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10 K EPR of an oxygen-hole aluminium centre, $[\text{AlO}_4]^0$, in x-irradiated zircon, ZrSiO_4

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Abstract. Precise parameter interaction matrix determinations, including ^{27}Al hyperfine and nuclear electric quadrupole matrices, are reported for an aluminium centre, with an electron removed from an adjacent oxygen and referred to as an oxygen-hole centre, in x-irradiated zircon based on 8.9 GHz EPR measurements at around 10 K. Each of the parameter interaction matrices exhibits monoclinic symmetry indicating sites of Laue class $2/m$ for both the hole-centre and the interacting ^{27}Al nucleus. Consideration of earlier reported results for two single electron-hole centres in zircon, and comparison with results for a similar centre in α quartz, show that the hole-centre is trapped at a short bonded ligand O in the zircon structure and interacts with an aluminium nucleus replacing Si at an adjacent site; each of the O and Si sites of the zircon structure have point group symmetry m .

1. Introduction

This paper is the second in a series which attempts to produce precise interaction matrix (tensor) directional data, in the microregion about an impurity centre, for paramagnetic species in x-irradiated zircon, ZrSiO_4 , from electron paramagnetic resonance (EPR) measurements at low temperatures. Some of these centres, for example $\text{Zr}^{3+}(\alpha)$ and the oxygen-hole centre reported herein have been measured and reported previously by Solntsev and Shcherbakova (1973) while others, like the electron-hole centres reported in our earlier paper (Claridge *et al* 1994), were, so far as we are aware, new results.

Our re-examination by EPR at low temperatures of some of these systems has a number of objectives. Firstly, while the descriptions of Solntsev and Shcherbakova (1973) of centres such as $\text{Zr}^{3+}(\alpha)$ and $[\text{AlO}_4]^{4-}$ (which we shall subsequently relabel $[\text{AlO}_4]^0$) are undoubtedly correct, the measurements of these authors were deficient in a number of respects. For example the interaction matrices are only known approximately and nuclear parameters of some interacting nuclei, particularly quadrupolar nuclei, are either only approximately known or are not reported at all. Secondly, less precise measurements do not allow one to compare interaction matrix (\bar{g} , \bar{A} , \bar{Q}) principal directions with specific bond directions, and hence to locate the paramagnetic centre with any certainty in the crystal. That such precise EPR measurements are practically realizable is amply illustrated by the oxygen-hole results of Nuttall and Weil (1981a, b, c) in the case of α quartz and our own results for zircon (Claridge *et al* 1994). Finally, only when precise parameter matrices have been obtained experimentally can meaningful comparisons be made between *ab initio* MO calculations of the centres, as exemplified by the calculations of Mombourquette *et al* (1984) and Mombourquette and Weil (1985) for α quartz, and experimental parameters, i.e., to precisely locate the electron-holes in specific orbitals.

In this paper, we report 10 K EPR measurements and precise parameter interaction matrix determination, including \bar{g} , \bar{A} (^{27}Al), \bar{Q} (^{27}Al), and \bar{g}_N (^{27}Al), for an oxygen-hole aluminium centre formed by x-irradiation of a synthetic zircon crystal at 77 K. Comparison with earlier results for two single electron-hole centres, Claridge *et al* (1994), further comparison with the results of Nuttall and Weil (1981a) for $[\text{AlO}_4]^0$ in α quartz, together with analysis of nuclear hyperfine and nuclear electric quadrupole matrices for ^{27}Al allow a determination of the location of the hole centre as almost certainly in the p orbitals of a short-bonded O atom of the zircon structure.

