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Two Ti^{3+} centres studied by X-band electron paramagnetic resonance at 10 K in zircon

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Abstract. Two previously unreported Ti^{3+} paramagnetic centres have been observed in zircon (zirconium silicate, ZrSiO_4) and studied by X-band electron paramagnetic resonance at ≈ 10 K. The first of these is shown to arise from a Ti^{3+} electron-trap centre where Ti substitutes into one of the Si^{4+} sites, point group symmetry $42m$ (D_{2d}), of the tetragonal crystal. A full spin-Hamiltonian analysis of the centre is given. The second centre arises from Ti^{3+} substituting for Zr^{4+} in the lattice and interacting with a 100% spin- $I = \frac{1}{2}$ nucleus, probably ^{31}P , in a nearby lattice site, thought to be a next-nearest-neighbour Si site. The point group symmetry of the site of this centre is 2 (C_2).

1. Introduction

We have reported in recent papers [1–3] detailed 10 K X-band electron paramagnetic resonance (EPR) studies of two Ti^{3+} centres in zircon single crystals. The first of these, labelled B(Ti^{3+}) and originally reported by Solntsev and Shcherbakova [4], was shown [1] to form following x-irradiation at 77 K, and electron capture by a Ti^{4+} substituting for Zr^{4+} in the crystal. The designation $[\text{TiO}_8]^-$ was suggested. A further more detailed study and more precise analysis [2] showed that the nuclear interactions of the $I = 5/2, 7/2$ quadrupolar nuclei of the $^{47,49}\text{Ti}$ isotopes required inclusion of terms of dimension BI^k, SI^k ($k = 3, 5$) in the spin Hamiltonian (SH) to describe the spectrum adequately. The parameters arising from these terms were found to be very much larger than observed previously for first-row transition ions. The second centre, reported in [3], also arises from a Ti^{3+} electron-trap centre associated with a Zr substitutional site. This centre exhibited hyperfine structure, apparently from a Y^{3+} ion substituted in the nearest-neighbour Zr site. We shall refer to the centre herein, following [3], as the Y centre. The designation $[\text{TiO}_8/\text{Y}]^-$ was suggested in [3] to describe the centre more completely.

The existence of the Y centre raised the possibility of further types of centre with Y^{3+} and Ti^{3+} in combination. Firstly, centres may be formed which have the Ti^{3+} in a Zr^{4+} site and the associated Y^{3+} ion in a next-nearest-neighbour Zr (as distinct from nearest-neighbour Zr as in the Y centre) site or, possibly, more remote sites. Centres in which the Ti^{3+} substitutes in the Si^{4+} site are also possibilities. We have subsequently begun a series of experiments to prepare and dope synthetic zircon crystals with various metal ions with a view to preparing and characterizing such centres.

We detail EPR measurements on a hitherto unreported Ti^{3+} electron-trap paramagnetic centre, labelled herein Si(Ti^{3+}), which was observed in some of the crystals doped with Ti

and subsequently x-irradiated at 77 K. This centre will be shown to originate from Ti^{3+} in a Si^{4+} lattice position, suggesting the designation $[\text{TiO}_4]^-$. A further previously unobserved centre, labelled P in figure 1 of [3], has also been analysed and is here reported. This centre is believed to be a Ti^{3+} centre situated at a Zr lattice position interacting with a nearby 100% $I = \frac{1}{2}$ nucleus; the interacting nucleus is most probably ^{31}P .

2. Experimental details

The P centre was observed in a nominally undoped zircon crystal supplied by Aerospace Corporation, CA, grown from molten $\text{Li}_2\text{SiO}_3\text{-MoO}_3$ as described by Chase and Osmer [5]. Defects in this crystal have been the subject of several earlier studies by the authors (see reference [1] and other references therein). As described, the number and nature of the paramagnetic defects observed depends on the previous heat treatment of the crystal, the type and temperature of the irradiation to which it is subjected, any subsequent heating and the temperature at which EPR observations are made. The $\text{Si}(\text{Ti}^{3+})$ centre was observed in a more recently synthesized crystal grown in an identical fashion, but with additional Ti^{4+} and Y^{3+} doping. This was achieved through the addition of 0.1 mol% TiO_2 and Y_2O_3 to the growth mixture. The undoped crystal used for the P-centre studies was in the form of a parallelepiped (dimensions $5.5 \times 3.5 \times 2$ mm) with rectangular faces parallel to the crystallographic a -, b - and c -axes of the tetragonal (space group $I4_1/amd$) system. The doped crystal was not cut, because it had natural faces parallel to the ac - and bc -planes which allowed precise alignments for the experimental measurements. The crystal orientation was confirmed by x-ray crystallography.

