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## 10 K electron paramagnetic resonance of a $d^1$ $\text{Ti}^{3+}$ centre in x-irradiated zircon (zirconium silicate)

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**Abstract.** A  $d^1$   $\text{Ti}^{3+}$  centre formed by x-irradiation of a synthetic zircon single crystal at 77 K has been studied by electron paramagnetic resonance (EPR) at 10 K. The  $\text{Ti}^{3+}$  ion occupies a substitutional site of point group symmetry  $\bar{4}2m$  ( $D_{2d}$ ). Absence of both site splitting in general crystal orientations and of superhyperfine structure from a +I ion indicated that a nearby charge compensator was not involved. Comparison with EPR measurements on  $\text{Ti}^{3+}/\alpha$  quartz centres, point charge calculations and  $^{29}\text{Si}$  hyperfine splittings indicated that the  $\text{Ti}^{3+}$  centre results from electron capture by  $\text{Ti}^{4+}$  occupying a  $\text{Zr}^{4+}$  site in the crystal; the designation  $[\text{TiO}_8]^-$  is suggested. Precise spin-Hamiltonian parameters, including  $^{47}\text{Ti}$  ( $I = \frac{5}{2}$ , 7.4%) and  $^{49}\text{Ti}$  ( $I = \frac{7}{2}$ , 5.4%) hyperfine, nuclear electric quadrupole and nuclear Zeeman parameter matrices, together with high-spin nuclear terms of dimension  $I^4$ ,  $I^3S$ ,  $I^5S$ ,  $BI^3$  and  $BI^5$  were determined. The set of terms  $BI$ ,  $BI^3$  and  $BI^5$  were found to be crucial in obtaining a good fit to the many 'forbidden' hyperfine lines observed. This resulted in determination of nuclear quadrupole and nuclear Zeeman parameters with precisions not hitherto attained in conventional single-crystal EPR measurements.

### 1. Introduction

This is the third paper in a series which attempts to produce precise interaction parameters to describe the environment of a paramagnetic ion in the microregion about the impurity centre in synthetic irradiated zircon,  $\text{ZrSiO}_4$ . Previously we have described the parameters for the  $\text{Zr}^{3+}(\alpha)$  and two oxygen-hole centres (Claridge *et al* 1994a) and the oxygen-hole  $[\text{AlO}_4]^0$  centre (Claridge *et al* 1994b). The  $\text{Zr}^{3+}(\alpha)$  and  $[\text{AlO}_4]^0$  centres have previously been reported by Solntsev and Shcherbakova (1973) but not with the degree of precision that is now possible and is exemplified by measurement of a wide variety of paramagnetic centres in  $\alpha$ -quartz (Weil (1984) and references therein) and other crystals of practical importance, such as calcium tungstate,  $\text{CaWO}_4$  (McGavin and Tennant 1985).

In this paper we detail 9 GHz EPR measurements of a  $d^1$   $\text{Ti}^{3+}$  centre at about 10 K in synthetic zircon. Our motives in repeating the measurements for this system earlier reported by Solntsev and Shcherbakova (1972) were several. Firstly, we wished to measure accurately the nuclear parameters via the  $^{47,49}\text{Ti}$  hyperfine and nuclear electric quadrupole interaction matrices; the former of these have previously only been determined approximately and the latter, as far as we are aware, had not measured at all. Comparison with EPR data for the centres  $[\text{TiO}_4]^-$  (Bailey *et al* 1992),  $[\text{TiO}_4/\text{Li}]_{\text{A,B}}^0$  (Isoya *et al* 1988, Bailey and Weil 1992) and  $[\text{TiO}_4/\text{H}]_{\text{A,B}}^0$  (Rinneberg and Weil 1972) in  $\alpha$ -quartz, for which the parameters were

all well determined, would possibly enable us to identify the centre as a compensated or non-compensated site. It was hoped also, to identify unambiguously the site of the impurity ion.

There have been a number of EPR studies of  $d^1$  ions, notably of  $Ti^{3+}$ ,  $V^{4+}$  and  $Nb^{4+}$ , in crystals such as  $\alpha$ -quartz and tetragonal crystals of the scheelite and zircon structures. The quartz work has been summarized in a review by Weil (1984) and includes centres  $[TiO_4/M^+]^0$  ( $M = H, Li, Na$ ) and  $[TiO_4]^-$ . In quartz Ti replaces Si and analysis of the  $\bar{g}$  and  $^{47,49}Ti$   $\bar{A}$ -parameter matrices establishes the ground state as predominantly  $3d_{z^2}$ . For  $d^1$  ions in zircon on the other hand (Solntsev and Shcherbakova 1972, Di Gregorio *et al* 1980, 1982) the ground states are apparently  $3d_{xy}$  but the site of the impurity ion is less certain since the two possibilities, replacement of either  $Si^{4+}$  or  $Zr^{4+}$ , have the same point group symmetry,  $42m$  ( $D_{2d}$ ), and it is not possible *a priori* to say which of these is the substitutional site. Di Gregorio *et al* (1982), on the basis of EPR and optical evidence, assigned  $d^1 V^{4+}$  to the 'tetrahedral' Si site while Di Gregorio *et al* (1980) assigned  $d^1 Nb^{4+}$  to the 'dodecahedral' Zr site.