2. Experimental details

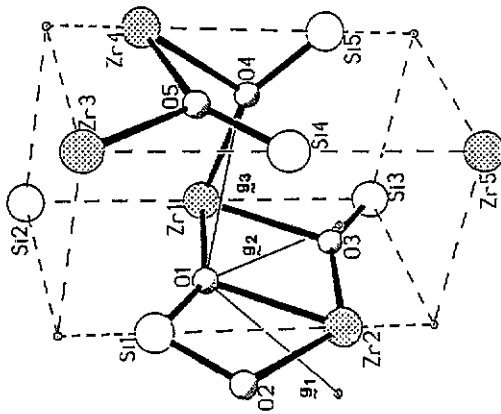
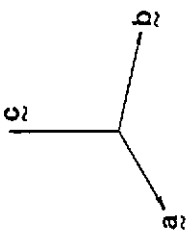
The crystal, the X-band Varian E12 spectrometer and the crystal goniometer used were as described earlier, Claridge *et al* (1994). The crystal was cut to a parallelepiped (dimensions $5.5 \times 3.5 \times 2$ mm) with faces parallel to the crystallographic a , b and c axes of the tetragonal (space group $I4_1/amd$) system. The crystal was irradiated at 77 K with x-rays from a tungsten tube and the crystal transferred cold to the Displex head of the EPR cavity-goniometer system. All measurements were made at about 10 K. Measurements were made in the bc and ab planes, and both sets of data initially used in the analysis. However, as described below, only the bc -plane data together with the technique of symmetry-related sites as described by Weil *et al* (1973) needed finally to be used.

3. Results

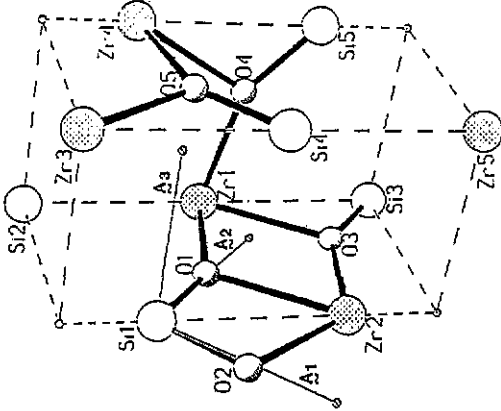
The spectrum with the static magnetic field parallel to the tetragonal axis c consisted of a sextet of lines with spacings around 0.08 mT. The position of the spectrum in relation to other reported EPR centres in zircon is shown in the c -axis spectrum in figure 1 of Claridge *et al* (1994). Along the c axis the g factors for the centres are: $[\text{AlO}_4]^0$ 2.025, D(hole) 2.010, RT(hole) 2.012, B(Ti^{3+}) 1.926, A($\text{Zr}^{3+}(\alpha)$) 1.866 and C($\text{Sn}^{3+?}$) 2.000. The sextet evidently arises from hyperfine interaction with a 100% abundant nucleus with nuclear spin $I = 5/2$ and comparison with similar spectra in α quartz make it clear that the nucleus in question is ^{27}Al . From the observed site splittings in the ab and bc planes, the site symmetry is evidently monoclinic, or possibly triclinic (Laue classes $2/m$ or $\bar{1}$ respectively): in the ab plane a maximum of two sites was observed and in the bc plane a maximum of three sites. In a general crystal orientation EPR spectra from four crystallographically equivalent sites were observed. Reference to the paper of Rae (1969) indicated therefore monoclinic symmetry for the centres with principal directions lying in the ac and bc planes as had previously been observed for two single electron-hole centres in zircon, Claridge *et al* (1994). Nevertheless, as a further check, we assumed initially only Laue class $\bar{1}$ for the paramagnetic site and fitted simultaneously data from both planes to the spin-Hamiltonian

$$(\mathcal{H})_i = \beta_e S \cdot \bar{g}_i \cdot B + S \cdot \bar{A}_i \cdot I - \beta_N I \cdot (\bar{g}_N)_i \cdot B + I \cdot \bar{Q}_i \cdot I \quad (1)$$

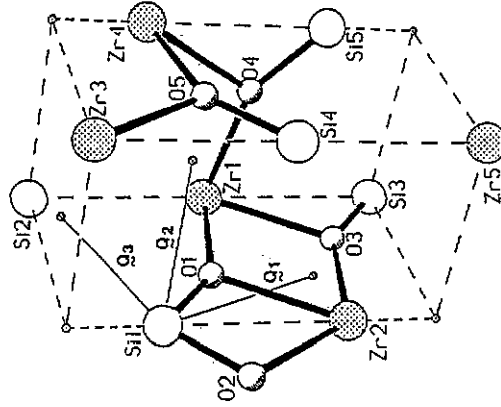
where the terms have their normal meanings and the subscript i refers to the $i = 1-8$ (triclinic symmetry, rotation group D_4), or $i = 1-4$ (monoclinic symmetry, rotation group C_4) symmetry-related sites. (Strictly the rotation group D_4 is required for each of these symmetries in a crystal of Laue class $4/mmm$, but the C_4 rotation matrices can be used because of site degeneracies when the site symmetry is monoclinic.) In (1), the \bar{g}_N matrix



