Since in all these alloys only an increase in $M_s$ is observed with temperature of ageing, it means that disordered alloys have a higher $M_s$ than the corresponding ordered alloys. This is in contrast to the situation found in Cu-Zn-Al systems where disordered alloys have a lower $M_s$ as compared to ordered alloys (Fig.6.2). This difference in responses to heat treatment in the two systems Cu-Zn-Mn and Cu-Zn-Al, as will be shown later, is due to the relative magnitudes of the ordering energies in the $\beta$- and $\alpha$-phases being different in the two systems.

6.4.3 Role of antiphase boundaries

The effect of low temperature heat treatment on as quenched specimens, as determined by tensile tests, are shown in Fig. 4.9. The $\sigma_{T}^{P-M}$ vs $T$ plots obtained for the 60 Cu/30 Zn/10 Mn (at.%) (A10) alloy in the as quenched condition and in the aged condition show that the straight line plot obtained for the as quenched specimen is altered on ageing at 100°C for an hour, to yield a curve that can be thought of as two straight lines with different slopes intersecting at a point. This feature persists even after long ageing at 100°C, the only difference being that the point of intersection of the two component straight lines is different in this case. The absence of such 'kinks' in the case of well annealed specimens given ageing treatment (Fig.4.10) suggests the possible influence of some quenched-in defects in the as quenched specimens. Cupshalk and Brown (119) have shown that, in $\beta$-brass, a large
number of non-equilibrium vacancies are created and retained on quenching from above the ordering temperature. Antiphase domain boundaries are also produced, and the excess vacancies tend to segregate to the APB's so produced. Ageing of the quenched specimen is found to result in dislocation nucleation predominantly at the APB's. Similar APB production and excess vacancy retention are quite likely in Cu-Zn-Mn alloys on quenching from above the ordering temperature $T_C$ (A2/B2). The APB's and the vacancies can be expected to play a significant role in affecting the nucleation of martensite\(^{(11)}\). The net effect of ageing after quench is the altering of the APB energy by promoting diffusion of excess vacancies, APB movements, and disordering appropriate to the ageing temperature. The plots of Fig. 4.9 corresponding to the cases of one hour and 65 hours ageing at 100°C, respectively, reflect the combined influence of all the factors mentioned acting simultaneously to change the APB energy and thereby the transformation characteristics. It can be reasonably inferred that Fig. 4.9 represents the intermediate situations before full elimination of APB\(^S\) and excess vacancies are achieved. However once ageing has proceeded to a level where all the APB\(^S\) and excess vacancies have been eliminated, subsequent low temperature ageing treatments alter only the degree of disorder the effects of which have been discussed in the previous section.
6.5 CORRELATION OF ORDERING THEORY WITH EXPERIMENT

6.5.1 General

In the calculations leading to free energy estimates in Cu-Zn and Cu-Zn-Mn systems in Chapter 5, it was tacitly assumed that in addition to the A2/B2 ordering transition, a further transition, B2 \( \rightarrow \) DO\textsubscript{3}/L\textsubscript{2\perp} should occur in both Cu-Zn binaries and the associated ternaries. The present results will now be examined to see how far they substantiate the existence of a secondary ordering reaction in the system Cu-Zn-Mn. Then the implications of the free energy analysis will be discussed.

6.5.2 Evidence for \((\text{DO}_{3}/L\textsubscript{2\perp}) \rightarrow \text{B2}\) transition in Cu-Zn and Cu-Zn-Mn alloys