Details of the Varian E12 spectrometer, crystal goniometer and cryogenic system have been described earlier [1]. Both crystals were irradiated for one hour at 77 K with x-rays from a tungsten tube (45 mA, 50 kV) and transferred cold to the previously cooled Displex head of the cavity goniometer system. Alignment of the crystal was confirmed by observing the previously determined $\text{Zr}^{3+}(\alpha)$ and $[\text{AlO}_4]^0$ centres each of which collapse from three symmetry-related species in planes containing the tetragonal axis to a single species for $B \parallel c$. Under these conditions the $\text{Si}(\text{Ti}^{3+})$ centre was readily observable in the Ti/Y-doped crystal. The Displex cooler was 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 re-cooled to 10 K for further measurements.

As observed in all earlier experiments on zircon crystals, this heat treatment removed most of the $\text{Zr}^{3+}(\alpha)$ centre and usually all of the $[\text{AlO}_4]^0$ centre but, in the doped crystal, also removed most of the $\text{Si}(\text{Ti}^{3+})$ centre. In contrast, the intensity of the P centre, in the undoped crystal, was largely unaffected by the above process. It was found that for determination of the g -matrix of the P centre, the removal of other centres by warming was desirable to minimize interference.

Measurements were carried out at 5–10° angular intervals in the bc -plane of both crystals. These data, from the doped crystal, were sufficient to characterize completely the $\text{Si}(\text{Ti}^{3+})$ centre. For the P centre further data were collected from the undoped crystal in planes obtained by rotating the crystal by 30°, 45° and 60° from b about c (hereafter these planes are referred to simply as the 30°, 45° and 60° planes respectively). Rotation angles were determined to within two minutes of arc. The magnetic field was measured with a Bruker Gaussmeter to ± 0.002 mT and the microwave frequency with a Systron Donner 6016 counter to ± 1 kHz.

3. Results

Figure 1 shows the 10 K X-band EPR spectra of the new $Si(Ti^{3+})$ centre and the earlier-reported [1, 2] $B(Ti^{3+})$ centre. The centre labelled H refers to an as-yet unidentified electron centre which may or may not be associated with one or more of the Ti centres. The relative positions of the $B(Ti^{3+})$, Y and P centres are shown in figure 1 of [3].

3.1. The $Si(Ti^{3+})$ centre

No site splitting was observed in any orientation in the crystal bc -plane, so the Ti impurity ion must occupy a site with tetragonal symmetry, i.e., must lie on one of the 4_1 axes of the tetragonal $I4_1/amd$ crystal space group. Observation of hyperfine multiplets corresponding to $I = 5/2$ and $I = 7/2$ with intensity ratios appropriate to the 47 and 49 isotopes of Ti (see figure 1) established beyond doubt that the EPR spectra did arise from Ti^{3+} . ‘Forbidden’ hyperfine lines, found to be crucial in the detailed analysis of the $B(Ti^{3+})$ centre [1, 2], were sought in intermediate orientations in the bc -plane, but none were found. Furthermore, the ^{47}Ti ($I = 5/2$) and ^{49}Ti ($I = 7/2$) isotope hyperfine lines were always, within experimental precision, coincident, except as regards the outermost ^{49}Ti lines.

The spectra were analysed using the matrix-diagonalization least-squares program EPRNMR developed by the University of Saskatchewan EPR group [6] and the SH

$$\mathcal{H} = \beta_e \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S} + \mathbf{I} \cdot \mathbf{P} \cdot \mathbf{I} - \beta_n \mathbf{B} \cdot \mathbf{g}_n \cdot \mathbf{I}. \quad (1)$$

The interaction matrices \mathbf{g} , \mathbf{A} , \mathbf{P} are in this instance necessarily diagonal and uniaxial. The matrices \mathbf{g}_n were set to the isotropic values for $^{47,49}Ti$: $-0.31539 \mathbf{U}$ and $-0.315477 \mathbf{U}$