(a)



(b)



(c)

Figure 1. $[AlO_4]^{10}$ centre principal directions in relation to zircon bond directions: (a) g tensor; (b) ^{27}Al A tensor; (c) ^{27}Al Q tensor. Tensor principal directions are portrayed as orthogonal 3 Å vectors.

for ^{27}Al was taken as the isotropic matrix $1.456601U$ where U is the 3×3 unit matrix. The spin-Hamiltonian (1) is simpler than that used by Nuttall and Weil (1981a) to analyse the EPR spectrum of $[\text{AlO}_4]^{0-}$ in α quartz since our spectrum was too weak to produce consistently measurable ^{29}Si hyperfine lines, and ^{17}O lines were not observed in any crystal orientation.

Data were fitted using the matrix diagonalization least squares programme EPR (McGavin *et al* 1989). In the two-plane fittings, only one off-diagonal matrix element in each parameter interaction matrix was, within error, non-zero thus confirming (within error) monoclinic site symmetry. In the bc plane there are generally, as noted earlier, three symmetry-related species. This is sufficient in the present instance to determine all parameter matrix elements c_{ij} ($i, j = 1, 3$) except c_{12} elements. However, allowing elements c_{23} to vary did not improve the fit of the bc -plane data and the c_{23} elements of all parameter matrices were found again, within error, to be zero. The final fittings therefore utilized data from the bc plane only and with monoclinic symmetry, $c_{12} = c_{23} = 0$, imposed; the parameters so obtained are listed in table 1. The final root-mean-squared deviation (RMSD) between calculated and observed resonant fields over 312 unit weighted data points was 0.0241 mT. In comparison to the peak-to-peak linewidth of around 0.033 mT this fit is rather poorer than that expected for inherent scatter in data points (ideally $\text{RMSD} \leq \frac{1}{3}$ peak-to-peak linewidth) but the precision of principal directions, table 1, is considered very good and we did not attempt to remeasure any data points.

Table 1. Spin-Hamiltonian parameters for RT^a and $[\text{AlO}_4]^{0-}$ centres: site 1 at about 10 K^b.

		Matrix Y		Principal values		Principal directions ^c	
				k	Y_k	θ_k ($^\circ$)	ϕ_k ($^\circ$)
<i>(a)</i> $[\text{AlO}_4]^{0-}$ centre							
\bar{g}	2.044 04(2)	0	-0.014 95(2)	1	2.051 73(2)	117.22(2)	0
		2.004 81(2)	0	2	2.014 98(2)	152.75(2)	180
			2.022 67(2)	3	2.004 81(2)	90	90
$\bar{A}({}^{27}\text{Al})/g_c\beta_c$ (mT)	-0.7412(19)	0	-0.0631(17)	1	-0.6735(19)	137.0(6)	0
		-0.8198(17)	0	2	-0.8001(20)	133.0(6)	180
			-0.7325(15)	3	-0.8198(17)	90	90
$\bar{Q}({}^{27}\text{Al})/g_c\beta_c$ (mT)	-0.1065(12)	0	0.0175(8)	1	0.0276(11)	158.4(1.2)	180
		-0.0041(18)	0	2	-0.0041(18)	90	90
			0.0207(14)	3	-0.0235(11)	68.4(1.2)	180
<i>(b)</i> RT centre							
\bar{g}	2.008 05(2)	0	-0.002 86(2)	1	2.013 40(3)	28.2(1)	180
		2.005 04(1)	0	2	2.006 52(3)	118.2(1)	180
			2.011 86(1)	3	2.005 04(3)	90	90

^a Data from Claridge *et al* (1994).

^b Error estimates in parentheses.

^c Angle θ measured from c and angle ϕ in a counterclockwise direction from a .