The main experimental techniques that can be employed for detection of the secondary ordering transformation \((\text{DO}_{3}/L\textsubscript{2\perp}) \rightarrow \text{B2}\) are resistance measurement with temperature and differential thermal analysis. Even though, theoretically, it should be possible to detect order by X-ray diffraction, it is difficult to do so in the system Cu-Zn and Cu-Zn-Mn because of the close proximity of the atomic numbers of the components involved. The same is true for electron diffraction method, even though it is possible to utilise selected area diffraction, as has been shown by Rapacioli and Ahlers\(^{(64)}\) to substantiate in an indirect way the existence of the B2 \( \rightarrow \text{DO}_{3}/L\textsubscript{2\perp}\) transition in \(\beta\)-Cu-Zn-Al alloys originally indicated by resistance measurements. Reistometric or calorimetric investigations directed solely towards detecting the B2 \( \rightarrow \text{DO}_{3}/L\textsubscript{2\perp}\) transition in binary Cu-Zn or ternary Cu-Zn-X \(\beta\)-phases other
than Cu-Zn-Al have not been reported, even though such investigations to detect ordering changes in the corresponding α-phases have been carried out in Cu-Al and Cu-Zn systems. Warlimont et al.¹²⁰ report DSC investigations of short-range order in α-Cu-Al alloys, and their DSC traces on α-Cu-Al alloys show that the SRO destruction is associated with a typical second-order transformation trace obtainable on a DSC. Clareborough et al.¹⁰⁵ have also obtained similar second-order DSC traces for short-range order destruction in α-brasses. Figure 4.13 shows that the β-phase alloys of Cu-Zn and Cu-Zn-Mn also exhibit such traces. Since theβ-phase is completely ordered on quenching and subsequent ageing at room temperature, there is no question of SRO destruction on heating in the low temperature range. Neither is there a possibility of a bainitic reaction, since the temperature region at which the transformation is detected (80 to 150°C) is well below the bainitic transition temperature. So it seems reasonable to infer that the transformation indicated by the change in slope of the DSC trace in the β-Cu-Zn and β-Cu-Zn-Mn alloys is indeed associated with the secondary ordering transition D\(_0^3\)/L\(_2^1\)+B\(_2\). The results of resistance measurements with increasing temperature in the Cu-Zn binary alloy, reported by Hummel⁴⁵ (Fig.2.18), also show that there is an increase in resistivity by about 3% in the same temperature region, which is consistent with the interpretation of the DSC traces as due to D\(_0^3\)→B\(_2\) disordering. In this connection, it is to be observed that DSC seems to be as sensitive a method as resistance measurements for detecting such transitions in
alloys where X-ray or electron microscopic methods are made difficult by close atomic numbers of the component elements involved.

In addition to the indication of the secondary ordering transitions, the DSC traces indicate a heat evolution consequent on quenching from intermediate temperatures (Fig.4.15). The DSC traces for alloys Al, A3, and A4 show that there is an evolution of heat when a sample quenched from above B2→DO₃/L2₁ transition temperatures is reheated to above room temperature. This confirms the observation by Brown\(^{(121)}\) that it is possible to quench in some degree of disorder in Cu-Zn if the quenching temperature is in the range 100 - 350°C. The heat evolution in Cu-Zn-In alloys when such quenched-in disorder was eliminated (during subsequent heating), is of the order of 12 - 25 J/mole. It is less than \(\frac{1}{10}\)th of the estimated heat associated with DO₃→B2 transition, (see Sec.6.5.4) \(\approx 300\) J/mol (Fig.5.10-5.12), which is in marked contrast to the much larger values of heat evolution found in quenched Cu-Zn-Al alloys (50 - 150 J/mol). This is consistent with the observation that it is easier to retain a greater degree of disorder in alloys containing trivalent ions than ions of lower valency\(^{(124)}\). Since it has been established that manganese behaves like zinc in affecting the \(M_s\), it is reasonable to presume that the rapid diffusion rates in Cu-Zn are not significantly reduced by manganese addition. Because of rapid diffusion, quenching after ageing above the B3→DO₃/L2₁ transition temperature in Cu-Zn-Mn alloys does not produce markedly different structures from those produced from quenching after ageing at lower temperatures.
6.5.3 Essential features of the free energy curves