## 2. Experimental details

The details of the Varian E12 spectrometer and the crystal goniometer and cryogenic system have been described earlier (Claridge *et al* 1994a). The crystal was cut to a parallelepiped ( $3.5 \times 5.5 \times 2.0$  mm) with faces parallel to the crystallographic  $a$ ,  $b$ , and  $c$  axes of the tetragonal (space group  $I4_1/amd$ ) crystal system. The crystal was irradiated at 77 K with x-rays from a W tube and transferred cold to the previously cooled Displex head of the cavity goniometer system. The alignment of the crystal was confirmed by observing the previously determined  $Zr^{3+}(\alpha)$  and  $[AlO_4]^0$  centres each of which collapse from three symmetry-related species in planes containing the tetragonal axis to a single species for  $B||c$ . The Displex cooler was then turned off and the cavity filled with He gas for efficient heat transfer. The crystal was allowed to warm for one hour to near room temperature, then recooled to 10 K for further EPR measurements. The heat treatment removed all evidence of the  $Zr^{3+}(\alpha)$  and  $[AlO_4]^0$  centres as well as other, as yet unreported centres. The two principal centres remaining were the B ( $Ti^{3+}$ ) centre and an as yet unreported centre which we have labelled C (see figure 1 of Claridge *et al* (1994a)). The B ( $Ti^{3+}$ ) and C centres could then be measured almost free of interference from other centres. Measurements were carried out at  $5$ – $10^\circ$  angular intervals in two planes, (110) and (100), containing the fourfold screw axis  $c$ . Angles were determined to within two minutes of arc and the magnetic field was measured with a Bruker Gaussmeter to  $\pm 0.002$  mT.

## 3. Results

The spectrum with the static magnetic field parallel to the tetragonal  $c$  axis consisted of a strong central line due to the even-mass-number (spinless) Ti isotopes ( $^{46}Ti$  8.0%,  $^{48}Ti$  73.7%,  $^{50}Ti$  5.3%) flanked by an octet of lines due to the two odd-mass-number Ti isotopes  $^{47}Ti$  ( $I = \frac{5}{2}$ , 7.5%) and  $^{49}Ti$  ( $I = \frac{7}{2}$ , 5.5%). Measurement of the relative intensities of the lines confirmed beyond question the assignment to a paramagnetic Ti species. The position of the spectrum in relation to other species in x-irradiated zircon is shown in the  $c$ -axis spectrum, before heat treatment, in figure 1 of Claridge *et al* (1994a). After annealing the B ( $Ti^{3+}$ ) (for which we shall subsequently suggest the label  $[TiO_8]^-$ ) and C centres were the only dominant spectral features. The intensity of the ( $Ti^{3+}$ ) centre was essentially

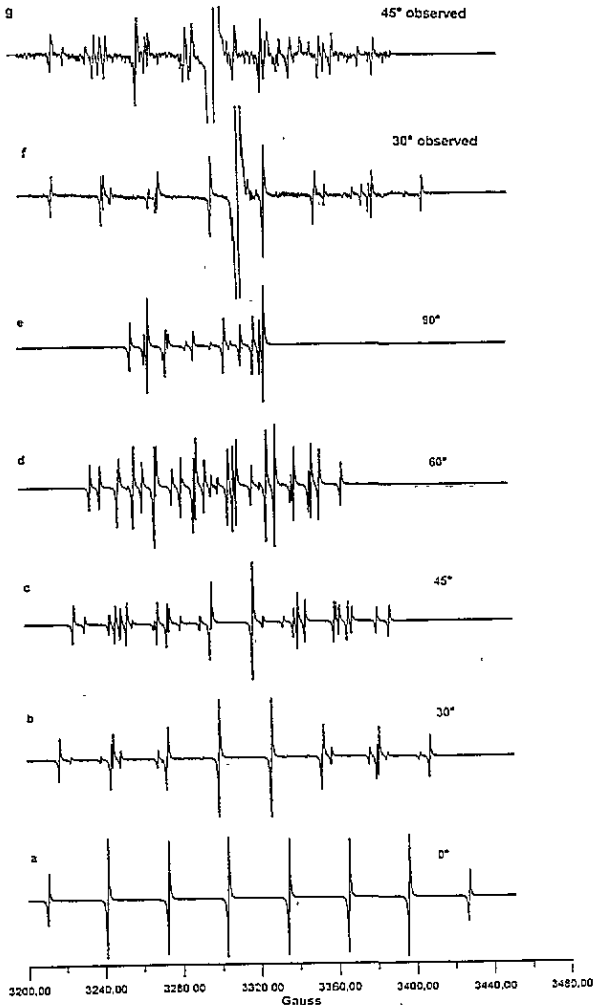


Figure 1. Calculated and experimental spectra for the  $d^1 \text{Ti}^{3+} [\text{TiO}_6]^-$  centre in zircon. (a)–(e): computer-simulated spectra for  $\text{Ti}^{47}$  ( $I = \frac{5}{2}$ , 7.4%) and  $\text{Ti}^{49}$  ( $I = \frac{7}{2}$ , 5.4%) in the (100) plane with  $B$  at various angles to the  $c$  axis. The data from tables 1 and 2 were used in the calculation. For clarity the central line for  $I = 0$  has not been included. (f), (g): experimental spectra in the (100) plane with  $B$  at  $30^\circ$  and  $45^\circ$  to the  $c$  axis.

unchanged following heat treatment.

In general crystal orientations only a single  $\text{Ti}^{3+}$  spectrum was observed, so the site of the paramagnetic ion must have the same Laue class as that of the host crystal (Rae 1969); the symmetry of the site is consequently necessarily uniaxial with the unique axes of each of the interaction matrices lying along the tetragonal  $c$  axis. In these circumstances one requires, in principle, only two crystal orientations to obtain all relevant spin-Hamiltonian (SH) parameters. However, we have followed our normal procedures in ensuring that all parameter interaction matrices are considerably over-determined. In fact we found it necessary, as outlined in the experimental section, to carry out measurements at  $5\text{--}10^\circ$  intervals in two crystal planes, (110) and (100). There were reasons other than the precision

of the parameter matrix determinations for this: firstly the  $^{47,49}\text{Ti}$  hyperfine lines were rather weak and the intensity fell away rapidly as the crystal was rotated away from the  $c$  axis; with  $B \perp c$  the intensities were approximately an order of magnitude lower. In intermediate orientations, because of the relative magnitudes of nuclear electric quadrupole and hyperfine interactions, 'forbidden' hyperfine lines with rather large intensity were observed which were sometimes stronger than the so-called 'allowed' transitions (see figure 1). There was therefore some doubt as to the correct assignment of the lines for crystal orientations more than about  $30\text{--}40^\circ$  from the  $c$  axis and we found it necessary to make assignments by performing successive cycles of refinement and simulation adding a new set of data for each orientation angle. As will be pointed out below, our values for the perpendicular components of the  $^{47,49}\text{Ti}$  hyperfine tensors are considerably smaller than those reported by Solntsev and Shcherbakova (1972) and we believe that their values of  $A_\perp$  to be in error, probably because of misassignment of lines in the perpendicular orientation of the crystal. The spin Hamiltonian used in the analysis was

