

Structure of multi oxygen related defects in erbium implanted silicon

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In a previous report, electron paramagnetic resonance measurements of erbium and oxygen implanted into silicon have revealed centres with monoclinic and trigonal symmetry. These centres were tentatively ascribed to different atomic configurations of O and Si atoms surrounding a central Er^{3+} ion. In light of recent calculations concerning the structure and stability of multi oxygen related defects in silicon more sophisticated models have now been developed. The structure of the monoclinic centers observed is attributed to an Er atom sitting at the tetrahedral interstitial site surrounded by six O atoms. In this model the O atoms are arranged in the form of three O interstitial dimers with each of the O atoms located near to the Si-Si bond centered positions. In the case of the prominent defect center which exhibited trigonal symmetry different possible structures for this center are explored including locating the Er^{3+} ion residing at the hexagonal interstitial site surrounded by six O atoms as well as a center consisting of an O decorated ring hexavacancy defect.

I Introduction

There is a growing realisation of the importance played by impurity and defect related complexes in understanding many of the electronic properties of silicon. [1] The study of the structure of multi oxygen related centers, in particular, has become important in recent times in order to understand the mechanism associated with the diffusion of O in Si. [2] Whilst it is generally accepted that single interstitial oxygen (O_i) atoms are located near to the bond centered (BC) position in the Si lattice forming two short ($\sim 1.6 \text{ \AA}$) Si-O bonds, the activation energy for diffusion of the O_i center is too high to explain the aggregation of O in Si and the resultant generation rates associated with thermal donor defects. [2, 3] It has been proposed that multi O centers, such as the O dimer (O_{2i}), behave as the fast diffusion species within the lattice, though the exact structure of these O_{2i} dimers has been the subject of considerable debate. [4, 5, 6] The results of *ab initio* calculations have proposed that two O atoms can be incorporated into neighbouring near BC sites in either a staggered ($-O_i-Si-O_i-$) configuration or in a skewed ($-O_i-Si-Si-O_i-$) configuration. [4-6] Although the reports differ on the binding energy of the different arrangements, partly due to differences in the details of the calculations, it appears that the staggered dimer configuration is more favourable than the skewed dimer. [4-6] In addition to dimers, O interstitial trimers (O_{3i}) have also been examined both in a staggered chain or in a ring configuration. Results from calculations of the different trimer structures have shown that it is the staggered arrangement of chains of O atoms which tends to be more stable than a ring arrangement of Si and O atoms. [4]

In addition to O_i and multi oxygen centers, the structure and properties of the vacancy and multivacancy aggregates as well as vacancy-oxygen (VO) related defects are being continuously refined [7]. In disordered Si smaller multivacancy centers, such as the divacancy, tend to be present along with the VO center. [8] However, in amorphised Si, larger multivacancies and open volume defects tend to be present. The early calculations of Chadi and Cheng [9] predicted the existence of a particularly stable multivacancy in the form of a puckered hexagonal ring, the ring hexavacancy, labelled V_6 . Further calculations, repeated at a more sophisticated level, confirmed this hypothesis

and introduced the concept of ‘magic number’ multivacancies, such as V_6 and V_{10} *etc.* . [7, 10] The predicted stability of the V_6 defect is due in part to a minimisation of the number of Si dangling bonds and upon reconstruction, results in the formation of a large void (~ 4.5 Å across) with trigonal (D_{3d}) symmetry. The V_6 center has been predicted to be electrically inactive as well as possessing a small dipole moment making it virtually undetectable to local mode infra red vibrational spectroscopy. [10] As a consequence the V_6 center and possible related configurations are therefore an important class of defect in Si. It has been postulated, for example, that H decorated V_6 centers are responsible for the 1.107 eV line emission [11] in Si and may also play a role in the formation of platelets. [12] Consequently, it is thus important to examine the possible structure/s of V_6 related centers which may be decorated with other atoms. One way that this can be accomplished is to make use of the partially shielded $4f$ electrons found in ions of the lanthanide series. These rare earth ions are shielded from the full extent of the host crystal field by the closed $5s$ and $5p$ electron shells and this shielding effect has been exploited as a valuable probe for the study of point defects.[13] In this paper we wish to make use of Er^{3+} implanted into Si to probe the EPR complexes involving O. Extensive research of the Er doped Si system has been performed since it is now well established as one of the most efficient ways to obtain light emission at the technological important $1.5 \mu\text{m}$ wavelength. The addition of O (or other light atoms such as F) has shown that the room temperature luminescence can be enhanced and this has been attributed to the formation of Er-impurity complexes. [14] The presence of light atoms also helps with increased rare earth incorporation in Si before the onset of silicide precipitation. It is thus important to examine the structure of these Si-O-Er centers not just to gain information relevant to the Si-Er system itself but from a fundamental study of multi oxygen related defects in Si as well.

In a previous paper the results of EPR measurements made on Er and O co-implanted Si were reported. [15] This paper reported the presence of several Er^{3+} related centres with monoclinic and trigonal symmetry. On the basis of comparison with known g values from other systems a tentative model for the monoclinic centre was proposed; no model for the centre which

exhibited trigonal symmetry was presented. It is the intention of this paper to revisit the original EPR results in light of recent calculations in a number of relevant materials systems. This paper is organised as follows. In part II a brief description of the samples used in the original study is presented and for convenience a summary of the main results and conclusions from the original EPR experiment is provided. The proposed different structures for the monoclinic and trigonal centres are then discussed in parts III (A) and (B), respectively.