We shall first consider the free energy curves obtained by the rigorous method for the three alloys of composition 60 Cu/40 Zn, 61.5 Cu/38.5 Zn, and 63 Cu/37 Zn, respectively. The three intersection points, $T_1^o$, $T_2^o$, and $T_3^o$, correspond to the equilibrium situations $\text{FCC}^{\text{dis}} + \text{BCC}^{\text{dis}}$, $\text{FCC}^{\text{dis}} + \text{BCC}^{\text{ord}}$, and $\text{FCC}^{\text{ord}} + \text{BCC}^{\text{ord}}$, respectively. The third intersection point, $T_3^o$, can be assumed to be equal to $M_s$ since the transformation is thermo-elastic with a very low hysteresis and a low value of elastic stored energy, and the martensitic structure can be considered as FCC with stacking faults whose contribution to the free energy of FCC is not likely to be very high. The variation of the three intersection points with composition clearly reproduces both the retrograde solidus, so characteristic of these alloys, and the variation of $M_s$ with zinc content (Fig.6.3). The presence of three critical transition points clearly places severe constraints on the input data, and it is surprising that such a good fit can be obtained merely by utilising the ordering data, phase stability information, and a single additional parameter which, in the range 37 - 40% Zn, turns out to be a destabilisation of the $\alpha$-phase by $\approx 440$ J/mol. Such a value is consistent with the magnitude of expected electronic ($\Delta G_{\text{elec}}$) contributions from Brillouin Zone effects (125). Although the intersections of the free energy curves are obviously very sensitive to the entropy difference between the phases, the chosen values of $\Delta S_{\text{Cu}}^{\alpha \rightarrow \beta}(2.51 \text{ J/mol/k})$ only differs by 0.83 from Kaufman's value, and is virtually identical to the value proposed by Kulkarni (126) (2.80 J/mol/k). The free energy curves (Figs.5.8-5.9) obtained by adopting the polynomial
FIG. 6.3: Variation of equilibrium temperatures $T_1^0$, $T_2^0$, and $T_3^0$ with composition in Cu-Zn system (calculated)
approximation for the ordering energy differ from the rigorous ones in predicting the precise values of the three transition temperatures and the 'destabilisation energy' $\Delta G_{\text{elec}}$. This is because of the inherent error in the polynomial approximation mentioned in Section 3.6.4. However, this does not alter the main conclusions derived on the basis of the rigorous calculations.

The free energy curves calculated for the ternary alloys by adopting the polynomial approximation show the same features as the binaries, i.e. there are three intersections corresponding to three transitions at $T_1^0$, $T_2^0$, and $T_3^0$ ($M_2$) respectively. Since the experimental quasi-binary sections of Cu-Zn-Mn up to 10% Mn show (Fig. 2.24) essentially the same retrograde solubility characteristic of the binary Cu-Zn phase diagram, the prediction of three transition temperatures by the present calculations in the ternary alloys confirms the validity of this approach and justifies the assumptions made. The value of the destabilising energy ($\Delta G_{\text{elec}}$) is higher than the corresponding value for the binary alloy (600 J/mol), but is still within the range of the expected electronic contributions from Brillouin Zone effects$^{(125)}$.

Two possible sources for such a difference are:

(1) Inherent error in polynomial approximation.

(2) Electronic contribution from manganese may not be equal to that of zinc.

It is difficult to separate these effects at the present stage.
6.5.4 Prediction from the free energy curves of the effect of low temperature ageing

It has already been suggested that the $M_s$ changes observed on low temperature ageing of the $\beta$-phase can be associated with disordering in the $\beta$-phase. A specific example of alloy 60 Cu/40 Zn, aged at 500°C and quenched to room temperature, will be considered. Assuming that the disorder corresponding to 500°C is present on quenching, the BCC free energy plot has been obtained and is shown in Fig.6.4. Since this disorder is inherited by the martensite on subsequent cooling, the free energy curve for the FCC phase reflects this, and is shown in the same figure. The first intersection of the BCC and FCC curves corresponds to $M_s$. The $M_s$ values so obtained for different quenching temperatures are plotted in Fig.6.5. It can be seen that substantial increases in $M_s$ with temperature of ageing are predicted, much larger than those observed experimentally, e.g., for the 60 Cu/40 Zn alloy, the rise predicted is by about 190°C when quenched from 475°C, as compared to the actual experimental value of ~12°C. This is actually to be expected, since we have already seen that the disorder induced at 475°C is not completely retained (see Section 6.5.2). This small amount of retained disorder is consistent with the corresponding small value of $\Delta M_s$.