$$\mathcal{H} = \beta_e S \cdot \bar{g} \cdot B + S \cdot \bar{A} \cdot I + I \cdot \bar{P} \cdot I - \beta_N I \cdot \bar{g}_N \cdot B + \text{extra terms} \quad (1)$$

where the terms have their normal meanings and the extra terms are detailed below. The matrices  $\bar{g}_N$  for  $^{47,49}\text{Ti}$  were taken initially to be respectively the matrices  $-0.31539 \mathbf{U}$  and  $-0.315477 \mathbf{U}$  where  $\mathbf{U}$  is the  $3 \times 3$  unit matrix. For uniaxial symmetry equation (1) can be further simplified since the parameter matrices  $\bar{g}$ ,  $\bar{A}$ ,  $\bar{P}$  and  $\bar{g}_N$  are necessarily all diagonal, together with the usual uniaxiality relationships. However, we did not impose uniaxial symmetry on our data until the magnitudes of off-diagonal matrix elements had been checked. Equation (1) is therefore the appropriate SH to use.

For  $S = 1/2$  and  $I > 2$ , symmetry-allowed terms of the form  $I^4$ ,  $SI^3$ ,  $SI^5$  may be added to equation (1). These are expressed (McGavin *et al* 1989) in terms of tesseral combinations of spherical tensor operators, the coefficients being expressed in the form  $B_{4,m}^{0,0,4} (I^4)$ ,  $B_{l,m}^{0,1,3} (SI^3)$  and  $B_{l,m}^{0,1,5} (SI^5)$  ( $l = 2, 4$ ;  $m = 0, 4$ ). Only the tetragonal symmetry terms with  $m = 0, 4$  need be retained for Laue class  $4/mmm$  (see McGavin *et al* (1990) for details). There are thus two  $I^4$ , three  $SI^3$  and four  $SI^5$ —i.e., a total of nine—extra symmetry-allowed terms which may be considered when  $I = \frac{5}{2}$  or  $I = \frac{7}{2}$ . The rationale for considering inclusion of such terms for the present experiments is outlined later when the necessity of including further symmetry-allowed high-spin terms is also discussed.

Data were analysed, as in our earlier papers in this series, using the matrix diagonalization least-squares program EPR developed by the University of Saskatchewan Group (McGavin *et al* 1989). Data from 14 crystal orientations in each of the (110) and (100) planes were refined as follows. For even isotopes: 46 unit-weighted data points with root mean square deviation (RMSD) between calculated and observed resonant fields equal to 0.0087 mT; for  $^{47}\text{Ti}$ : RMSD over 201 unit-weighted data points equal to 0.0146 mT; for  $^{49}\text{Ti}$ : RMSD over 202 unit-weighted data points equal to 0.0174 mT. Linewidths ( $lw$ ) ranged from about 0.02 mT ( $B \parallel c$ ) to 0.08 mT ( $B \perp c$ ). The RMSD is therefore in the range  $1/3 lw \leq \text{RMSD} \leq lw$ , so the fit is on average to within the inherent scatter in the data. The SH parameters so obtained are listed in tables 1 and 2.

#### 4. Discussion

The unit cell structure (see Wyckoff 1965) of zircon consists of alternating  $\text{SiO}_4^{4-}$  tetrahedra and  $\text{Zr}^{4+}$  ions along the crystallographic  $c$  axis (the fourfold screw axis). Each  $\text{Zr}^{4+}$  ion is surrounded by eight  $\text{O}^{2-}$  ions from the  $\text{SiO}_4^{4-}$  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  $\text{ZrO}_8$

**Table 1.** SH parameters for the (Ti<sup>3+</sup>) centre at about 10 K with error estimates in parentheses.

	Matrix $\bar{Y}$	Principal values <sup>a</sup>	
		$Y_{\parallel}$	$Y_{\perp}$
Even isotopes, $I = 0$	$\bar{g}$	1.926 83(1)	1.940 67(1)
No of unit-weighted data points= 46			
RMSD= 0.0087 mT			
<sup>47</sup> Ti, $I = \frac{5}{2}$	$\bar{g}$	1.926 86(1)	1.940 66(2)
	$\bar{g}_N$	-0.417(118)	-0.267(25)
	$\bar{A}/g_e\beta_e$ (mT)	2.9768(8)	0.8453(30)
	$\bar{P}/g_e\beta_e$ (mT)	-0.1698(5)	0.0849(3)
No of unit-weighted data points= 201			
RMSD= 0.0146 mT			
<sup>49</sup> Ti, $I = \frac{7}{2}$	$\bar{g}$	1.926 83(1)	1.940 66(2)
	$\bar{g}_N$	FV <sup>b</sup>	FV <sup>b</sup>
	$\bar{A}/g_e\beta_e$ (mT)	2.9700(9)	0.8459(5)
	$\bar{P}/g_e\beta_e$ (mT)	-0.0667(10)	0.0334(5)
No of unit-weighted data points= 202			
RMSD= 0.0174 mT			

<sup>a</sup> The parallel values,  $Y_{\parallel}$ , lie along the  $c$  axis.

<sup>b</sup> FV fixed at  $1.00028 \times$  <sup>47</sup>Ti values.

and four SiO<sub>4</sub><sup>4-</sup> groups each set of which are both crystallographically and magnetically equivalent; both have  $\bar{4}2m$  (D<sub>2d</sub>) point group symmetry.