4. Discussion

Solntsev and Shcherbakova (1973) described their so-called $[\text{AlO}_4]^{4-}$ EPR spectrum in γ -irradiated natural zircon, which we believe to be the same as the species reported herein, as

an electron-hole centre, with the defect located on a ligand O position, interacting with a ^{27}Al nucleus located in an adjacent Si lattice position. All experimental evidence presented here, and the comparative results of Nuttall and Weil (1981a) for α quartz, is in agreement with this description. Consideration of stoichiometric charges for initially electrically neutral $[\text{Zr}^{4+}][\text{SiO}_4^{4-}]$ pairs subsequently balanced by compensating Al^{3+} for Si^{4+} replacement and electron removal by irradiation leads to a labelling of the centre as $[\text{AlO}_4]$, as in α quartz, and we shall subsequently label the centre accordingly. In the unirradiated sample, the Al centre is generally thought to involve a +1 compensator, H^+ , Na^+ or Li^+ . In α quartz, Nuttall and Weil (1981a, b) have observed the compensated centre, $[\text{AlO}_4/\text{M}^+]^+$, when the crystal is irradiated and transferred cold to the EPR cavity. The formation of the trapped electron-hole means that the +1 compensator is no longer necessary and, upon warming the crystal, it moves away; the $[\text{AlO}_4/\text{M}^+]^+$ centres disappear leaving only $[\text{AlO}_4]^0$. In zircon we have never observed a +1 compensated site inferring that either the compensation is remote or that the compensator is able to diffuse away even at 77 K. We note that in α quartz the +1 compensator is not invariably observed in cold transfer samples (Nuttall and Weil 1981b).

The g and ^{27}Al A principal values given by Solntsev and Shcherbakova (1973) agree in magnitude with those of table 1, although contrary to their results, and in agreement with the expectations of a monoclinic site, the A matrix is not uniaxial. The g tensor principal directions given by these authors also do not agree with table 1. We noted earlier (Claridge *et al* 1994), in the case of the $\text{Zr}^{3+}(\alpha)$ centre, that Solntsev and Shcherbakova (1973) appeared to have wrongly identified axes: their g -tensor principal axes and ours are related by a 45° rotation about c . There is however no such simple relation between the g tensor principal directions for $[\text{AlO}_4]^0$ and we believe the directional data reported by these authors to be in error. They did not report principal directions for the ^{27}Al A and Q tensors and we believe that our present data are new. We have followed Nuttall and Weil (1981a) in assigning a negative value to the isotropic part of the ^{27}Al A matrix, taken to agree with the sign of the Fermi contact interaction, when the signs of all three principal values are negative. The signs of $Q(^{27}\text{Al})$ are then known relative to those of A so that the sign of the electric field gradient at ^{27}Al is positive as found for the comparable centre in α quartz. All three interaction matrices have in common one principal direction, the crystallographic b axis in the case of site 1 (table 1), but the principal directions in the plane perpendicular to b are non-coaxial as would be generally expected of a monoclinic site.

The $[\text{AlO}_4]^0$ centre was produced by irradiation at 77 K. On warming above 77 K the lines of the centre broaden and disappear but reappear on cooling. After some hours at higher temperatures the signals are irreversibly destroyed. We earlier reported two single electron-hole centres in x-irradiated zircon, each with monoclinic site symmetry. One, labelled D, was only measurable below 77 K and decayed irreversibly as the temperature was raised above this. The second centre, labelled RT, was found to be stable at elevated temperatures. The $[\text{AlO}_4]^0$ centre also evidently arises from an electron-hole trapped at a site of Laue class $2/m$ and it is reasonable to assume that this site would be one of the O ligand sites each of which has point group symmetry m . The Si sites also have point group symmetry m so that the interaction matrices of ^{27}Al substituting for Si would be expected to exhibit monoclinic symmetry, as observed. The rather similar behaviour of the RT centre and the $[\text{AlO}_4]^0$ centre makes it interesting to compare the spin-Hamiltonian parameters for the two. This is done in table 1. Direct comparisons between the two centres are best made in terms of the relations of each to structural features of the ZrSiO_4 lattice. This is outlined in table 2 and described below. Crystallographic data were taken from the book by Wyckoff (1965).