The situation remains more or less the same in ternary Cu-Zn-Mn alloys, where the retained disorder on quenching is of a similar order and the $M_s$ rises, as determined by DSC, are also similar. Now the question arises as to whether parent phase disordering will always result in $M_s$ elevation. Under
FIG. 6.4: FCC and BCC free energy curves for composition 60 Cu/40 Zn corresponding to retained disorder from 500°K.
FIG. 6.5: $M_s$ variation with quenching temperature for composition 60 Cu/40 Zn assuming retained disorder corresponding to the quenching temperature.
the conditions where the product phase always inherits the order of the parent phase, any disordering of the β-phase will result in a rise of $M_S$ provided the ordering energy of the α-phase is smaller than the ordering energy of the β-phase. Table 6.2 shows the calculated ordering energies of β- and α-phases at $0^\circ$K in one Cu-Zn and one Cu-Zn-Mn alloy. It can be seen that in both cases the ordering energy for the α-phase is lower than the corresponding ordering energy for the β-phase, and so it is not surprising that any disorder retained in the β-phase as a result of low temperature ageing treatment results in elevating the $M_S$ in both Cu-Zn and Cu-Zn-Mn alloys.

**TABLE 6.2**

Comparison of Ordering Energies.

<table>
<thead>
<tr>
<th>Composition (in at.%)</th>
<th>$\Delta G^{\text{dis} \rightarrow \text{ord}}$ of β-phase (J/mol)</th>
<th>$\Delta G^{\text{dis} \rightarrow \text{ord}}$ of α-phase (J/mol)</th>
</tr>
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<tbody>
<tr>
<td>60 Cu/40 Zn</td>
<td>-3138</td>
<td>-1196</td>
</tr>
<tr>
<td>60 Cu/30 Zn/10 Mn</td>
<td>-2577</td>
<td>-1217</td>
</tr>
</tbody>
</table>

In Cu-Zn-Al alloys, where the product phase also inherits the order of the parent phase, $M_S$ is depressed by disordering the parent phase. This should mean that the ordering energy of the α-phase in Cu-Zn-Al alloys must be greater than that of the corresponding β-phase (see the recently published work of Ahlers and Rapacioli\(^{129}\)) or some similar effect due to changes
of the electronic contribution must occur as a result of ordering. A similar situation probably prevails in Au-Ag-Cd and Cu-Al-Ni alloys that show comparable ageing behaviour to Cu-Zn-Al. Because of lower diffusion rates, quenching from higher temperature results in higher retention of disorder in these systems, as compared to Cu-Zn or Cu-Zn-Mn. On ageing the parent phase at low temperature, the order corresponding to the ageing temperature is restored, raising the $M_s$. According to the free energy curve, there should be no qualitative difference between disorder in the $\text{DO}_3/L2_1$ lattice and subsequent further disordering of the $\text{B}2\text{lattice}$. The full effect of $\beta$-disorder is difficult to study because rapid $\alpha$-phase precipitation occurs at higher temperatures.

### 6.6 SIGNIFICANCE OF THE ASSUMED ENERGY PARAMETERS

The agreement between the experimentally observed and predicted behaviour of the martensitic transformation in the Cu-Zn and Cu-Zn-Mn systems on the basis of the free energy calculations can be taken to justify the several assumptions made regarding the ordering temperatures (see Section 5.5 and 5.6) and the heats of formation shown in Table 6.3.

<table>
<thead>
<tr>
<th>System</th>
<th>BCC $\Delta H^F_{C=0.5}$ kJ/mol</th>
<th>FCC $\Delta H^F_{C=0.5}$ kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Zn</td>
<td>-10.5</td>
<td>-8.5</td>
</tr>
<tr>
<td>Mn-Zn</td>
<td>-6.3</td>
<td>-15.0</td>
</tr>
<tr>
<td>Cu-Mn</td>
<td>-4.2</td>
<td>+3.0</td>
</tr>
</tbody>
</table>
It can be seen that the formation energy of BCC and FCC phases differs by -2.0, +8.7, and -7.2 KJ/mol in the three binaries Cu-Zn, Mn-Zn, and Cu-Mn, respectively. In the case of Cu-Zn, it is well within the error limits assumed by Miedema, whereas the other two values differ considerably from these limits. It is also significant that the calculated formation energy of the metastable $\beta$-Cu-Mn phase is actually of a different sign than that of the FCC phase.