The B (Ti<sup>3+</sup>) centre arises, as does the earlier-reported Zr<sup>3+</sup>( $\alpha$ ) centre (Solntsev and Shcherbakova 1973, Claridge *et al* 1994a), from the capture of an electron by a substitutional Ti<sup>4+</sup> ion following x-irradiation at 77 K. The question as to which of the possible tetragonal substitutional sites, Zr or Si, is occupied by Ti<sup>3+</sup> we defer until later in the discussion. It seems, because of lack of observable evidence of a charge compensator, that the centre can be labelled as either [TiO<sub>8</sub>]<sup>-</sup> or [TiO<sub>4</sub>]<sup>-</sup>. However, we note that in  $\alpha$ -quartz the equivalent [TiO<sub>4</sub>]<sup>-</sup> centre is unstable relative to the alkali-metal-compensated centres [TiO<sub>4</sub>/M]<sup>0</sup> formed when the crystal is warmed. In zircon the observed centre is stable to ambient temperatures. Evidently, either the (Ti<sup>3+</sup>) centre in zircon is more stable, or there are no alkali ions or protons available in the structure to act as compensators. The latter is a distinct possibility since the synthetic zircon is grown in a high-temperature melt (Chase and Osmer 1966) whereas  $\alpha$ -quartz synthetic crystals are normally grown hydrothermally.

From the data of table 1 it is clear that the (Ti<sup>3+</sup>) centre reported here has distinctly different parameters to that of the [TiO<sub>4</sub>]<sup>-</sup> centre in  $\alpha$ -quartz. (We note that in  $\alpha$ -quartz the various Ti centres all exhibit C<sub>2</sub> symmetry but the parameters are in all cases not too distorted from uniaxial. We can therefore reasonably compare the 'unique' principal values with the 'parallel' principal values in zircon.) The principal  $g$ -values follow the expectation of different ground states for the two systems: predominantly  $d_{z^2}$  in  $\alpha$ -quartz but predominantly  $d_{xy}$  (or  $d_{x^2-y^2}$ , see below) in zircon. Thus, from table 1,  $g_{\parallel} < g_{\perp}$  while in  $\alpha$ -quartz the 'unique'  $g$ -value is the greatest. The principal  $A$ -values are even more disparate. In zircon,  $A_{\parallel} (> A_{\perp})$  is the larger while in  $\alpha$ -quartz the 'unique'  $A$ -value is ' $A_{\parallel}$ ' ( $\ll A_{\perp}$ ). One cannot infer therefore, from a comparison of these parameters, that Ti<sup>3+</sup> occupies the same type of site, i.e., the SiO<sub>4</sub> 'tetrahedron' in each case. Indeed the widely different values of the hyperfine principal values might lead one to opt for Zr<sup>4+</sup> as the substitutional site for Ti in zircon. The same pattern of relative magnitudes of  $g$ -

**Table 2.** Values of high-spin parameters  $B_{l,m}^{I_B J_S J_I}$  for  $^{47,49}\text{Ti}$  at about 10 K, with error estimates in parentheses.

	$^{47}\text{Ti} (I = \frac{5}{2})$		$^{49}\text{Ti} (I = \frac{7}{2})$	
(a) Terms of dimension $I^4 (\times 1/g_e \beta_e \text{ (mT)})$	$B_{4,0}^{0,0,4}$	$B_{4,4}^{0,0,4}$	$B_{4,0}^{0,0,4}$	$B_{4,4}^{0,0,4}$
	-0.0009(3)	0.0005(10)	-0.0034(2)	-0.0012(4)
(b) Terms of dimension $SI^3 (\times 1/g_e \beta_e \text{ (mT)})$	$B_{l,0}^{0,1,3}$	$B_{l,4}^{0,1,3}$	$B_{l,0}^{0,1,3}$	$B_{l,4}^{0,1,3}$
$l = 2$	0.011(9)	—	0.065(8)	—
$l = 4$	0.012(9)	0.19(5)	0.058(7)	0.19(1)
(c) Terms of dimension $SI^5 (\times 1/g_e \beta_e \text{ (mT)})$	$B_{l,0}^{0,1,5}$	$B_{l,4}^{0,1,5}$	$B_{l,0}^{0,1,5}$	$B_{l,4}^{0,1,5}$
$l = 4$	0.004(5)	0.09(6)	0.015(1)	0.06(1)
$l = 6$	0.005(6)	0.02(2)	0.011(1)	0.055(6)
(d) Terms of dimension $BI^3$ (unitless)	$B_{l,0}^{1,0,3}$	$B_{l,4}^{1,0,3}$	$B_{l,0}^{1,0,3}$	$B_{l,4}^{1,0,3}$
$l = 2$	-0.055(7)	—	-0.063(3)	—
$l = 4$	-0.016(5)	-0.018(13)	-0.006(3)	-0.042(8)
(e) Terms of dimension $BI^5$ (unitless)	$B_{l,0}^{1,0,5}$	$B_{l,4}^{1,0,5}$	$B_{l,0}^{1,0,5}$	$B_{l,4}^{1,0,5}$
$l = 4$	0.025(6)	-0.023(11)	0.021(1)	-0.012(1)
$l = 6$	0.020(6)	0.052(7)	0.009(1)	0.028(1)

and  $A$ -values is also found in the  $\text{Zr}^{3+}(\alpha)$  centre found in irradiated zircon (Claridge *et al* 1994a).