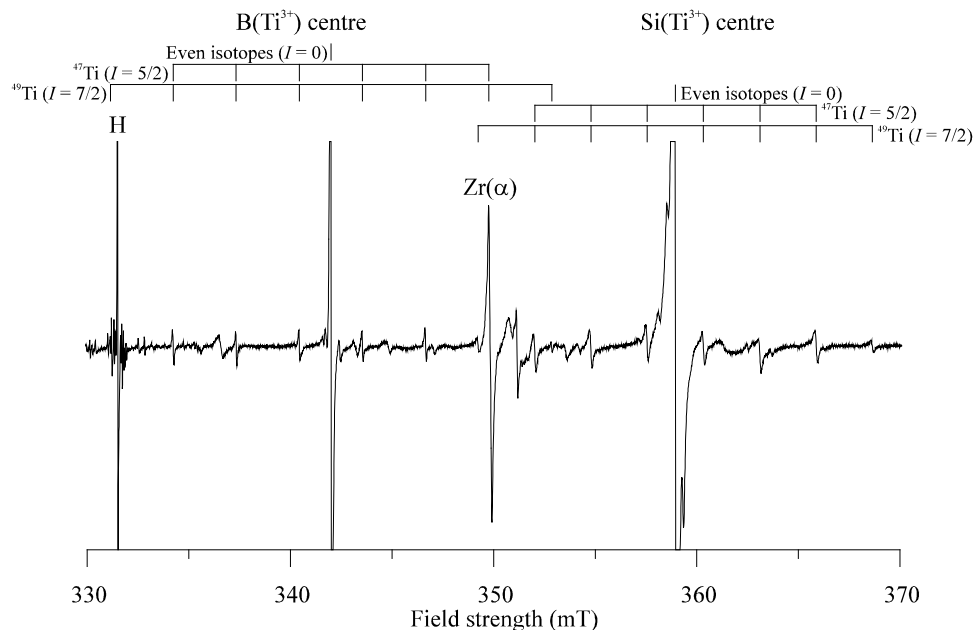


Figure 1. The c -axis spectrum at ≈ 10 K and 9.224 GHz depicting the relative positions of the $Si(Ti^{3+})$ and $B(Ti^{3+})$ centres. Hyperfine transitions for both centres are shown. The centre labelled H is an as-yet uncharacterized electron centre. The g -factors for H, $Si(Ti^{3+})$ and $B(Ti^{3+})$ are respectively 1.9931, 1.9337 and 1.8524.

Table 1. SH parameters for the Si(Ti³⁺) at ≈ 10 K; error estimates are given in parentheses.

Matrix \mathbf{Y} :	⁴⁷ Ti parameters, principal values		⁴⁹ Ti parameters, principal values		Spinless isotopes, principal values	
	Y_{\parallel}	Y_{\perp}	Y_{\parallel}	Y_{\perp}	Y_{\parallel}	Y_{\perp}
g	1.83615(1)	1.98061(1)	1.83615(1)	1.98047(1)	1.83617(2)	1.98055(2)
A / $g_e\beta_e$ (mT)	2.5299(9)	0.7274(12)	2.5302(7)	0.7268(10)		
P / $g_e\beta_e$ (mT)	0.0157(20)	-0.0078(10)	0.0067(18)	-0.0034(9)		
g_n	-0.31539	-0.31539	-0.315477	-0.315477		
Data points	138		184		23	
Unit-weighted data points	96		127		22	
RMSD (mT)	0.0113		0.0141		0.0081	

respectively, where \mathbf{U} is the 3×3 unit matrix. Data sets for the 47 and 49 Ti isotopes and the spinless isotopes were refined separately; the SH parameters are listed in table 1. One might question the reliability of the ⁴⁹Ti parameters of table 1 since, as noted above, the data set used differs from that of ⁴⁷Ti only in respect of the outer two lines of the ⁴⁹Ti multiplets. In the absence of any hyperfine anomaly [7], the corresponding hyperfine matrices would be expected to differ only as the ratio of their isotropic nuclear g -factors, i.e., $^{49}A = 1.00028^{47}A$. The calculated ⁴⁹ A -values are then $A_{\parallel} = 2.5306$ mT, $A_{\perp} = 0.7276$ mT which, within error, agree nicely with the fitted parameters. Similarly, in the absence of pseudo-nuclear electric quadrupolar effects [7] such as are observed for the B(Ti³⁺) centre [1, 2], the nuclear quadrupole interaction matrices would be expected to be related by [1, 2, 8] $^{47}P/^{49}P = (21/10)^{47}Q/^{49}Q$ where the Q s are the respective nuclear quadrupole moments. The calculated ⁴⁹ P -parameters are then $P_{\parallel} = 0.0060$ mT and $P_{\perp} = -0.0030$ mT, again in good agreement with the fitted values.

3.2. The P centre

From the site splittings observed in specific crystal planes, the site of the P centre evidently has point group symmetry $2 (C_2)$, or very close to this: two twofold-degenerate lines were observed for all crystal orientations in the bc -plane. In the 30° , 45° and 60° planes of the undoped crystal four, three and four lines respectively were observed in general orientations. The point group symmetry, $2 (C_2)$, differs importantly from those of nearly all other non-uniaxial paramagnetic centres in zircon so far studied. Most of the many oxygen hole centres reported in the literature have point group symmetry $m (C_s)$ where the (implied) twofold axis lies along the crystal a - or b -axes, i.e., perpendicular to the mirror planes containing the paramagnetic centres. In this laboratory all centres hitherto studied exhibit either uniaxial (tetragonal) symmetry or point group symmetry m [1, 2, 3, 10].