The ordering temperatures for the FCC phases of Cu-Zn and Cu-Mn, which have been assumed from indirect experimental evidence, cannot be far away from the actual ordering temperatures since the free energy curves based on them lead to reasonable predictions. In this case, one would predict no chemical long-range ordering in $\alpha$-Cu-Mn in the vicinity of Cu$_3$Mn, as the assumed ordering temperature is 0°K. This seems to be experimentally borne out by the fact that long time annealing at low temperatures of $\alpha$-Cu$_3$Mn does not result in any increase of order\(^{(112)}\). As for the Cu-Zn system, the ordering temperature for $\alpha$-Cu$_3$Zn is likely to be lower than 275°K\(^{(105)}\), but not completely non-existent (as in Cu-Mn).
Martensitic transformation in the system Cu-Zn-Mn has been investigated with a view to determining the role of order in influencing the transformation characteristics. The experimental results and theoretical calculations lead to the following conclusions.

(1) The effects of manganese on the martensitic transformation characteristics in the system Cu-Zn are essentially the same as those of zinc.

(2) A secondary ordering transformation B2 → DO₃/L₂₁ exists at low temperatures in binary and ternary β-phases of Cu-Zn and Cu-Zn-Mn systems, respectively, in addition to the high temperature A₂ → B₂ ordering transformation. The rapid diffusion characteristics of Cu-Zn alloys are not affected by manganese additions.

(3) Ageing and quenching from above the B2 → DO₃/L₂₁ transformation temperature does not result in markedly different structures compared to ageing at lower temperatures. However, it is still possible to retain a certain amount of disorder by such quenching procedures which anneals out very fast on further ageing at low temperatures.

(4) The effects of low temperature ageing on the martensitic transformation temperature can be associated with disordering effects. The martensite inherits the order of the parent phase under such circumstances, and disordering of the β-phase will result in a rise of Mₛ provided the ordering
energy of the martensitic phase is smaller than the ordering energy of the $\beta$-phase.

(5) Free energy calculations made by combining ordering data for both FCC and BCC phases, with a regular solution model and phase stabilities, confirms this is to be the case for binary Cu-Zn and Cu-Zn-Mn alloys.

(6) Useful free energy curves can be obtained from ordering data, phase stability information, and a single additional parameter which takes into account the expected electronic contribution from Brillouin zone effects.

(7) The free energy curves for the BCC and FCC phases of binary Cu-Zn and ternary Cu-Zn-Mn alloys cross three times, which is in conformity with the known phase equilibrium in Cu-Zn and Cu-Zn-Mn alloys. The variation of the three intersection points with composition clearly reproduces both the retrograde solidus so characteristic of these alloys and the variation of $M_s$ with zinc content.

(8) Low temperature ageing effects are not permanent, and tend to anneal out without producing any major change.

(9) The energy parameters deduced for FCC Cu-Mn alloys make it unlikely that a true chemical long-range ordering transformation exists in $\alpha$-Cu$_3$Mn alloy.

(10) In shape memory devices using Cu-Zn-Al alloys the sensitivity of $M_s$ to low temperature ageing may be a drawback. Addition of Mn to the Cu-Zn-Al alloy is likely to reduce this sensitivity to low temperature ageing in such applications.
SUGGESTIONS FOR FURTHER STUDY