II Summary of results

Multiple energy implants of Er to a dose of 10^{15} cm^{-2} were performed into float zone Si at 77 K, which resulted in a uniform concentration of $10^{19} \text{ Er cm}^{-3}$ extending nearly 2 μm below the surface. Some samples were co-implanted with O ions to achieve an average O concentration of 3×10^{19} or 10^{20} cm^{-3} overlapping that of the Er concentration. The samples were then subsequently annealed at 450°C for 30 mins and then 620°C for 3 hours with some samples further annealed at 900°C for 30 s. The low temperature EPR measurements were performed in a modified Bruker EPR spectrometer employing 100 kHz field modulation and at a microwave frequency of 9.23 GHz. From the samples with no O or with a 3:1 O:Er impurity ratio, no sharp EPR lines were observed. By contrast, from the sample with a 10:1 impurity ratio sharp EPR lines were observed whether the sample was annealed to 620°C for 3 hours only or had an additional 900 °C anneal for 30 s. These sharp lines were shown to be associated with Er^{3+} centers with either monoclinic or trigonal symmetry and their g values, along with the associated point symmetry, are reported in table 1. The appearance of these sharp lines as the O:Er concentration ratio increased from 3:1 to 10:1 implies that well defined Si-O-Er complexes with a high coordination number of O atoms have formed.

One centre, which exhibited monoclinic symmetry, labelled OEr-1, was attributed to an Er ion surrounded by six O atoms in a configuration similar to that found in the monoclinic configuration of Er doped Y_2O_3 , which has the same structure as Er_2O_3 . [16] The measured g values for Er^{3+} in Y_2O_3 , are also reported in table 1. [17] The C phase of Er_2O_3 is known to occur

with two different coordinations each of which consists of an Er^{3+} ion surrounded by six O atoms, though neither ErO_6 structure is in the form of an octahedron. The EPR measurements, revealed Er to be in sites with monoclinic C_2 and trigonal C_{3i} (S_6) symmetry (*c.f.* table 1). In the case of the monoclinic centre the O-Er distances and the O-Er-O angles are not all equal, but come in three pairs as shown in Fig. 1. A second monoclinic centre, labelled OEr-3, was also reported in ref. 15 and based upon the similarities of the g values and point symmetry of centre OEr-3 to centre OEr-1, these two centres are believed to have very similar structures. However, the exact arrangement of these defect complexes within the Si lattice was unknown. Two centers, labelled OEr-2 and OEr-4, which exhibited trigonal symmetry were also observed though the intensity of center OEr-2 was considerably higher than that of OEr-4. The g values of these centers were sufficiently different from the trigonal center found in erbium oxide or any other known Er^{3+} center that no structures for these centers were proposed in the original study. The structure of these different centers will be discussed later though the discussion will concentrate on centers OEr-1 and OEr-2.

Subsequent extended X-ray absorption fine structure (EXAFS) measurements made on the same samples investigated by EPR confirmed the original hypothesis that the first coordination shell consisted of O. [18] It was found that in samples with an O:Er impurity ratio of 10:1, the average number of O atoms surrounding the Er atom was 5.1 ± 0.5 and the average Er-O separation was 2.26 \AA , close to the average value found in erbium oxide (2.27 \AA). It is important to realise that the EXAFS measurements probe the environment of all the Er ions (both divalent and trivalent) whereas the EPR results are from the EPR active trivalent Er^{3+} centers. Consequently the average number of 5.1 ± 0.5 O atoms surrounding the Er atom obtained in the EXAFS study indicates that there is a distribution of Si-O-Er centers present. The results from the EPR measurements therefore reflect a subset of all Er related centres in the samples investigated.

III Discussion of the structure of the Si-O-Er centers

(A) Monoclinic center

In order to analyse the g values found in the Si-O-Er system the crystal field experienced by the Er ion is taken, as a first approximation, to be cubic on to which a smaller lower symmetry crystal field is superimposed. This is referred to as the cubic crystal field (CCF) approximation. If the magnitude of the non-cubic component of the crystal field is sufficiently small to be treated as a perturbation to the cubic crystal field then the average of the trace of the g tensor, g_{av} , as defined by

$$g_{av} = 1/3 (g_1 + g_2 + g_3), \quad (1)$$

is conserved and would equal the g value found in cubic symmetry, g_c . [19] In this way the average g value can be used as a quantitative measure of the local crystal field around a paramagnetic rare earth ion. This establishes the use of rare earth ions as probes of the local structure of defects in semiconductor and insulator materials. From table 1, it is evident that not only are the g values of the center OEr-1 (and OEr-3) similar to those found in Er doped Y_2O_3 but that g_{av} for OEr-1 is almost identical at 6.27 to the average value found in the oxide (6.28). It was on this basis that centre OEr-1 consists of six O atoms surrounding the Er ion in a manner similar to that found in the oxide though this original assignment [16] failed to indicate how this ErO_6 complex was positioned within the lattice. Figure 2 now addresses this issue and shows the proposed structure of center OEr-1. Firstly in order for this center to possess the correct observed monoclinic C_{1h} symmetry the defect center must exhibit a single plane of reflection corresponding to a $\{110\}$ plane of the Si lattice. The center consists of an Er ion located at the tetrahedral interstitial site (T_i) surrounded by three sets of oxygen interstitial dimers. The O atoms in Fig. 2 have been located at exactly the bond centered positions, the significance of which will be discussed later. At any point surrounding the rare earth ion the Si-O bonding arrangement can be viewed as $\dots(Si-O-Si-O-Si)-(Si-O-Si-O-Si)\dots$. The presence of the central Si-Si bond effectively isolates one dimer from the other dimers present. Such O incorporation is strongly driven since it is well known that the energy gained by breaking a single Si-Si bond and replacing it by two Si-O bonds is 7 eV, making O incorporation near to the