The principal  $g$ - and  $A$ -values may be analysed by a crystal-field/ligand-field approach as has been done by other authors for  $d^1$  and  $d^9$  ions; the principles are those outlined by McGarvey (1969). The axis system is chosen conventionally with the highest-fold rotation axis as  $z$ , the fourfold screw axis in the zircon case, which then necessarily defines the orientation of the  $d_{z^2}$  orbital. The choice of  $x, y$  axes is at the disposal of the experimenter and determines which of  $d_{xy}$  or  $d_{x^2-y^2}$  becomes the ground state under  $D_{2d}$  symmetry. We follow Prather (1961) and Golding (1969) in choosing the usual dodecahedral axes (i.e.,  $x$  as one of the twofold axes) when the  $d_{x^2-y^2}$  ( $B_1$  representation) is the ground state; a rotation by  $45^\circ$  about  $z$  sees  $x$  and  $y$  coinciding with the tetragonal  $a$  and  $b$  axes and the ligand atoms are contained in the  $xz, yz$  planes; in this case  $d_{xy}$  (the  $B_2$  representation) is lowest. The ligand-field treatment produces identical  $g$ - and  $A$ -values for the two cases (see Golding (1969), pp 289–94). For the  ${}^2B_1$  ground state one obtains:

$$g_{\parallel} = g_e - 8\zeta/\Delta E_1 \quad (2)$$

$$g_{\perp} = g_e - 2\zeta/\Delta E_2 \quad (3)$$

$$A_{\parallel} = -\mathcal{P}[4 + 7(g_e - g_{\parallel}) + 3(g_e - g_{\perp}) + 7\kappa]/7 \quad (4)$$

$$A_{\perp} = \mathcal{P}[4 - 11(g_e - g_{\perp}) - 14\kappa]/14 \quad (5)$$

where  $g_e = 2.0023$ ,  $\zeta$  is the spin-orbit coupling constant,  $\Delta E_1 = E_{xy} - E_{x^2-y^2}$ ,  $\Delta E_2 = E_{xz,yz} - E_{x^2-y^2}$ , and  $\kappa$  is treated as a parameter; the product  $\mathcal{P}\kappa$  ( $= K$  in the later discussion) is the isotropic contact term and  $\mathcal{P} = g_e g_N \beta_e \beta_N \langle r^{-3} \rangle_{3d}$ . We have followed common practice and replaced the orbital coefficients in equations (4) and (5) by the equivalent  $g$ -values obtained from equations (2) and (3).

As a preliminary to this analysis, we follow the Morton and Preston (1978) procedure and compare the isotropic and anisotropic parts of the experimental hyperfine tensors to the theoretical parameters  $A^c$  and  $P^d$  respectively. From table 1,  $A_{iso} = (A_{\parallel} + 2A_{\perp})/3 = 44.06$  MHz and the anisotropic parameter  $b_{3d} = 19.70$  MHz. Then from table 1 of Morton and Preston (1978) the spin-density contributions are: for Ti 4s,  $44.06/782.0 = 0.056$  (5.6%); and for Ti 3d,  $19.7/((2/7) \times 73.64) = 0.936$  (93.6%). Therefore, based on this analysis,  $\sim 100\%$  of the spin density lies on the  $\text{Ti}^{3+}$  ion and the bulk (93.6%) is in the d orbital.

So far as we are aware no optical study of  $\text{Ti}^{3+}$  in zircon has been carried out, so the relevant crystal-field splittings are not available. If one takes the splittings  $\Delta E_1 = 13\,600$   $\text{cm}^{-1}$  and  $\Delta E_2 = 6\,400$   $\text{cm}^{-1}$  obtained by Di Gregorio *et al* (1982) for  $d^1 V^{4+}$  in zircon as order-of-magnitude approximations, then with  $\zeta = 154$   $\text{cm}^{-1}$ , the free-ion value, one obtains from equations (2) and (3),  $g_{\parallel} = 1.912$  and  $g_{\perp} = 1.954$  in reasonable, but not good, agreement with the experimental values (table 1). The generally observed condition for a  $d_{x^2-y^2}$  ground state,  $g_{\parallel} < g_{\perp} < g_e$ , is however apparent.

Treating the ratios  $\zeta/\Delta E_{1,2}$  as adjustable parameters and using the experimental  $g$ -values from table 1, we obtain, from equations (2) and (3) with  $\zeta = 154$   $\text{cm}^{-1}$ ,  $\Delta E_1 = 16\,324$   $\text{cm}^{-1}$  and  $\Delta E_2 = 4\,997$   $\text{cm}^{-1}$ . These could be modified by orbital reduction, leading to a decrease in the effective spin-orbit coupling constant, and by Jahn-Teller distortion in the  ${}^2E$  ( $d_{xz,yz}$ ) excited states. Jahn-Teller splitting of the  ${}^2E$  excited states is not possible under  $D_{2d}$  symmetry and the effects of a dynamic Jahn-Teller effect, as discussed by Di Gregorio *et al* (1982) for  $V^{4+}$  in zircon, would, we believe, be very small in our case due to the very small mixing coefficients of the excited states (the coefficients are  $\zeta/\Delta E_1 = 0.0094$  and  $\zeta/\Delta E_2 = 0.0154$  respectively for the  ${}^2B_2$  and  ${}^2E$  states). A 20% decrease in the free-ion spin-orbit coupling constant would, however, give  $\Delta E_1 = 13\,060$   $\text{cm}^{-1}$  and  $\Delta E_2 = 3\,990$   $\text{cm}^{-1}$ .

Turning next to the hyperfine interaction constants, equations (4) and (5), we first treat both  $\mathcal{P}$  and  $K = \mathcal{P}\kappa$  as adjustable parameters and obtain from the experimental  $A$ -values of table 1  $\mathcal{P}/hc = -24.84 \times 10^{-4}$   $\text{cm}^{-1}$  and  $K/hc = -25.93 \times 10^{-4}$   $\text{cm}^{-1}$ .  $\mathcal{P}$  is in good agreement with the theoretical value of  $P_{3d} = \mu_0 g_e g_N \beta_e \beta_N \langle r^{-3} \rangle_{3d}/4\pi = -23.61 \times 10^{-4}$   $\text{cm}^{-1}$  (Isoya *et al* 1988). Alternatively, if one substitutes the theoretical value  $P_{3d}$  in equations (4) and (5), and the above value for  $K$ , one obtains  $A_{\parallel} = 2.950$  mT and  $A_{\perp} = 0.946$  mT in good agreement with experiment.