Since $M_g$ is depressed by ageing treatments in the Cu-Zn-Al system, the ordering energy of the $\beta$-phase must be smaller than that of the $\alpha$-phase. Similar calculations on the lines adopted for the Cu-Zn-Mn system should be performed to see whether it is, indeed, the case in this system. The systems Cu-Zn-Ni and Cu-Mn-Al can be studied to test whether the approach adopted here can be utilised to successfully explain the ordering behaviour and the effects on martensitic transformations in systems for which very little additional data is required, since two sets of information regarding $W^{(1)}$ and $W^{(2)}$ already exist. The same technique could be applied to other systems like Ti-Ni, etc., thereby showing that this approach can provide a general picture of the martensitic transformation in the shape memory alloys.
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NEW BINA  
10 REM PROGRAM FOR CALCULATION OF ORDER DISORDER TEMPERATURES  
30 REM A&B MOLE FRACTIONS OF A&B COMPONENTS  
40 REM W1&W2 EXCHANGE ENERGIES IN "NN" AND "NNN" RESPECTIVELY  
50 INPUT A,B  
60 INPUT W1,W2  
70 PRINT "COMPOSITION OF ALLOY" ;A*100,B*100  
80 PRINT "EXCHANGE ENERGIES" ;W1,W2  
90 LET T1=A*B*(8*W1-6*W2)  
100 PRINT "A2/B2 ORDER DISORDER TEMPERATURE T-X= " ;T1  
110 PRINT "X(LRO)" ;"T-Y" ;"DF/DX AT T-Y"  
120 FOR X=0 TO B STEP 0.1E-1  
130 LET C=A+X  
140 LET D=A-X  
150 LET E=B+X  
160 LET F=B-X  
170 LET L1=6*W2*D*E  
180 LET T2=L1  
190 LET L2=C**2*E**2  
200 LET L3=D**2*F**2  
210 IF (L3)<0 THEN 270  
220 LET L2=L2/L3  
230 IF (L2)<0 THEN 270  
240 LET L1=L1*LOG(L2)  
250 LET L1=L1-8*(4*W1-3*W2)*X  
260 PRINT X,T2,L1  
270 NEXT X  
280 END  
  
COMPOSITION OF ALLOY  60  40  
EXCHANGE ENERGIES  615  325  
A2/B2 ORDER DISORDER TEMPERATURE T-X= 712.8  
X(LRO) T-Y DF/DX AT T-Y  
.397  314.592 -189.809  
.39772  315.261 -151.102  
.3974  315.029 -109.239  
.3976  314.797 -63.712  
.3978  314.565 -13.878  
.398  314.332  41.0891  
  
FINISHED
APPENDIX II
NEW LORD1
20 PRINT "T-Y CALCULATION FOR CU-ZN -MN ALLOYS (INDEN'S METHOD)"
40 REM COMPOSITIONS A, B, C
50 INPUT A, B, C
60 PRINT "COMPOSITION OF ALLOY IN AT%" 
70 PRINT A*100, B*100, C*100
80 INPUT W1, W2, W3, W4, W5, W6
90 PRINT "INPUT ENERGY PARAMETERS (BW6 VALUES IN K-UNITS)"
100 PRINT W1, W2, W3, W4, W5, W6
120 LET M=8*(W3+W5-W1)-6*(W4+W6-W2)
130 LET F2=W4+W6-W2
140 LET F1=A*C*(4*W5-3*W6)+B*C*(4*W3-3*W4)
150 LET F1=F1+A*B*(4*W1-3*W2)
160 LET F2=(2*F1)**2
170 LET F2=F2-4*A*B*C*(8*W5-6*W6)*(8*W3-L*W4)-0.25*N1**2
180 LET F2=0.5*SQR(F2)
190 LET F1=F1+F2
200 PRINT "A2/B2 ORDER DISORDER TEMPERATURE T -X=";F1
205 PRINT "X-CU", "X-ZN", "T-Y", "DF-DXA", "DF-DXB"
210 IF (A)>(1-A) THEN 240
220 LET Q=A
230 GOTO 260
240 LET Q=A-1
250 GOTO 280
260 LET S=A
270 GOTO 290
280 LET S=1-A
290 FOR X1=0.33 TO S STEP 0.01E-1
300 IF (-B)<=C-X1 THEN 330
310 LET K=-B
320 GOTO 340
330 LET K=-C-X1
340 IF (B)<=C-X1 THEN 370
350 LET I=C-X1
360 GOTO 380
370 LET I=B
380 FOR X2=K TO I STEP 0.01E-1
390 LET T1=W6*(B+C+X1)*(A-X1)
400 LET T1=T1+W4*(A+C+X2)*(B-X2)
410 LET T1=T1-M2*(B-X2)*(A-X1)
420 LET T1=3*T1
430 LET T2=T1**2-9*(4*W6*W4-W2**2)*(A-X1)*(B-X2)*(C+X1+X2)
440 IF (T2)<0 THEN 640
450 LET T1=T1+SQRT(T2)
460 IF (T1)<0 THEN 640
470 LET L1=4*(8*W5-6*W6)*X1**2*M1*X2
480 LET R1=(A+X1)**2*(C+X1+X2)**2
490 LET R2=(A-X1)**2*(C-X1-X2)**2
500 IF (R2)<0 THEN 550
510 LET R1=R1/R2
520 IF (R1)<0 THEN 550
530 LET D1=T1+LOG(R1)
540 LET N1=L1-D1
550 LET L2=4*(8*W3-6*W4)*X2**2*M1*X1
560 LET R3=(B+X2)**2*(C+X1+X2)**2
570 LET R4=(B-X2)**2*(C-X1-X2)**2
580 IF (R4)<0 THEN 640
590 LET R3=R3/R4
600 IF (R3)<0 THEN 640
610 LET D3=T1+LOG(R3)
620 LET N3=L2-D3
621 IF (ABS(N1))>45 THEN 640
622 IF (ABS(N3))>45 THEN 640
630 PRINT X1, X2, T1, N1, N3
640 NEXT X2
650 NEXT X1
660 END
T-Y CALCULATION FOR Cu-Zn -MN ALLOYS (INDEN'S METHOD)