BC position highly favourable. It was also established, that in the case of the isolated staggered O_{2i} dimer, that the dimer structure is more stable than two single interstitial O_i atoms by 0.2-0.6 eV [4, 6]. Locating the O atoms at exactly the BC positions results in an overall orthorhombic (C_{2v}) symmetry in which are present two {110} mirror planes containing the C_2 axis of rotation. In order to lower the symmetry to the observed monoclinic C_{1h} symmetry it is simply a matter of removing the C_2 axis of rotation. This can be readily accomplished by moving some of the O atoms away from the exact BC positions to near to the BC site resulting in the Er-O separations no longer being equal to one another. This is directly analogous to the situation discussed earlier for the configuration of the monoclinic site found in Er_2O_3 (*c.f.* Fig. 1 (a)). *Ab initio* calculations also favour such an O migration away from the BC site, since it was reported that a favoured configuration for O_{2i} dimers is for the Si-O-Si bond angle to be 131° , different from the 180° corresponding to the ideal BC position. [4]

Secondly the T_i site was chosen for the location of the Er ion since it has been previously established, both experimentally, using emission channelling [20], and theoretically, using *ab initio* calculations, that in O free Si that this is the most favoured position. [21, 22] The T_i site has sufficient space to accommodate the large Er ion and also does not result in the breaking of Si-Si bonds. Furthermore if the relaxation of the O atoms away from the BC positions is small, the Er-O separation should be approximately equal to the distance from the T_i site to the BC site (2.25 Å). This is close to the average Er-O separation (2.27 Å) found in the centers with monoclinic symmetry in Er_2O_3 . [23] To date there have been very few theoretical studies of the structure of the Si-O-Er centres. Recent first principles calculations by Hashimoto and others have attempted to determine the most stable atomic configurations of the ErO_6 system. [24] They calculated the formation energies of a number of different ErO_6 configurations in Si and found that the two lowest energy structures had orthorhombic (C_{2v}) and monoclinic (C_2) symmetry. The structure of the center C_{2v} symmetry is similar to that discussed above whilst the center with C_2 symmetry was observed to be 0.44 eV higher in energy than the orthorhombic center. They also considered the effects of

relaxing this structure and found a more relaxed C_{2v} state similar to that associated with centre OEr-1. In summary, the structure proposed in Fig. 2 explains not only the magnitude and the average of the observed g values but also the point symmetry around the Er^{3+} ion as measured by EPR. The structure is simultaneously mimicking the local structure of the monoclinic site in Er_2O_3 as well as gaining energy through the breaking of Si-Si bonds and replacing them by strong Si-O bonds with the O atoms near the BC positions.

(B) Trigonal Center

The discussion of the structure of the monoclinic centers was based on comparison with the known structure and g values for the corresponding low symmetry center found in Er doped Y_2O_3 . Likewise it is possible to begin the discussion of the dominant trigonal center, OEr-2, found in the Si-O-Er system by comparing it with the trigonal center found in the oxide (Fig. 1 (b)). From table 1, the g values of the trigonal C_{3i} center observed in $Y_2O_3:Er^{3+}$ are clearly different (with $g_{\parallel} > g_{\perp}$) from the g values found for the OEr-2 center ($g_{\parallel} < g_{\perp}$). Note that in both cases, however, the values of g_{\perp} are almost the same with $g_{\perp} = 3.24$ in Si-O-Er system and $g_{\perp} = 3.32$ in the oxide. The major difference between the two centers is found in the value of g_{\parallel} . This may indicate that the crystal field around the Er ion and hence the local structure around the Er ion in the plane perpendicular to the trigonal defect axis are similar. [25] To conclusively prove that a particular structure is associated with a particular EPR center a thorough *ab initio* study would have to be performed. Since this is beyond the scope of this paper, we first explore the magnetic resonance analysis for a center with cubic symmetry and then extend the analysis to the case of trigonal symmetry. In the case of Er^{3+} in cubic symmetry the different irreducible representations can be readily obtained from group theory and can be represented by $\Gamma_6 + \Gamma_7 + 3\Gamma_8$. The Γ_6 and Γ_7 irreducible representations of the cubic group are twofold degenerate and each of the three Γ_8 levels is fourfold degenerate. For each of the cubic irreducible representations Γ_6 , Γ_7 and Γ_8 the values of m_J in the eigenvector expansion will differ by four to reflect the presence of a 4-fold axis of rotational

symmetry. In such a situation the CCF approximation, and hence the corresponding cubic crystal field eigenstates, can be employed in which the cubic rare earth crystal field Hamiltonian [26] can be expressed as

$$H = B_4 (O_4^0 + 5 O_4^4) + B_6 (O_6^0 - 21 O_6^4), \quad (2)$$

where O_n^m are the crystal field equivalent operators and the coefficients B_4 and B_6 determine the crystal field splitting. Equation (2) can be solved through the introduction of two parameters x and W defined such that