The  $P$ -tensor values of table 1 agree rather well in magnitude with those for the  $[\text{TiO}_4]^-$  centre in  $\alpha$ -quartz but have the opposite sign. The sign of  $P$  is, from the fittings, known to be relative to that of  $A$ , assumed here to be positive following Rinneberg and Weil (1972). The ratio  ${}^{47}P_{\parallel}/{}^{49}P_{\parallel}$  is 2.27 compared to 2.54 obtained from the ratios of the corresponding quadrupole moments which are proportional to  $Q/[I(2I-1)]$ . Isoya *et al* (1988) obtained also 2.27 for this ratio in their study of  $[\text{TiO}_4/\text{Li}]_A^0$  centre and speculated that the difference between the  $P$ -ratio and that obtained from the quadrupole moments may arise from neglect of higher-order terms of dimension  $I^4$ ,  $SI^3$  and  $SI^5$ . We have included these terms in our analysis since, for the  $4/mmm$  Laue class of the  $\text{Ti}^{3+}$  site in zircon, the required number of



terms is small. From table 2, terms in  $I^4$  are significant but terms in  $SI^3$  and  $SI^5$  are only occasionally larger than the errors in their measurement and there is only a small ( $< 1\%$ ) diminution in the RMSD resulting from their inclusion.

We also investigated the effects of varying  $g_N$ , initially constrained as isotropic, in some of the refinements. Surprisingly, there was a significant diminution in the RMSD ( $> 10\%$ ) and some 'forbidden' hyperfine lines which seemed to show systematic errors, outside the precision of the overall fit, were now well fitted; the refined  $g_N$ -values were around zero. We could not accept that the linear nuclear Zeeman interaction alone was directly responsible for these observations. Rather, we believed that terms of dimension  $BI^3$  and  $BI^5$ , also allowed on symmetry grounds (see McGavin *et al* 1990) when  $I > 2$ , also needed to be included in the SH analysis. We had not previously considered  $BI^3$ - and  $BI^5$ -terms to be of importance for systems with  $I > 2$  since they would be expected to provide only a small perturbation on an already small linear nuclear Zeeman interaction. (It should be pointed out that terms of dimension  $BSI^2$  and  $BSI^4$  are also symmetry allowed in the SH when  $I \geq 2$ . As outlined in McGavin *et al* (1990), these terms involve decomposition of triple-vector spherical tensor operators,  $T_{l,m}(B, S, I)$ . The decompositions are not unique and have not, so far as we are aware, been carried out; the terms were consequently not available to us using the program EPR. In a negative sense we can say that an excellent fit to our data was obtained in their absence, but we cannot discount the possibility that an even better (or perhaps different) fit would be obtained when they were included.)

$BI^3$ - and  $BI^5$ -terms are also not yet included in the program EPR, but we were able to obtain refined values for the SH parameters arising from them by the following 'subterfuge'. If one interchanges the spins  $S$  and  $I$  in the program EPR—i.e., treats the  $S = \frac{1}{2}$ ,  $I = \frac{5}{2}$ ,  $\frac{7}{2}$  systems as  $S = \frac{5}{2}$ ,  $\frac{7}{2}$ ,  $I = \frac{1}{2}$  then the correspondences given in table 3 apply.

Table 3. Correspondences.

$S = \frac{1}{2}, I > 2$		$S > 2, I = \frac{1}{2}$
Term/term type	Term/term type	Apparent/actual parameter matrix
$\beta_e B \cdot \bar{g} \cdot S$	$\beta_e B \cdot \bar{g}' \cdot I$	$\bar{g}' = \bar{g}_N \beta_N / \beta_e$
$I \bar{A} S$	$S' \bar{A}' I$	$\bar{A}' = \bar{A}$
$-\beta_N B \cdot \bar{g}_N \cdot I$	$-\beta_N B \cdot \bar{g}_N' \cdot S$	$\bar{g}_N' = \bar{g} \beta_e / \beta_N$
—	$S' \bar{D}' S$	$\bar{D}' = \bar{P}$
$I \bar{P} I$	—	—
$I^4: B_{l,m}^{0,0,4}$	$S^4: B_{l,m}^{0,4,0}$	$B_{l,m}^{0,4,0} = B_{l,m}^{0,0,4}$
$SI^3: B_{l,m}^{0,1,3}$	$S^3 I: B_{l,m}^{0,3,1}$	$B_{l,m}^{0,3,1} = B_{l,m}^{0,1,3}$
$SI^5: B_{l,m}^{0,1,5}$	$S^5 I: B_{l,m}^{0,5,1}$	$B_{l,m}^{0,5,1} = B_{l,m}^{0,1,5}$
$(BI^3: B_{l,m}^{1,0,3})$	$BS^3: B_{l,m}^{1,3,0}$	$B_{l,m}^{1,3,0} = B_{l,m}^{1,0,3} \beta_N / \beta_e$
$(BI^5: B_{l,m}^{1,0,5})$	$BS^5: B_{l,m}^{1,5,0}$	$B_{l,m}^{1,5,0} = B_{l,m}^{1,0,5} \beta_N / \beta_e$

As a check on this procedure we initially held the 'new'  $BI^3$ -,  $BI^5$ -parameters at zero and allowed all other new parameters to vary; we obtained a completely identical fit to that obtained with the 'old' parameter set. The  $BI^3$ - and  $BI^5$ -parameters were then allowed to vary. The values of these parameters are listed in parts (d) and (e) of table 2. They are generally significant (mean error of estimation: 18%) and in general the agreement between the  $^{47}\text{Ti}$  and  $^{49}\text{Ti}$  values is within the combined errors for the two.