COMPOSITION OF ALLOY IN AT%

<table>
<thead>
<tr>
<th></th>
<th>60</th>
<th>30</th>
<th>10</th>
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INPUT ENERGY PARAMETERS (BWG VALUES IN K-UNITS)

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<tr>
<th></th>
<th>615</th>
<th>325</th>
<th>505</th>
<th>115</th>
<th>300</th>
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<td>107</td>
<td></td>
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A2/B2 ORDER DISORDER TEMPERATURE T -x = 543.04

<table>
<thead>
<tr>
<th>X-CU</th>
<th>X-ZN</th>
<th>T-Y</th>
<th>DF-DXA</th>
<th>DF-DXB</th>
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<tr>
<td>-2.635</td>
<td>-2.685</td>
<td>415.629</td>
<td>5.64668</td>
<td>55.8638</td>
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<tr>
<td>-2.635</td>
<td>-2.685</td>
<td>415.501</td>
<td>-1.32831</td>
<td>.649811</td>
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<tr>
<td>-2.635</td>
<td>-2.675</td>
<td>415.373</td>
<td>-7.29395</td>
<td>-15.346</td>
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<tr>
<td>-2.64</td>
<td>-2.685</td>
<td>415.278</td>
<td>-1.28627</td>
<td>8.57649</td>
</tr>
<tr>
<td>-2.64</td>
<td>-2.685</td>
<td>415.15</td>
<td>-7.2478</td>
<td>-7.64095</td>
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FINISHED
MAST WISE
C PROGRAM FOR FREE ENERGY CALCULATION OF BCC AND FCC
C PHASES FOR AN ALLOY OF SAME COMPOSITION.
C TWO ORDERING REACTIONS IN BCC AND ONE DISCONTINUOUS
C ORDERING REACTION IN FCC ARE CONSIDERED
D I M E N S I O N B T ( 1 0 0 ) , B T O U ( 1 0 0 ) , F T ( 1 0 0 ) , F T O U ( 1 0 0 ) , B D F ( 1 0 0 ) , F D F ( 1 0 0 )
C VALUES OF EPSILON, THETA, T CRITICAL, BF2, USO1, USO2, COF1, COF2, FF1-INPUT DATA
C X1, Y1, Z1-PERCENT Cu, Zn AND Mn RESPECTIVELY.
C N=NUMBER OF TEMPERATURE INTERVALS
READ ( 1 , 1 0 ) X 1 , Y 1 , Z 1 , U S O 1 , U S O 2 , C O F 1 , C O F 2 , B F 2 , F F 1 , N
10 FORMAT ( 9 F 0 , 4 D )
WRITE ( 2 , 1 2 0 ) X 1 , Y 1 , Z 1
120 FORMAT ( 1 H , 1 1 H COMPOSITION , 2 X , 3 H C U = , F 5 , 2 , 3 H Z N = , F 5 , 2 , 2 X ,
* X H M N = , F 5 , 2 )
20 FORMAT ( 3 F 0 , 4 D )
READ ( 1 , 2 0 ) E P S I , T H E T , T C R I
WRITE ( 2 , 3 0 ) E P S I , T H E T , T C R I
30 FORMAT ( 1 H , 8 H EPSILON= , F 7 , 1 , 2 X , 6 H THETA= , F 4 , 1 , 2 X , 1 0 H CRITICALT= , F 5 , 1 )
DO 5 I = 1 , N
BDF ( I ) = U S O 1 + B F 2
5 F D F ( I ) = F F 1
B T ( I ) = 0.
F T ( I ) = 0.
DO 4 0 I = 1 , N
BT ( I + 1 ) = BT ( I ) + 50.
BT O U ( I ) = B T ( I ) / T C R I
IF ( B T O U ( I ) . G E . 1 . ) G O T O 5 0
BDF ( I ) = EPSI + T H E T I * T C R I I * B T O U ( I ) + B D F ( I )
BDF ( I ) = B D F ( I ) - ( 3 * E P S I + 2 * T H E T * T C R I I I * B T O U ( I ) ) * 2
BDF ( I ) = B D F ( I ) * ( 2 * E P S I + T H E T I * T C R I I I * B T O U ( I ) ) * 3
50 BDF ( I ) = B D F ( I )
4 0 CONTINUE
READ ( 1 , 2 0 ) E P S I , T H E T , T C R I
WRITE ( 2 , 3 0 ) E P S I , T H E T , T C R I
WRITE ( 2 , 1 3 0 )
130 FORMAT ( 1 H , 3 X , ' T ' , 6 X , ' G - B C C ' )
DO 6 0 I = 1 , N
BT ( I + 1 ) = BT ( I ) + 50.
BT O U ( I ) = B T ( I ) / T C R I
IF ( B T O U ( I ) . G E . 1 . ) G O T O 7 0
BDF(I) = EPSI + THET * TCRI * BTU(I) + BDF(I)
BDF(I) = BDF(I) - (3. * EPSI + 2. * THET * TCRI) * BTU(I) ** 2
BDF(I) = BDF(I) + (2. * EPSI + THET * TCRI) * BTU(I) ** 3