$$B_4 F(4) = W x \text{ and } B_6 F(6) = W (1 - |x|), \quad (3)$$

where W is an energy scale factor that depends on the electrostatic potentials and $F(4)$ and $F(6)$ are numerical constants. [26] The quantity x is the crystal field mixing term ($\sim B_4/B_6$) and runs from -1 to +1. With labelling appropriate to T_d symmetry, the Γ_7 representation lies lowest for $-1 < x < -0.46$, the Γ_6 representation for $-0.46 < x < 0.58$ and the Γ_8 representation for $x > 0.58$. From the crystal field eigenstates, the g values associated with transitions within the Γ_6 and Γ_7 states are 6.80 and 6.00 and are independent of x . For centers with less than cubic symmetry it is possible to use Eq. (1) to relate the observed principal g values to the g value associated with a center with cubic symmetry, g_c . [19] Since the average g value for center OEr-2 is 2.39 and is far enough removed from the cubic g values for a Γ_6 state (6.8) or Γ_7 state (6.0) we can conclude that this center is not associated with an Er^{3+} ion surrounded by four tetrahedrally arranged O atoms for which $x < 0$. Neither can this center be associated with an environment of six octahedrally coordinated O atoms for which $0 < x < 0.58$. For the remaining region of $0.58 < x < 1$, (also associated with octahedral coordination), corresponding to a Γ_8 level lying lowest, the use of the average g value is not valid. This is also the case for $W < 0$ for $-1 < x < 0.8$. In this case it is necessary to calculate the g values for each value of x and use the associated cubic crystal field eigenstates, labelled P and Q in the notation of reference [19], to calculate the principal g values g_{\parallel} and g_{\perp} via

$$g_{\parallel} = g_J (P-Q) \text{ and } g_{\perp} = g_J (P+Q). \quad (4)$$

where the Landé g value is taken to be $6/5$. Figure 3 shows the calculated g values determined by this method using intervals for x of 0.01 for both $W>0$ and $W<0$. It is evident from Fig. 3 that no unique value of x exists for which calculated values of g_{\parallel} approach the observed value of 0.69 and g_{\perp} approaches 3.24. We therefore conclude that center OEr-2 does not originate from a trigonally split Γ_8 ground state. The overall result is that center OEr-2 cannot be associated with an Er^{3+} ion either tetrahedral or octahedral O coordination.

Since simple octahedral oxygen coordination has been ruled out as a possible explanation for center OEr-2, alternative models are required. It is possible to adapt the three O_{2i} dimer model presented in Fig. 2 by rearrangement of some of the O atoms to different (near) BC positions to give overall trigonal symmetry as shown in Fig. 4. In this configuration the Er-O separations are all equal and the overall symmetry is C_3 . The dimers are again separated by Si-Si bonds as in the model proposed for monoclinic center. However the *ab initio* calculations of Hashimoto *et al.* showed that this structure was 2.42 eV less stable than the structure of the centers investigated [24] and consequently it is not believed that this is the structure of the OEr-2 trigonal center.

Other atomic positions and coordinations therefore need to be considered. There exist a number of other positions for impurity atoms in the Si lattice which can give rise to trigonal symmetry. Two such sites are defects located at the BC position and also the hexagonal interstitial (H_i) position. Locating an Er atom at the BC site would result in the formation of two Er-Si bonds with the nearest neighbours being Si rather than O atoms. Furthermore in order to accommodate a large number of O atoms a large defect center is desirable. Figure 5 shows the arrangement of atoms at the hexagonal interstitial site in which each nearby Si-Si bond has been replaced by two Si-O bonds with the O atoms located exactly at the BC sites and the Er^{3+} ion located at the H_i site. In Si, the distance from the H_i site to the BC site is only 1.92 Å and to the unrelaxed Si to be 2.25 Å. Although this arrangement of atoms has trigonal D_{3d} point symmetry and is consistent with the magnetic resonance data, it is not believed to be the optimal arrangement of center OEr-2 for two reasons. Firstly in the atomic arrangement of Fig. 5 the bonding around the hexagonal ring

alternates evenly between Si and O atoms with each O atom being shared between two Si atoms. The calculations of Pesola *et al.* [4] examined the formation and binding energies of placing three O atoms in a ring arrangement or in a staggered arrangement. Both of these configurations also consisted of alternate Si-O bonding. They noted that for these arrangements there was a stronger tendency for the O atoms to prefer to form the staggered chains rather than a ring arrangement. Pesola *et al.* also found that the ring configuration of O_{3i} is stabilised by only 0.2 eV when compared to splitting into three O_i whereas the corresponding binding energy for the staggered chain was 0.7 eV against splitting into three O_i atoms. Consequently such ring arrangements are believed to be less stable than chain arrangements.