For the P centre the twofold axis lies along the crystal [110] direction, one of the two dihedral twofold axes of the zircon structure. These point group symmetries, $2 (C_2)$ and $m (C_s)$, are contained in the same Laue class, $2/m (C_{2h})$. Since the paramagnetic species has $2/m$ Laue class, the data can be refined and all parameters obtained from data collected in a single plane of measurement using the method of symmetry-related sites [9]. As discussed in [10], the appropriate 3×3 proper rotation matrices relating the symmetry-related sites are, for a site with $2/m$ Laue class in a tetragonal crystal, those of the C_4 proper rotation group, while noting that the full proper rotation group is D_4 . These matrices are listed in table II of reference [9]. The SH to be used is again equation (1). Since ^{47,49}Ti hyperfine structure

was not measured, there is no nuclear quadrupole term included and nuclear spin I refers to a 100% abundant nucleus which, as discussed later, we consider to be ^{89}Y or ^{31}P . The g_n -matrix in equation (1) is then set to the corresponding isotropic g_n -matrix. See table 2.

Table 2. SH parameters for the P centre at ≈ 10 K; the error estimates are given in parentheses.

	Matrix \mathbf{Y}	k	Principal values, Y_k	Principal directions			
				θ_k (deg)	ϕ_k (deg)		
\mathbf{g}	1.936005(5)	0.0	0.018066(4)	1	1.963878(3)	42.51(0)	315
	1.936005(5)	-0.018066(4)		2	1.936005(5)	90	45
		1.940460(4)		3	1.912587(3)	132.51(0)	315
$\mathbf{A}^{(31}P)/g_e\beta_e$ (mT)	0.126(6)	0	0.0017(13)	1	0.126(6)	89.4(1)	315
	0.126(6)	-0.0017(13)		1	0.126(6)	90	45
		-0.0819(9)		3	-0.082(1)	179.4(6)	315
$\mathbf{g}_n(^{31}P)$	2.26320	0	0				
		2.26320	0				
			2.26320				

To identify the P centre as arising unequivocally from Ti, one needs to be able to locate and measure the 47 and/or 49 Ti isotope hyperfine lines. c -axis data were collected with a very long accumulation time. While some pairs of lines were observed, they could not be assigned unambiguously to Ti hyperfine structure. However, even in the absence of definitive hyperfine evidence, it is reasonable to infer that the centre is a Ti centre because of the similarity of the g -matrix principal-value magnitudes and anisotropy to those observed for other Ti centres in zircon [1–3]. The experimental principal g -values, both considerably less than 2.0023, eliminate the possibility that the species is a hole centre.

4. Discussion

4.1. The $Si(Ti^{3+})$ centre

The EPR spectrum in this instance clearly corresponds to an ion in a lattice position with uniaxial point group symmetry. The site of the impurity Ti must therefore be one or other of the Zr or Si positions in the unit cell each of which has dodecahedral, $\bar{4}2m$ (D_{2d}), point group symmetry. An analysis of the $B(Ti^{3+})$ g - and A -values based on a ligand-field model, point charge calculations of energy levels and inferences drawn from observed superhyperfine structure [1] led to the conclusion that Ti replaced Zr in the crystal. From the relative magnitudes of the g - and A -values of the $Si(Ti^{3+})$ centre (table 1), the ground state is again $d_{x^2-y^2}$ ($\sim b_1$) and a similar analysis can be used. From [1, 2], the equations relating g - and A -values to the orbital levels under D_{2d} point group symmetry are, to second order in the perturbation [2, 11],

$$g_{\parallel} = g_e(N^2 - 4yN - x^2 + y^2) \quad (2)$$

$$g_{\perp} = g_e(N^2 - xN + xy - y^2) \quad (3)$$

$$A_{\parallel} = -\mathcal{P}(4N^2 + 56yN + 6xN + 8x^2 + 4y^2 + 6xy + 7\kappa)/7 \quad (4)$$

$$A_{\perp} = \mathcal{P}(2N^2 - 11xN + 11xy - 2y^2 - 7\kappa)/7 \quad (5)$$

where $N = (1 - \frac{1}{2}x^2 - y^2)^{1/2}$, $x = \zeta/\Delta E_2$, $y = \zeta/\Delta E_1$ and $\mathcal{P}\kappa$ is the isotropic contact interaction where $\mathcal{P}_{3d} = \mu_0 g_e g_N \beta_e \beta_N \langle r^{-3} \rangle_{3d}/4\pi$ and κ is a parameter representing core

polarization of the s electrons (see [2] for further details). $\Delta E_1 = E_{b_2} - E_{b_1}$, $\Delta E_2 = E_c - E_{b_1}$ and ζ is the free-ion spin-orbit coupling constant. Since the orbital reduction factors are not known, x and y are treated as parameters to be obtained from the experimental g -values and equations (2), (3). Following the procedures detailed in [2], equations (2) and (3) were solved iteratively to obtain x and y from the experimental g -values and then \mathcal{P} and κ obtained from equations (4), (5) using the experimental A -values. The parameters so obtained, together with some related derived quantities, are listed in table 3. For comparison, the corresponding values for B(Ti³⁺) are also listed in table 3.