Table 2. $[\text{AlO}_4]^0$ principal directions in relation to crystal bond directions^a.

g matrix			Hole-centre at O(1) (0.32, 0, 0.07)			
g_k	θ_k	ϕ_k	direction to	$r(\text{\AA})$	θ	ϕ
2.05174	117.2	0	bisector O(2)–Zr(2)	—	118.8	0
2.01498	152.8	180	O(3)	2.49	159.5	180
2.00481	90	90	O(5)	3.36	78.8	90
$A(^{27}\text{Al})$ matrix			Al replacement at Si(1) ($\frac{1}{2}, 0, \frac{1}{4}$)			
A_k	θ_k	ϕ_k	direction to	$r(\text{\AA})$	θ	ϕ
–0.6735	137.0	0	O(2)	1.61	131.5	0
–0.8001	133.0	180	O(1)	1.61	131.5	180
–0.8198	90	90	bisector Zr(3)–Si(4)	—	90	90
$Q(^{27}\text{Al})$ matrix			Al replacement at Si(1) ($\frac{1}{2}, 0, \frac{1}{4}$)			
Q_k	θ_k	ϕ_k	direction to	$r(\text{\AA})$	θ	ϕ
0.0276	158.4	180	bisector O(1)–Zr(2)	—	155.8	180
–0.0041	90	90	bisector Zr(3)–Si(4)	—	90	90
–0.0235	68.4	180	Si(2)	3.66	65.8	180

^a Fractional coordinates of some atoms in parentheses.

The unit cell structure of zircon consists of alternating SiO_4^{4-} tetrahedra and Zr^{4+} ions along the crystallographic c axis (fourfold screw axis). Each Zr^{4+} ion is surrounded by eight O^{2-} ions from the SiO_4^{4-} groups arranged as two distorted tetrahedra of short (2.131 Å) and long (2.268 Å) bonded oxygens. In the unit cell there are four ZrO_8 and four SiO_4^{4-} groups each set of which are both crystallographically and magnetically equivalent; both have $42m(D_{2d})$ point group symmetry (the label $42m$ given for this site in Claridge *et al* (1994) is a typographical error).

In the following discussion we need refer only to the various parameter matrices for site 1. The atoms to which we shall refer are illustrated in figure 1, part of the zircon unit cell. The RT centre has been described, Claridge *et al* (1994), as an electron–hole trapped at the short-bonded ligand O(1) when the g_1 and g_2 principal directions lie respectively 4° away from the O(1)–Zr(2) direction and 13.1° away from the O(1)–Si(1) direction. The third principal direction, as required by symmetry, lies along b and 11.2° away from the O(1)–O(5) direction. If the $[\text{AlO}_4]^0$ centre is also regarded as arising from an electron–hole trapped at the same short-bonded O atom, O(1), then figure 1(a) and table 2, g_2 lies 6.7° away from the O(1)–O(3) direction and g_1 lies 1.6° away from the bisector to O(2) and Zr(2). The two g tensors have in common the symmetry direction b and are related by a 55.4° counterclockwise rotation about this common axis.

The principal directions of the A_{Al} and Q_{Al} tensors can similarly be sensibly related (see figure 1(b), (c) and table 2) to local structural features when O(1) is regarded as the electron–hole trapping site interacting with a ^{27}Al nucleus replacing Si(1) at an adjacent site, fractional coordinates ($\frac{1}{2}, 0, \frac{1}{4}$) and distance 1.61 Å. Thus (see figure 1(b)) A_2 lies 1.5° away from the direction joining Al(Si(1) in figure 1) to O(1), the proposed site of the trapped hole. A_1 lies 5.5° away from the Al–O(2) direction. We note that if the AlO_4 tetrahedron distorted in such a way to accommodate these principal directions exactly along Al–O bond directions, then this needs to be merely an in-plane (e.g., ac plane in this instance) distortion to retain the point group symmetry m of the site and the observed monoclinic symmetry in the A tensor.