Secondly as O aggregation in the ring increases, incorporation of the six O atoms required in Fig. 5, will result in an increase in the strain energy in the ring until it becomes energetically favourable for the formation of a VO_n complex with the release of a Si self interstitial (Si_i). The maximum size of O_{ni} can be estimated as follows; taking the formation energy of Si_i to be 4.2 eV, and using the formation energies quoted by Pesola *et al.* of 1.1 eV for O_i and 3.7 eV for a VO center, the reaction $O_i \rightarrow VO + Si_i$ is seen to be highly endothermic requiring over 6.8 eV. Since the formation energy of the silicon interstitial is constant, the relative difference between the formation energies of interstitial oxygen and the VO center is only 2.6 eV. This reduces to 1.6 eV for the case of the O_{2i} dimer for which Pesola quotes formation energies of 2.1 and 3.7 eV for O_{2i} and VO_2 , respectively. This reduction in the energy difference between O_{ni} and VO_n as the number of O atoms increases and will ultimately result in the reaction $O_{ni} \rightarrow VO_n + Si_i$ becoming exothermic before a six atom O hexamer will form. This proposition has been recently confirmed by Jones *et al.* who show that the reaction for the kick out of the Si_i and the formation of VO_n becomes exothermic for n equal to four. [27]

We propose an alternative model that is stable against the dissolution of the Si-O rings and is consistent with the EPR results and is based on the H_i site model discussed above. However, the model proposed reflects the likelihood of a high number of vacancy and multi vacancy centers

produced by the MeV ion implantation. In this model, shown in Fig. 6, the Er atom is placed in the center of a ring hexavacancy decorated by six O atoms. In the ideal geometry of the undecorated V_6 center, twelve Si atoms are the nearest neighbouring atoms of the vacant sites such that each pair of atoms shares a single vacant site. Pairs of Si atoms are displaced toward each other to form a weak reconstructed Si-Si bond. A total of six Si-Si reconstructed bonds each with a bond length of around 2.6 Å forms [7]. After reconstruction V_6 possesses trigonal D_{3d} symmetry with an idealised distance across the defect of 4.5 Å. The model proposes that the O atoms enters into or near to the center of the reconstructed bonds, effectively producing six Si-O-Si bonds, but unlike the H_i site model described earlier, are effectively isolated from each other. Examination of Fig. 6 shows that the bonding arrangement is Si-O-Si-Si-O-Si which will minimise the O-O interaction and allow electrons to be gathered from the Si and from the Er by O. This model is also consistent the trigonal symmetry observed in the EPR measurements. In this model the atomic arrangement along the defect axis consists of two pairs of reconstructed Si-Si bonds and the Er ion. A decorated hexavacancy related center is plausible in these materials considering the non-equilibrium method of Er and O incorporation (ion implantation) into the Si.

The decorated hexavacancy model previously discussed is not just confined to the case of rare earth incorporation. MeV ion implantation which generates large quantities of multi vacancy centers may act as gettering centers for metal atoms. Estreicher has modelled the situation of Cu incorporation into Si containing V_6 centers and reported multi decoration of the V_6 centers with Cu ions. [28] Whether the formation of a decorated ring hexavacancy occurs will depend on whether the vacancy centers are stable upon annealing. This in turn will be affected by the presence of strong metal gettering centers and whether the presence of O atoms are able to break the reconstructed Si-Si bonds forming strong Si-O-Si bonds. In this way the O decorated ring hexavacancy can be formed by ion implantation of MeV heavy ions into Si in the presence of O atoms.

IV Conclusions

In conclusion different models for multi O related centers in Si by incorporation of the rare earth ion erbium are explored. In the case of a center exhibiting monoclinic symmetry, the structure of the center is explained in terms of six O atoms arranged around an Er^{3+} ion located at the T_i site in the Si lattice. The O atoms are grouped into three dimers with the O atoms near to bond center positions. In this way the proposed structure is consistent with the observed g values as well as the point symmetry as measured by EPR. The center is stabilised though the breaking of Si-Si bonds and replacing them with strong Si-O bonds in which the Er-O separation is close to that found in the erbium oxide. Three possible models for the observed trigonal center were examined, including a variation of the monoclinic center, a center based on Er located at the hexagonal interstitial site and thirdly a model in which the Er atoms is at the center of an O decorated ring hexavacancy center. The structure of the different centers was examined in each case and the relevance to the study of defect in MeV high dose implantation into Si.

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Table 1: Principal g values for different Er^{3+} related centers

Center	g_1	g_2	g_3	Symmetry, τ (degrees) ^{a)}	g_{av}
OEr-1	0.80	5.45	12.55	Monoclinic, 56.9	6.27
OEr-2	0.69	3.24	3.24	Trigonal, 54.7	2.39
OEr-3	1.09	5.05	12.78	Monoclinic, 48.3	6.31
OEr-4	2.00	6.23	6.23	Trigonal, 54.7	4.82
Er_2O_3	1.64	4.89	12.31	Monoclinic	6.28
Er_2O_3	12.17	3.32	3.32	Trigonal	6.27

a) The angle τ is the angle that g_1 and g_3 principal axes in the Si-O-Er system are rotated about g_2 as measured relative to [001] and [010]. The direction of g_2 is along a [110] direction having being rotated by 45° from [100].

Figure captions

Figure 1. Arrangement of O atoms around a central Er atom found in (a) the monoclinic C_2 and (b) trigonal C_{3i} configurations of the C phase of Er_2O_3 . In (a) the O atoms are not at equal distances from the Er ion and this is indicated by the O atoms not residing on the corners of the cube. Pairs of atoms at the same Er-O distance are indicated by 1, 2 and 3. In (b) all the Er-O distances are equal.

Figure 2. Proposed structure of center OEr-1. The six O atoms surround the Er atom which is located at the tetrahedral interstitial site in Si. The O atoms are arranged in three sets of interstitial dimers. In the configuration presented the O atoms are located at the bond center positions giving C_{2v} symmetry. By eliminating the C_2 axis of rotation, such as a small movement of some of the O atoms away from the BC position, the symmetry is reduced to the observed C_{1h} .