Table 3. Electronic and nuclear properties derived from equations (2)–(6) and the g - and A -values of table 1.

Quantity	Si(Ti ³⁺) ⁴⁷ Ti isotope ^b	B(Ti ³⁺) ^a ⁴⁷ Ti isotope
ζ/Δ_1	0.02073	0.03036
ζ/Δ_2	0.01022	0.00908
Δ_1^c	7430 cm ⁻¹	16967 cm ⁻¹
Δ_2^c	15064 cm ⁻¹	5072 cm ⁻¹
\mathcal{P}	-16.5628×10^{-4} cm ⁻¹	-21.3081×10^{-4} cm ⁻¹
κ	0.6807	0.6325
$\langle r^{-3} \rangle_{3d}$	1.6476 au	2.1227 au
$\mathcal{P}\kappa/2g_n\beta_n$	7.0297 T	8.403 T

^a From reference [2].

^b See the text for relations to the corresponding ⁴⁹Ti values.

^c Based on $\zeta = 154$ cm⁻¹, the free-ion spin-orbit coupling constant.

It is useful to compare the g - and A -matrices for the Si(Ti³⁺) centre with those of the earlier-determined B(Ti³⁺) centre [1, 2]. The magnitudes of the g -matrices are ordered in the same way, i.e., $g_{\parallel} < g_{\perp}$ in both cases, but the isotropic and anisotropic parts are very different. In particular, as a measure of the latter, the uniaxial parameters given by $(g_{\parallel} - g_{\perp})/3$ are 0.048 15 and 0.004 65 respectively for the Si(Ti³⁺) and B(Ti³⁺) centres, i.e., an order of magnitude greater in favour of the new centre. The A -matrices on the other hand are fairly similar. Following the Morton and Preston procedure [12], where one compares the isotropic and anisotropic parts of the experimental hyperfine matrix with the theoretical parameters A^C and p^d , it is shown that 85% of the spin density for the centre lies on the Ti³⁺ ion with around 80% in the d orbital. If the remaining 15% is situated in the d orbitals of the two nearest-neighbour Zr ions, then a value 0.12 mT is predicted for the hyperfine uniaxiality parameter b_0 . As discussed later, this is in reasonable agreement with the observed Zr superhyperfine splittings. The situation is considerably different from that for the B(Ti³⁺) centre, where around 100% of the spin density lies on the Ti³⁺ ion with about 94% in the d orbital.

If one compares the numerical values of the quantities in column 2 of table 3 with the corresponding values for the B(Ti³⁺), column 3, then there are clearly some marked differences. Firstly the ordering of the energies of the orbital states is different: for the B(Ti³⁺) centre the order is [1] $d_{xy} > d_{xz,yz} > d_{x^2-y^2}$ with $\Delta E_1/\Delta E_2 = 3.345$ while for the new Si(Ti³⁺) centre the order is $d_{xz,yz} > d_{xy} > d_{x^2-y^2}$ with $\Delta E_1/\Delta E_2 = 0.493$. This latter ordering is just what was calculated from a point charge model for Ti in the Si site of zircon (see figure 2 and associated calculations in [1]). It seems certain therefore that the present centre arises from Ti³⁺ substituting for Si in the lattice.

It is useful to compare the quantities \mathcal{P} , κ (and $K = \mathcal{P}\kappa$) and $\langle r^{-3} \rangle_{3d}$ of table 3 for the Si(Ti³⁺) centre with those for the B(Ti³⁺) centre. \mathcal{P} and $\langle r^{-3} \rangle_{3d}$, treated here as variable parameters, are both considerably smaller than the corresponding values for the B(Ti³⁺) centre.