We finally allowed  $\bar{g}_N$ —now, as demanded by site symmetry, constrained to be uniaxial—to vary using the data for the  $I = \frac{5}{2}$  isotope. There was a further small diminution in the RMSD and a small, but 'sensible', departure from isotropic values (see table 1).  $\bar{g}_N$

can also be expressed in irreducible tensor form using the relations given in equations [26] of McGavin *et al* (1990). Thus uniaxial  $\bar{g}_N$  is expressed in terms of two coefficients  $B_{0,0}^{1,0,1}$  and  $B_{2,0}^{1,0,1}$ , which are found to be 0.546 and  $-0.097$  respectively. The first is given by the relation  $B_{0,0}^{1,0,1} = -\text{Tr}(\bar{g}_N)/\sqrt{3}$  and this may be compared to the accepted nuclear value  $-(3 \times -0.31539)/\sqrt{3} = 0.54627$ .

We shall not speculate here as to the meanings of the parameters, but we believe that they are real on three grounds: (i) their inclusion results in  $\sim 20\%$  diminution in the RMSD; (ii) the fit of previously poorly fitted forbidden hyperfine lines is generally now within  $\pm$ RMSD; and (iii) the ratio  $^{47}P_{\parallel}/^{49}P_{\parallel}$  became  $2.55 \pm 0.05$  in excellent agreement with the 'correct' value  $2.54 \pm 0.18$  obtained from nuclear measurements (Channapa and Pendlebury 1965, Gabathuler and Hundt 1971).

The presence of high-spin terms of the forms used in this paper affects the spectra in a number of ways. There is a predicted angular dependence of lines in the (001) plane, arising from fourth- and sixth-rank tensors, which would be absent in the presence of only second-rank tensors in the SH. Unfortunately, we were unable to check this angular dependence in any detail because the spectra were too weak in the perpendicular orientation of the crystal; in addition some of the lines whose calculated shifts were greatest had transition probabilities calculated to be zero. For the six lines checked in the perpendicular orientation in the (110) plane for the  $^{47}\text{Ti}$  isotope the shifts in line positions due to high-spin terms were as predicted to within  $\pm$ RMSD; the numerical values of the shifts were in the range 0.04–0.09 mT (i.e.,  $(2.7\text{--}6.2) \times \text{RMSD}$ ). Most affected by the presence of high-rank tensors are the forbidden hyperfine lines; there are also smaller shifts in all lines in all crystal orientations except  $B \parallel c$ , being maximal for  $B \perp c$ . Fortunately, the choice of (100) and (110) planes of measurement turned out by calculation to be those—for the present combination of terms—where the shifts due to high-spin terms are most sensitive. Again for the  $^{47}\text{Ti}$  isotope data, 56 of 135 transitions in the (110) plane and 27 of 100 in the (100) plane were forbidden lines. In the absence of high-spin terms the mean deviation of these forbidden lines was 0.034 mT and the RMSD over all lines was 0.0277 mT. With high-spin terms included the RMSD was halved (0.0146 mT) and the mean deviation of forbidden lines was within  $\pm$ RMSD.

It should be emphasized that values of the  $g_N$ -parameters (constrained to be uniaxial) in table 1 are obtained *only* in combination with refinement of coefficients of higher-order terms of dimension  $BI^3$ ,  $BI^5$ . The set of terms of dimension  $BI$ ,  $BI^3$ ,  $BI^5$  may be regarded collectively as describing the nuclear Zeeman interaction where the first term is the *linear* nuclear Zeeman term and the second and third terms are the high-spin nuclear Zeeman terms. There is an obvious 1:1 correspondence to the electronic Zeeman terms  $BS$ ,  $BS^3$ ,  $BS^5$  which are detailed in McGavin *et al* (1990) and which have proved to be of considerable importance in a recent low-temperature study of  $\text{Fe}^{3+}$  in calcium tungstate (present authors, manuscript in preparation).

The rather large nuclear electric quadrupole interaction has its most marked effect in the production of 'forbidden' hyperfine lines in all crystal orientations except  $B \parallel c$ . This is illustrated in figures 1, (a)–(e), showing computer-simulated spectra, obtained using the parameters of tables 1 and 2, with the static magnetic field at angles  $0^\circ$ ,  $30^\circ$ ,  $45^\circ$ ,  $60^\circ$ , and  $90^\circ$  to the  $c$  axis in the (100) plane; at  $60^\circ$  the forbidden lines predominate. Figures 1(f) and 1(g) showing the experimental spectra obtained at  $30^\circ$  and  $45^\circ$ . There is obviously very good agreement with the corresponding simulated spectra.

It remains to assign the impurity paramagnetic ion to either the Zr or the Si substitutional site. We believe the former is the correct assignment on four grounds. Firstly, as already

discussed, there is no correspondence between the  $[\text{TiO}_4]^-$  parameters in  $\alpha$ -quartz with those in zircon. The site symmetries are of course different— $C_2$  for  $\alpha$ -quartz and  $D_{2d}$  for zircon—but the  $\text{SiO}_4$  'tetrahedra' in each case are very similar. Secondly, on the basis of crystal ionic radii ( $\text{Si}^{4+}$ , = 0.42 Å;  $\text{Zr}^{4+}$ , = 0.79 Å;  $\text{Ti}^{4+}$ , = 0.68 Å) the Zr site would again seem to be more likely, although it is clear from the  $\alpha$ -quartz example that Ti certainly *can* substitute for Si. Di Gregorio *et al* (1982) have argued convincingly for  $\text{V}^{4+}$  (0.63 Å) for  $\text{Si}^{4+}$  substitution, but  $\text{Nb}^{4+}$  (0.74 Å) for  $\text{Zr}^{4+}$  substitution in zircon; the crystal ionic radius of  $\text{Ti}^{4+}$  is intermediate between these two.