70 BDF(I) = BDF(I) - COF1 * BT(I)
WRITE(2,140)BT(I),BDF(I)

140 FORMAT(1H,F5.0,F4X,F8.0)

60 CONTINUE
READ(1,20)EPSI,THET,TCRI
WRITE(2,30)EPSI,THET,TCRI
WRITE(2,150)

150 FORMAT(1H,'3X,T',8X,6=FCC')
DO 80 I=1,N
FT(I+1) = FT(I) + 50.
FTU(I) = FT(I) / TCRI
IF(FTU(I) .GE. 1.) GO TO 90
FDF(I) = FDF(I) + EPSI + THET * TCRI * FTU(I)
FDF(I) = FDF(I) - (3. * EPSI + 2. * THET * TCRI) * FTU(I) ** 2
FDF(I) = FDF(I) + (2. * EPSI + THET * TCRI) * FTU(I) ** 3

90 FDF(I) = UDOZ - COF2 * FT(I) + FDF(I)
WRITE(2,160)FT(I),FDF(I)

160 FORMAT(1H,F5.0,F4X,F8.0)
80 CONTINUE
STOP
FINISH

COMPOSITION: CU=60.00 ZN=30.00 MN=10.00
EPSILON= -557.0 THETA= 1.6 CRITICAL= 416.0
EPSILON= -2027.0 THETA= 3.5 CRITICAL= 598.0

T  G=BCC
  0.  -6931.
  50.  -7139.
  100.  -7325.
  150.  -7500.
  200.  -7676.
  250.  -7863.
  300.  -8072.
  350.  -8313.
  400.  -8598.
  450.  -8931.
<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Energy Value (eV)</th>
</tr>
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<tbody>
<tr>
<td>500</td>
<td>-9300</td>
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</tr>
<tr>
<td>900</td>
<td>-13086</td>
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<tr>
<td>950</td>
<td>-13571</td>
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</table>

**Epsilon = -1217.0**  
**Theta = 5.3**  
**Critical = 365.0**
THE END

*****