Apparently the more compact fourfold-coordinated site of the $Si(Ti^{3+})$ centre results in a rather smaller value of $\langle r^{-3} \rangle$, i.e., a larger radial distribution of the single 3d electron, which in turn affects the core polarization field. \mathcal{P} is observed to be smaller than any other fitted value that we can find for comparable Ti^{3+} centres. (Isoya *et al* [8] report a value of $-18.79 \times 10^{-4} \text{ cm}^{-1}$ for the $[TiO_4/H]_A^0$ centre in α -quartz.) The core polarization field at the nucleus given by $K = \mathcal{P}\kappa/hc = -1.27 \times 10^{-4} \text{ cm}^{-1}$ agrees almost exactly with that found for the comparable centre $[TiO_4]^-$ in α -quartz [13].

For a single d electron the experimental parameter P_{\parallel} is related to the nuclear quadrupole moment Q by [2, 7]

$$P_{\parallel} = 3e^2 Q \langle r_q^{-3} \rangle_{3d} / 7I(2I - 1). \quad (6)$$

As discussed in [2] (see also reference [7], p 686), the quantity $\langle r_q^{-3} \rangle$ is normally expected to be different from the $\langle r^{-3} \rangle$ of equations (4), (5) due to electrostatic shielding of the nucleus. From the experimental fittings, the sign of P_{\parallel} is not established. We have assumed, following [2], that the electric field gradient (efg) at the nucleus arises predominantly from the unpaired single d electron, as was shown to be the case for the $B(Ti^{3+})$ centre. The sign of P_{\parallel} is then determined by the signs of the valence contribution to the efg and Q —both positive for $^{47,49}Ti$. However, in the present instance, P_{\parallel} is an order of magnitude smaller and this assumption needs to be examined more closely. The single unpaired electron in the $d_{x^2-y^2}$ orbital makes a theoretical contribution $q_{val} = +4\langle r^{-3} \rangle_{3d}/7$ to the efg and the resulting contribution to P_{\parallel} is [2, 7] $3e^2 q_{val} Q/40 = +0.179 \text{ mT}$ (in units $1/g_e \beta_e$). This contribution is reduced by electrostatic shielding of the nucleus [7] through the relation [2, 7] $\langle r_q^{-3} \rangle_{3d} = (1 - R)\langle r^{-3} \rangle_{3d}$ and taking the factor R estimated for $B(Ti^{3+})$, 0.28, a value of 0.129 mT is estimated for P_{\parallel} , which is around an order of magnitude too large. For the apparently more compact four-coordinate site of the $Si(Ti^{3+})$ centre, the shielding factor could of course be somewhat larger. There is also a lattice contribution to the efg due to four negative O ions in a distorted tetrahedron about the Ti^{3+} ion. On the basis of a simple point charge model, this contribution to P_{\parallel} is -0.00858 mT , but it is increased by Sternheimer anti-shielding [7] by a factor $(1 - \gamma_{\infty})$ which has been estimated [14] for Ti^{3+} to lie between +10 and +15. P_{\parallel} might then lie between 0.0005 and 0.0434 mT, a result which agrees moderately well with experiment. However, the lattice calculations are very crude and the valence contributions to the efg will, in this instance, be modified by covalent forces which may considerably modify the calculated result. The best that can be said is that the calculated magnitude is about right and the sign of P_{\parallel} is probably positive.

Clearly visible in the c -axis spectrum of figure 1 are a pair of hyperfine lines, spacing 0.75 mT, flanking the spinless isotope Ti line. These lines merge into the main line as the crystal is rotated away from c and reappear when B lies along b . If the Ti^{3+} ion substitutes for Si^{4+} as proposed, then superhyperfine lines can be expected from, principally, nearest-neighbour ^{91}Zr ($I = 5/2$, 11.15%) nuclei at positions $[\frac{1}{2} \frac{1}{2} \frac{1}{2}]$ and $[\frac{1}{2} \frac{1}{2} -\frac{1}{2}]$. Assuming that the two lines observed arise from the outer transitions of a ^{91}Zr hyperfine sextet, the c -axis spectrum was simulated using Lorentzian first-derivative lineshapes and shown to give a very good fit to the observed spectrum. The ^{91}Zr hyperfine splitting factor was estimated as $0.75/5 = 0.15 \text{ mT}$. No attempt was made to obtain a ^{91}Zr hyperfine matrix because even the outer transitions of the sextet of lines were unresolved in intermediate crystal orientations in the bc -plane.

4.2. The P centre

The exact nature of the P centre is not, at this time, understood completely. As noted earlier, the site point group symmetry is 2 (C_2) with the symmetry axis lying along one of the dihedral twofold axes of the zircon unit cell. The g -parameter matrix is defined, very precisely, to

have this symmetry by the line degeneracies in the plane of measurement (bc). (Actually the g_{12} -element is not determined in the bc -plane but, by simultaneously refining data from the bc -plane and any one of 30° , 45° or 60° planes, the g_{12} -element was found to be, within error, zero.) There is no change, to well within the fitting errors, of either the principal values or of the RMSD if one constrains the g -matrix to have this C_2 symmetry. It seemed sensible therefore to constrain the $I = \frac{1}{2}$ superhyperfine matrix to have the same symmetry; superhyperfine splittings were clearly observable along the c -axis and decreased to zero (or possibly small negative values) about 40° away from c . The g - and A -parameter matrices obtained with the above constraints are listed in table 2. The assignment of the A -matrix to ^{31}P is discussed below.