The third ground is based on point charge calculations for the possible sites. We carried out point charge calculations for both the  $\text{SiO}_4$  'tetrahedron' and the  $\text{ZrO}_8$  'dodecahedron' using the ideal, undistorted, crystallographic atom positions (data from Wychoff 1965) and the procedure outlined by Hutchings (1964) to obtain the crystal-field splittings in each case. The d-orbital energies are obtained in the form

$$E(d_\alpha) = (vp + w)(\langle r^4 \rangle / a^5) e^2 Z' \quad (6)$$

where  $\alpha = z^2, yz, xz, xy$  or  $x^2 - y^2$ ;  $p = a^2 \langle r^2 \rangle / \langle r^4 \rangle$  with  $a = 2.13$  Å (4.02 au) for  $\text{ZrO}_8$  and 1.61 Å (3.04 au) for  $\text{SiO}_4$ ;  $\langle r^2 \rangle$  and  $\langle r^4 \rangle$  are the radial expectation values for the d orbitals. Following Golding (1969) (p 184) we evaluate the ratio  $p$  using the Slater 3d radial function for  $\text{Ti}^{3+}$  as an approximation; this gives  $p = 2.057$  for  $\text{ZrO}_8$  and  $p = 1.175$  for  $\text{SiO}_4$ . From the tables of relativistic Hartree–Fock–Slater eigenvalues given by Lu *et al* (1971),  $\langle r^2 \rangle_{3d} = 2.5952$  au and  $\langle r^4 \rangle_{3d} = 18.6969$  au from which we obtained  $p = 2.2486$  for  $\text{ZrO}_8$  and  $p = 1.2847$  for  $\text{SiO}_4$ . (These tabulations of  $\langle r^2 \rangle$ ,  $\langle r^4 \rangle$  are in fact for free atoms, but comparison of the Hartree–Fock 3d basis functions for  $\text{Ti}^{3+}$  and  $\text{Ti}^0$  indicates that the error involved is small.) The energy levels in units of  $(\langle r^4 \rangle / a^5) e^2 Z'$  using these latter values are plotted in figures 2(a) and 2(c) for  $\text{ZrO}_8$  and  $\text{SiO}_4$  respectively; for the latter the levels are scaled by a factor  $(1.61/2.13)^5$ . Alternatively,  $p$  can be treated as a parameter to be obtained from experiment. From the observed  $g$ -values and equations (2) and (3) we obtain  $\Delta E_1 / \Delta E_2 = 3.2668$  for the  $\text{ZrO}_8$  'dodecahedron' and 0.0654 for the  $\text{SiO}_4$  'tetrahedron' (the value calculated using the Hartree–Fock–Slater radial expectation values and equation (6) is 2.3847). Then using equation (6) we obtained  $p = 1.7814$  for  $\text{ZrO}_8$  whence the calculated energy levels are as depicted in figure 2(b). One cannot apply a similar procedure to  $\text{SiO}_4$  because the calculated value of the parameter  $p$  is negative, which is clearly impossible. The reliability of such point charge calculations is open to question but it is clear that the  $\text{ZrO}_8$  dodecahedron agrees moderately well with observation while the  $\text{SiO}_4$  tetrahedron does not.

Finally, the observed hyperfine structure is qualitatively in agreement with the Zr substitutional site. Each Ti in a Zr site would be expected to interact with two types of Si. Taking Zr as the centre of symmetry, fractional coordinates [000], there are two equivalent Si atoms at positions  $[00 \pm \frac{1}{2}]$  and distance 2.99 Å bound by bridging long-bonded (2.27 Å) O atoms and four equivalent Si atoms at positions  $[\pm \frac{1}{2} 0 \frac{1}{4}]$ ,  $[0 \pm \frac{1}{2} 0]$  and distance 3.63 Å bound by non-bridging short-bonded (2.13 Å) O atoms. In most crystal orientations in the planes of measurement, no hyperfine structure was observed on the intense line of the spinless  $\text{Ti}^{3+}$  isotopes, implying splittings  $\leq$  the linewidth,  $\sim 0.05$  mT. At  $30^\circ$  to the  $c$  axis in the (100) plane (see figure 1(f)) two pairs of weak hyperfine transitions were observed with splittings of approximately 0.5 and 0.25 mT and with intensities roughly in accord with that expected for  $^{29}\text{Si}$  (natural abundance 4.6%). The tables of Morton and Preston (1978) show that the isotropic contribution to spin density from such Si hyperfine splittings would be negligible and that the previously unaccounted for spin density of around 1% would be completely accounted for by anisotropic parameters,  $b$ , of 0.04 and 0.02 mT respectively.

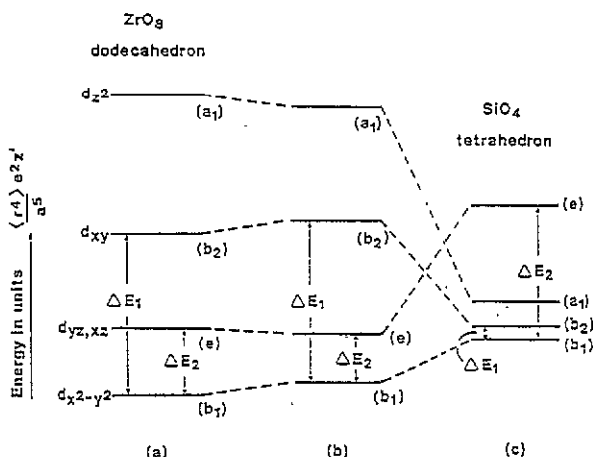


Figure 2. Calculated crystal-field splittings: (a)  $ZrO_8$  dodecahedron; (b)  $ZrO_8$  dodecahedron splittings obtained using observed  $g$ -values (see the text for details); (c)  $SiO_4$  tetrahedron.

These latter are reasonable upper-limit estimates of unresolved anisotropic splittings.

We suggest in conclusion that the  $Ti^{3+}$  centre discussed herein should henceforth be assigned the label  $[TiO_8]^-$ .

## Appendix A.

During refereeing, one of the referees remarked that our description led one to the conclusion that  $g_N$  and  $BI^3$ ,  $BI^5$  appeared correlated and pointed out, correctly, that this would be unacceptable for orthogonal tensors. That these parameters are not in fact correlated is easily shown: examination of the variance-covariance matrix in the output from the program EPR showed that the covariances between  $g_N$  and  $BI^3$ ,  $BI^5$  were very small indeed, indicating negligible correlation.

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