The two larger Q_{Al} principal values, Q_1 and Q_3 , also have their principal directions in the ac plane (see figure 1(c)). Q_1 , the largest, does not however lie along the Al–O(1)

direction (it is actually 23.3° away from this direction) but rather lies 2.6° away from the bisector to atoms O(1)–Zr(2). In the $[\text{AlO}_4]^0$ centre in α quartz the electric field gradient is dominated by the electron-hole, and Q_z (the largest-magnitude principal value of the Q matrix) points exactly at the short-bonded O atom at which the hole is trapped. In the present instance, however, the electric field gradient is influenced clearly by both the trapped hole and also by the adjacent Zr^{4+} ion. Q_3 lies 2.6° away from the Al–Si(2) direction. Q_2 and A_3 have in common the symmetry direction b which is also the bisector of Zr(3)–Si(4).

There is also another significant difference between the interaction matrices of $[\text{AlO}_4]^0$ in α quartz and zircon. In α quartz the twofold symmetry of the Al(Si)–O₄ ideal quartz site is lowered to triclinic by the presence of the trapped hole at one of the short-bonded oxygens. Nevertheless, the symmetry approximates reasonably to uniaxial as evidenced by the magnitude of the asymmetry parameter $\eta = (Q_1 - Q_2)/Q_3 = 0.184$ (η is zero for exactly uniaxial symmetry); Nuttall and Weil (1981a) refer to Q_3 as the 'unique' principal value. In zircon in this work, however, the monoclinic symmetry of the Al(Si) site is, within error, retained but the distortion from uniaxial symmetry is very significant, $\eta = 0.703$ (the maximum distortion from uniaxial symmetry occurs when $Q_1 = -Q_3$, $Q_2 = 0$ and $\eta = 1$). It is evident that the Q tensor centred at Al(Si(1)) is dominated by in-plane interactions with neighbouring Zr(2), O(1) (the site of the electron-hole) and Si(2) all of which are coplanar in the ac plane. The third principal value, Q_2 in this case, required by symmetry to lie along b , is close to zero magnitude.

Comparison of the isotropic part of the ^{27}Al hyperfine matrix, $a = \frac{1}{3}(\text{Tr } \bar{A})$, with the atomic parameter A^c from table 1 of Morton and Preston (1978) suggests that there is negligible delocalization of the hole spin density to the ^{27}Al nucleus: even a 1% delocalization would produce an isotropic hyperfine matrix with approximately correct magnitudes but positive sign whereas we have taken the values to be negative. In this we have followed Nuttall and Weil (1981a) in arguing that the negative sign for a arises from core polarization when g_N is positive. The dipolar contributions to $\bar{A}(^{27}\text{Al})$ may however be influenced by the trapped hole in a non-bonding p orbital of the oxygen. In the absence of observable ^{17}O hyperfine structure it is not yet possible to carry out a detailed analysis of the distribution of the spin density as attempted by Nuttall and Weil (1981a). However the similar magnitudes of \bar{g} , $\bar{A}(^{27}\text{Al})$ and $\bar{Q}(^{27}\text{Al})$ matrices for the $[\text{AlO}_4]^0$ centres in both α quartz and zircon give confidence to the assumption that the non-observed $\bar{A}(^{17}\text{O})$ matrix will also be similar, and that the hole spin density resides in a non-bonding p orbital of the trapping O atom. In α quartz Nuttall and Weil (1981a) showed that $\approx 80\%$ is in the non-bonding p orbital.

If the O atom, O(1) (figure 1) is bonded by approximately sp^2 hybrid orbitals to the neighbouring coplanar Zr(2), Zr(1) and Si(1) atoms, then there will be a non-bonding p orbital available perpendicular to this plane to trap the electron hole. In α quartz the principal direction of the smallest magnitude g value is almost coincident with the 'unique' direction of $\bar{A}(^{17}\text{O})$, the assumed axis of non-bonding p orbital. In zircon, the minimum magnitude g principal direction is a symmetry direction and therefore must also be a principal axis of $\bar{A}(^{17}\text{O})$ and by analogy with α quartz, can be assumed to be the 'unique' principal direction of $\bar{A}(^{17}\text{O})$. Our present studies indicate, however, that on the EPR time scale, the average position of the hole is in-plane since *all* measured tensors for the $[\text{AlO}_4]^0$ centre are within experimental error, monoclinic.

Acknowledgments

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