The P centre undoubtedly lies, at least on the EPR timescale, on the twofold axis along $[110]$ (or $[\bar{1}10]$), and interacts with a single $I = 1/2$, 100% nucleus. The previously reported $[\text{TiO}_8/\text{Y}]^-$ centre [3], herein labelled Y, was shown to arise from Ti^{3+} substituting for Zr^{4+} (fractional coordinates $[\frac{1}{2}\frac{1}{2}\frac{1}{2}]$) with superhyperfine structure supposedly arising from ^{89}Y ($I = \frac{1}{2}$, 100%) in a nearest-neighbour Zr lattice site at fractional coordinates $[0\frac{1}{2}\frac{1}{4}]$ (or one of three other symmetry-related sites).

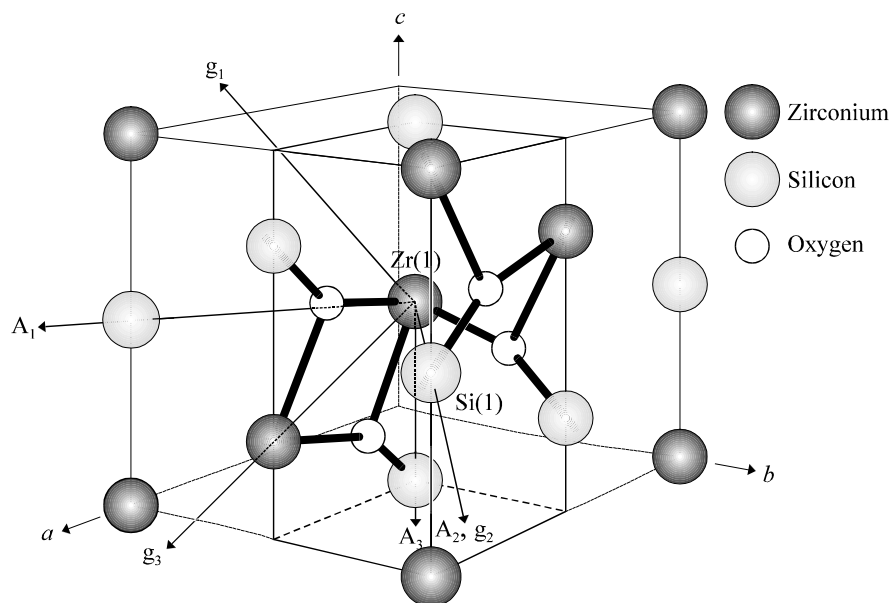


Figure 2. The unit cell of zircon depicting the sites and principal directions of the interaction matrices of the P centre discussed in this paper. For clarity, not all atom positions are shown.

It seems necessary, to explain the C_2 symmetry of the P centre, to have *both* the Ti^{3+} and the interacting $I = \frac{1}{2}$ nucleus on the twofold (dihedral $[110]$) axis. This restricts the choice of lattice positions for the Ti^{3+} and the interacting nucleus to one or other of Zr $[000]$ (Zr(1) in figure 2) and Si $[\frac{1}{2}\frac{1}{2}0]$ (Si(1) in figure 2). There is also the possibility, albeit remote, of an interstitial compensating ion located in one of the large channels and lying on the twofold axis. We note in passing that, although the presence of +1 charge-compensating ions is usually proposed to account for the charge balance when the various paramagnetic centres involving transition ions are formed during x-irradiation, there is no direct EPR evidence of such counter-ions in zircons grown from melts. Although there is much EPR evidence, particularly for natural zircon crystals, for the presence of the ^{89}Y nucleus as the source of

superhyperfine structure in observed spectra, we have in this laboratory had reason to question whether this is necessarily the only source of such structure. We have recently re-examined the EPR spectrum of the so-called $Zr^{3+}(\alpha)$ centre [10] and found that superhyperfine structure, previously ascribed to ^{89}Y , unequivocally arises from ^{31}P ; the evidence is principally the correct prediction, both as regards positions and intensities, of ^{31}P spin-flip transitions. It is to be noted that the $Zr^{3+}(\alpha)$ centre was formed in the same (nominally) undoped zircon crystal as the P centre.