Figure 3. Calculated principal g values for an Er^{3+} ion in site of trigonal symmetry for $W > 0$ (solid lines) and $W < 0$ (dashed lines). The calculation assumes that the trigonal field is small so that cubic eigenstates can be used. Close to $x = -0.5$ it is observed that g_{\perp} becomes close to zero.

Figure 4. Possible structure of center OEr-2 using three O_{2i} dimers. The Er atom is located at the T_i site and the Er-O distances are all equal to each other. The overall symmetry is C_3 .

Figure 5. Possible structure of center OEr-2 with the Er atom located at the hexagonal interstitial site and each of the Si-Si bonds in the hexagonal ring is replaced by two Si-O bonds. The O atoms are located at exactly BC position and the overall symmetry is D_{3d} .

Figure 6. Possible structure of center OEr-2 with the Er atom located at the center of an O decorated ring hexavacancy center. Each of the reconstructed Si-Si bonds in the ring is replaced by two Si-O bonds. The overall symmetry is D_{3d} .

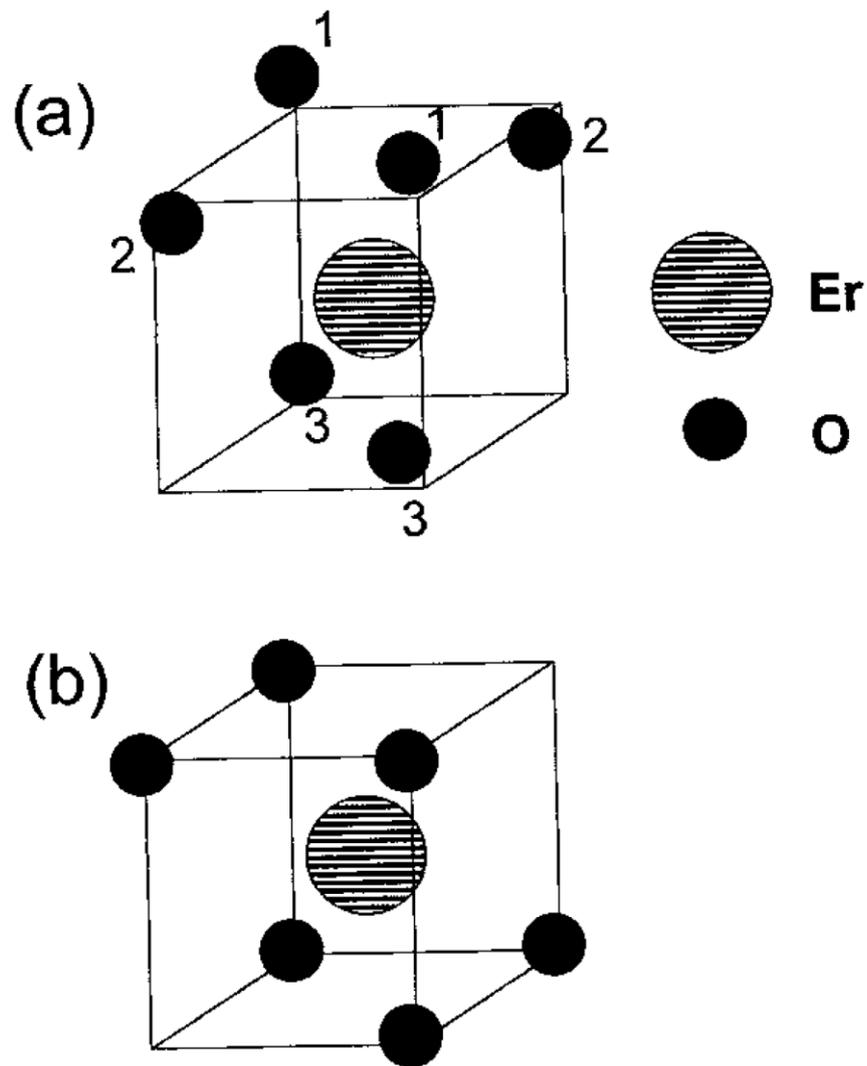


Figure 1

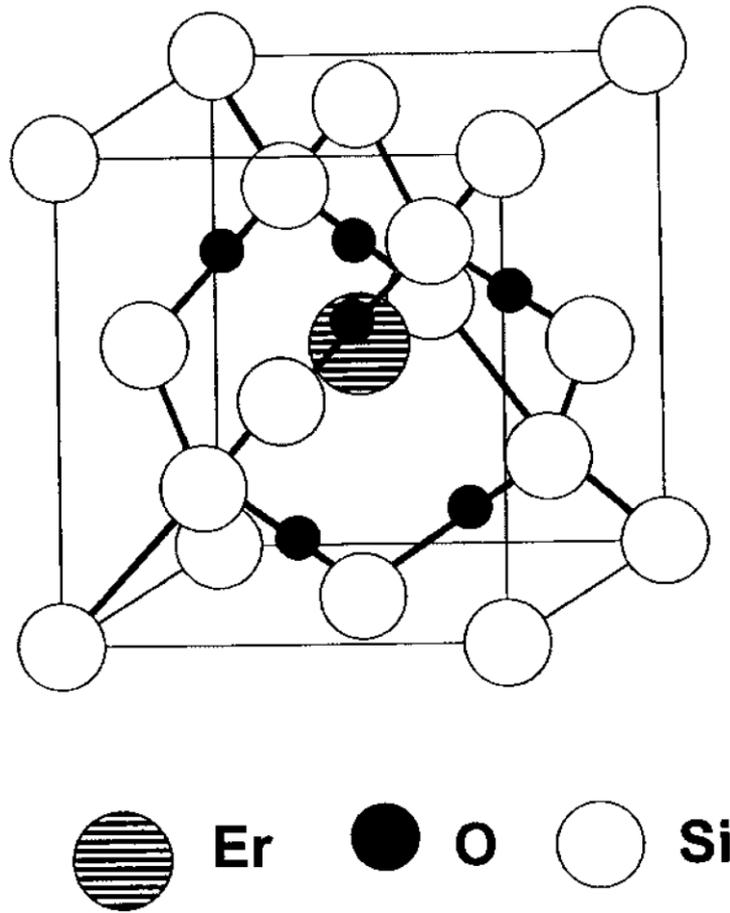


Figure 2

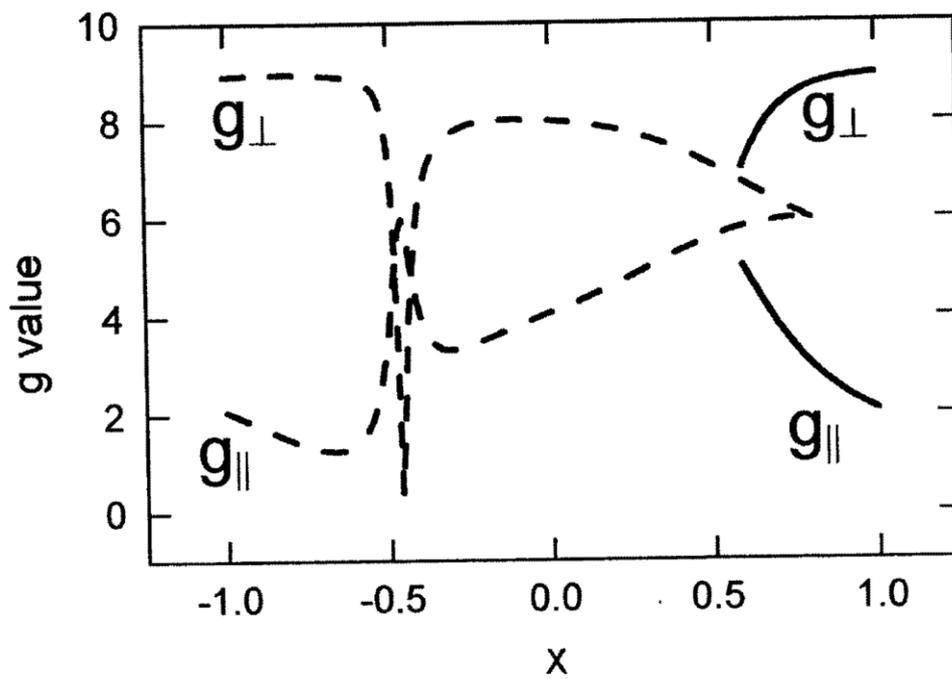


Figure 3

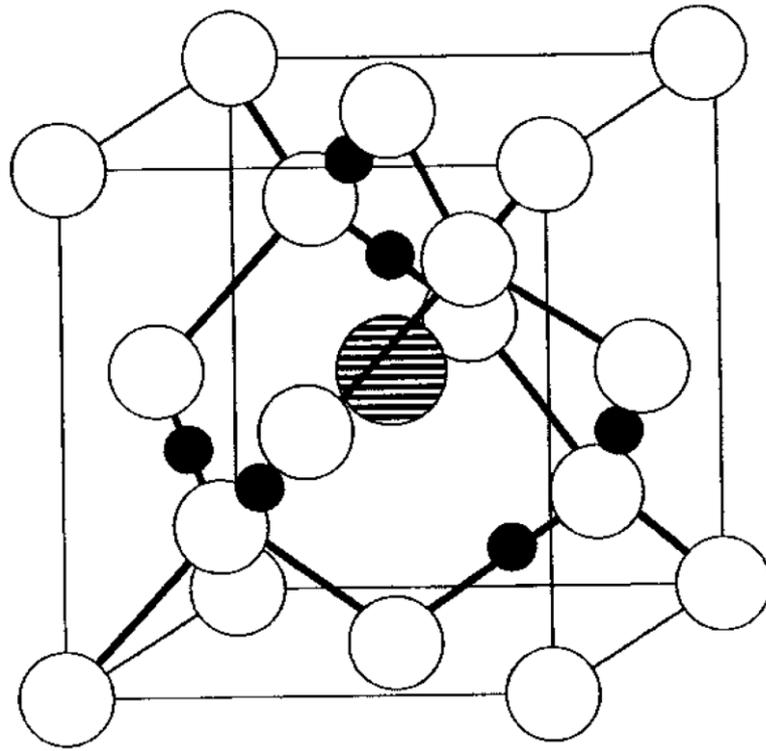


Figure 4

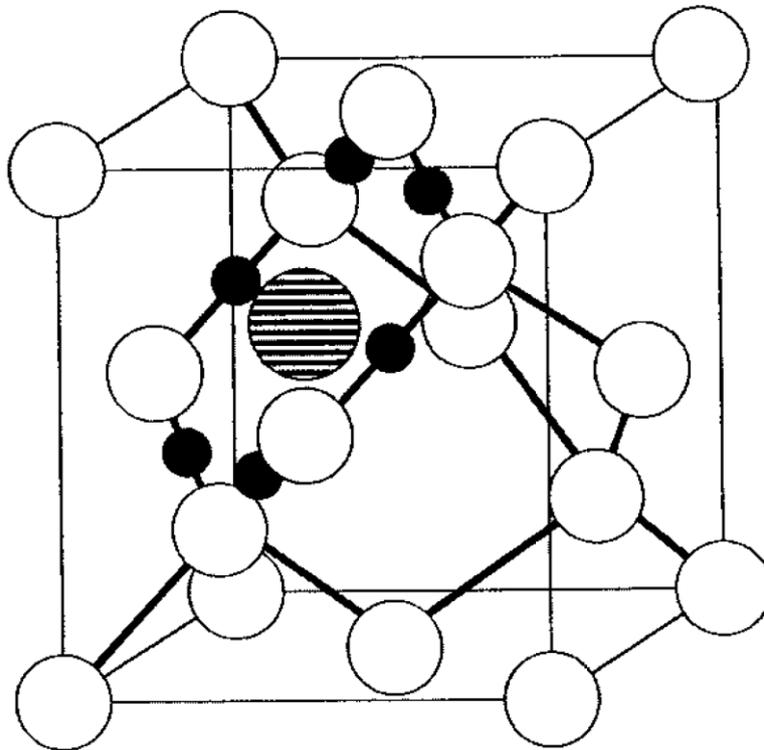


Figure 5

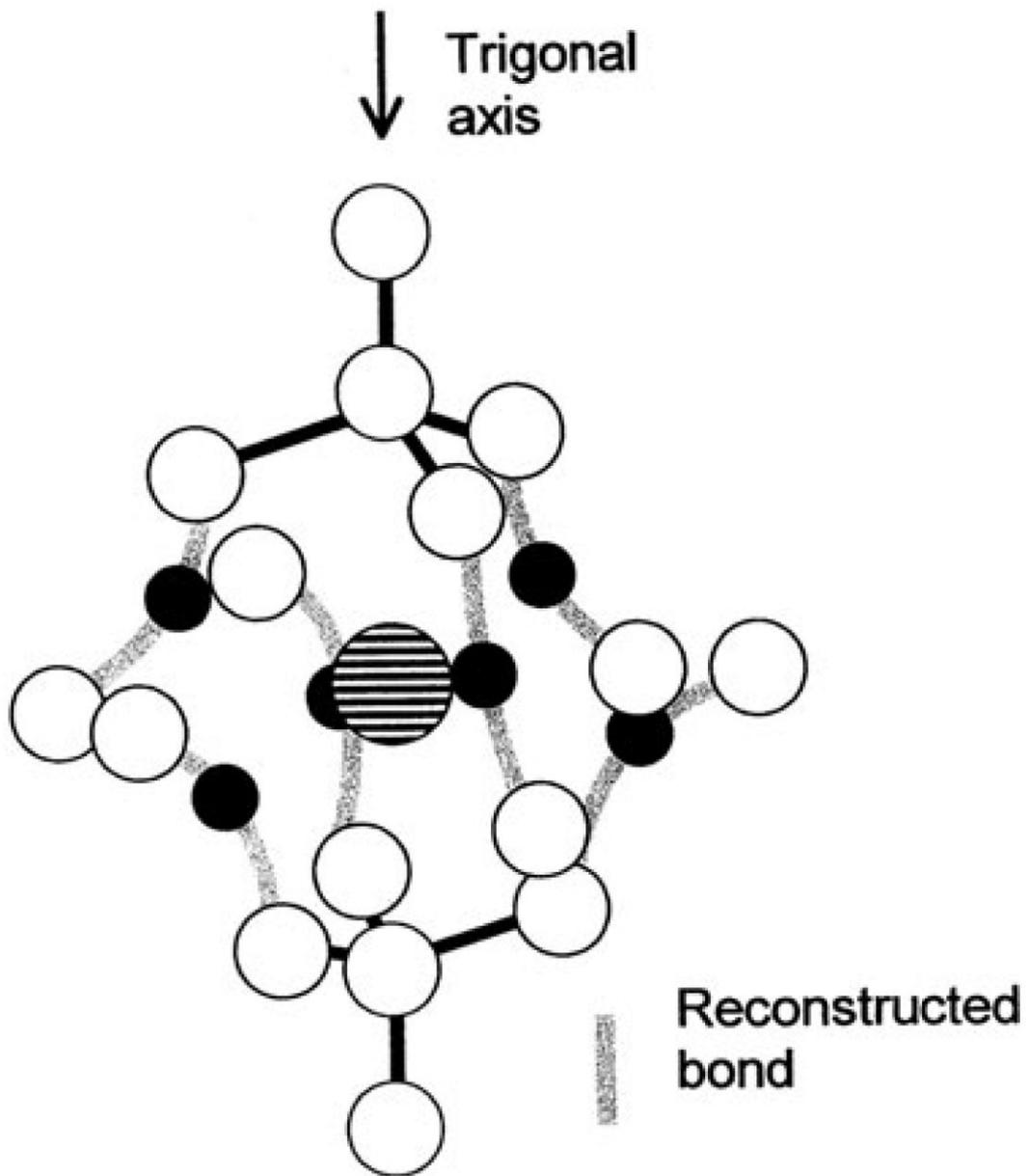


Figure 6