From the discussion of the preceding paragraph we can then propose two alternative structures for the P centre in the undoped crystal: (i) Ti^{3+} substitutes for Zr(1) (see figure 2) and the interacting $I = \frac{1}{2}$ nucleus is ^{31}P substituting for Si(1); or (ii) Ti^{3+} substitutes for Si(1) and the interacting $I = \frac{1}{2}$ nucleus is ^{89}Y substituting in the Zr(1) position. Experimentally the differences between these two possibilities are small. The main difference lies in the signs and magnitudes of the nuclear g -factors for the two nuclei: $-0.274\ 836$ for ^{89}Y and $+2.263\ 20$ for ^{31}P . Substitution of either of these values into equation (1) leads in the fitting procedure, after adjustment of the level labels, to distinctly different superhyperfine matrices but with around a 50% reduction in RMSD in favour of the ^{31}P . Furthermore, some elements of the superhyperfine matrix for ^{89}Y were statistically ill-defined. Because of the low intensity of the spectra, it was not possible to observe any distinguishing features such as ^{31}P nuclear spin flips. We nevertheless favour the first of the two models for the following reasons: (i) the crystal is the same one in which the $Zr(\alpha)$ spectrum, now known to involve interaction with a ^{31}P nucleus, was observed; (ii) although Ti^{3+} is known, from the work reported in this paper, to enter the Si site, the $Si(Ti^{3+})$ centre is not observed in the undoped crystal; (iii) the hyperfine structure on the main lines appears to arise only from the $I = \frac{1}{2}$ 100% nucleus; there is no evidence of minor structure, for example, from two adjacent ^{91}Zr nuclei ($I = 5/2$, 11.23%) as would be expected of Ti^{3+} in position Si(1) (see the discussion on $Si(Ti^{3+})$ in the previous section; and (iv) the ^{31}P principal hyperfine directions are sensibly related to special crystallographic directions while those of the fitted ^{89}Y matrix are not (see further discussion on this below).

There is no *symmetry* requirement for either of the two principal values g_1 or g_2 (see table 2) of the g -parameter matrix to be aligned along any special crystallographic directions in the plane perpendicular to $[110]$. The largest g -value lies about 15° from the direction to Zr at fractional coordinates $[00\frac{1}{2}]$ and that corresponding to the smallest g -value lies about 10° away from Zr at fractional coordinates $[00-\frac{1}{2}]$ (refer to figure 2). The two larger-magnitude A -matrix (^{31}P) principal directions lie almost in the ab -plane with A_2 lying exactly along $[110]$ and A_1 lying almost along $[-110]$. The ^{31}P A -matrix is in fact almost uniaxial about the crystal c -axis.

In further studies, now in progress, we plan to pursue the temperature dependence of the centres herein described, and their possible relations to other Ti^{3+} centres as well as to other simultaneously observed centres, with a view to clarifying the above proposals. It is clear that such studies should attempt also, by producing synthetic crystals deliberately doped with phosphorus, to obtain unequivocal evidence of ^{31}P superhyperfine structure.

The designations $[TiO_4]^-$ and $[TiO_8/P]^-$ respectively are suggested for the two new centres reported here.

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Appendix

The secular determinant of the matrix

$$\begin{bmatrix} a & 0 & c \\ 0 & a & -c \\ c & -c & b \end{bmatrix}$$

to which the interactions of the P centre evidently conform, factorizes and the eigenvalues and eigenvectors can be obtained in explicit algebraic form:

$$\begin{aligned} \varepsilon_1 &= a \\ \varepsilon_{\pm} &= \frac{a+b}{2} \pm \frac{1}{2}\{(a-b)^2 + 8c^2\}^{1/2} \\ \phi_1 &= \left\{ \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0 \right\} \\ \phi_{\pm} &= \left\{ \left(\frac{-\rho+b}{c} \right) Z^{-1/2}, \left(\frac{\rho-b}{c} \right) Z^{-1/2}, 2Z^{-1/2} \right\} \end{aligned}$$

where

$$Z = 2 \left\{ \left(\frac{-\rho+b}{c} \right) + 2 \right\}$$

and $\rho = \varepsilon_+$ or ε_- .

From the eigenvalues one can readily obtain algebraic expressions for the variation of g or A in any specific plane. Of some interest is the g - and A -variation in the ab -plane of the crystal for the P centre. The g -variation turns out to depend on the value of the principal direction designated θ_1 in table 2. For the g -matrix, with fitted value $\theta_1 = 42.51^\circ$, the angular dependence is calculated to be almost isotropic; it is exactly isotropic in the plane for angle $\theta_1 = 42.32^\circ$. This behaviour is closely followed for the principal values of the ^{31}P A -matrix: within error one principal value lies along the crystal c -axis and the remaining two principal values are almost isotropic in the ab -plane.

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