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X-band electron paramagnetic resonance of a new Ti^{3+} centre in x-irradiated zircon

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Abstract. A new $d^1 \text{Ti}^{3+}$ centre formed by x-irradiation of a synthetic zircon crystal at 77 K has been found and studied by electron paramagnetic resonance at 10 K. The impurity ion is believed to occupy a Zr^{4+} substitutional site, as was the case for the earlier reported $\text{B}(\text{Ti}^{3+})$ centre. Interaction with an ^{89}Y nucleus in a nearest-neighbour Zr^{4+} site lowers the site symmetry from $\bar{4}2m$ (Laue class, $4/mmm$) tetragonal to m (Laue class, $2/m$) monoclinic.

1. Introduction

In a recent paper (Claridge *et al* 1995) a detailed analysis of an 8.9 GHz electron paramagnetic resonance (EPR) spectrum of a Ti^{3+} centre observed in x-irradiated zircon (ZrSiO_4) at about 10 K was presented. This spectrum had been reported originally by Solntsev and Shcherbakova (1972). Lack of observed site splitting in the spectra indicated that the Ti^{3+} impurity ion in question occupied a site of point group symmetry $\bar{4}2m$ (D_{2d}) in the tetragonal zircon structure which could have included either Si^{4+} or Zr^{4+} as substitutional sites; no charge compensation was involved. Comparison with the EPR parameters for the equivalent uncompensated Ti^{3+} spectrum in α -quartz (designated $[\text{TiO}_4]^-$ Bailey *et al* 1992), point-charge calculations and analysis of observed superhyperfine structure indicated unequivocally that in zircon the Ti^{3+} occupied the Zr^{4+} site. The designation $[\text{TiO}_8]^-$ was therefore adopted and the centre is referred to herein as $\text{B}(\text{Ti}^{3+})$.

In this paper a second, previously unreported Ti^{3+} EPR spectrum is described. This species displays superhyperfine structure from a nearby 100% abundant atom with nuclear spin $I = \frac{1}{2}$. The centre, as with $\text{B}(\text{Ti}^{3+})$, is formed after x-irradiation at 77 K, cold transfer to the EPR cavity, annealing to room temperature and subsequent recooling to 10 K. The following analysis will show that this new centre is an analogue of the $\text{B}(\text{Ti}^{3+})$ with the Ti^{3+} substituted in a Zr^{4+} lattice site in association with a Y^{3+} ion in a nearest-neighbour Zr^{4+} site.

2. Experimental details

The main features of the Varian E12 spectrometer, the crystal goniometer and the cryogenic system have been presented earlier (Claridge *et al* 1994). A 10 MHz (accuracy, 1 part in 10^{10}) time base derived from an HP5061A caesium beam clock is now used as a reference signal for all frequency and field measurements. An improved signal-to-noise ratio has been achieved by signal averaging and computer control of the field scan.

The crystal was cut to a parallelepiped (3.5 mm \times 5.5 mm \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. Following irradiation at 77 K with x-rays from a W tube the crystal was transferred cold to the previously cooled Displex head of the cavity goniometer. The alignment of the crystal was confirmed by observing, at about 10 K, the previously determined $Zr^{3+}(\alpha)$ and $[AlO_4]^0$ centres each of which collapse from up to four symmetry-related species to a single species for $B\parallel c$. The crystal was rapidly warmed to room temperature by filling the cavity with helium and after about 1 h recooled to about 10 K. The heat treatment destroyed all traces of the $Zr^{3+}(\alpha)$ centre and most of the $[AlO_4]^0$ centre together with other, as yet unreported temperature-unstable centres. In addition to the two prominent centres B(Ti^{3+}) (Claridge *et al* 1995) and C, (Claridge *et al* 1996) a number of centres with a low intensity are observable, subsequent to annealing, with values of g in the range 1.91–1.96. Data were collected for one of these centres in two distinct crystal planes, b – c and the plane containing c obtained by rotating from the b – c plane by 60° about the c axis; this plane is referred to hereafter as the 60° plane. Measurements were made over a 180° range in 5 – 10° angular intervals. Angles were determined to within $2'$, the magnetic field (with a Bruker ER 033M NMR gaussmeter) to ± 0.002 mT and the microwave frequency (with a Systron Donner 6016 counter) to ± 1 kHz.

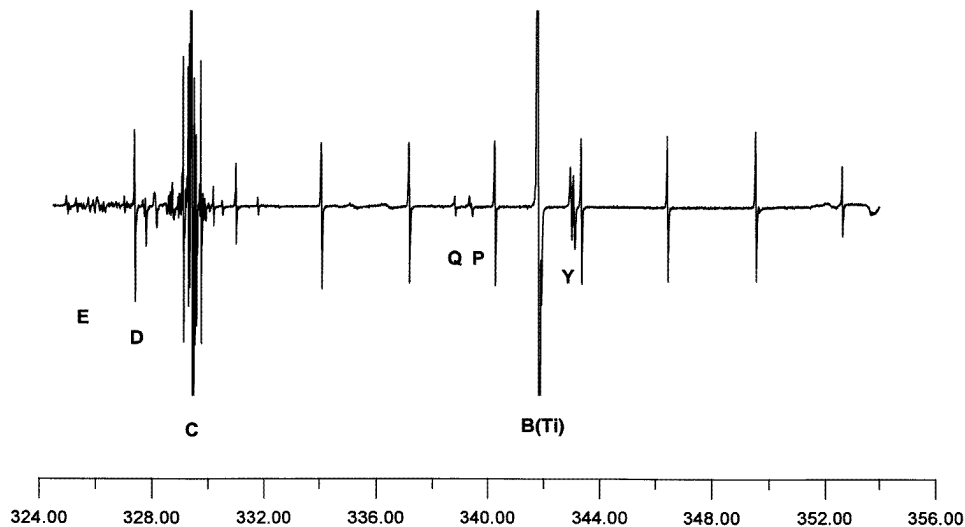


Figure 1. 10 K EPR spectrum of zircon with $B\parallel c$ after annealing to room temperature: B(Ti), uncompensated B(Ti^{3+}) centre; Y, $[TiO_8/Y]^-$ centre, the subject of this paper; C, C–Z centre triradical species; D, hole centre; E, remnants of $[AlO_4]^0$; Q, P, other, as yet unreported Ti centres.

3. Results

The EPR spectrum with the static magnetic field parallel to the tetragonal c axis, recorded at 10 K for the annealed crystal is shown in figure 1. The centre which is the subject of this work is labelled Y and, in the c axis orientation, consists of a pair of equally intense lines

with splittings around 0.097 mT attributed to ^{89}Y superhyperfine structure. The peak-to-peak linewidths along the *c* axis were around 0.03 mT and increased to a maximum of around 0.06 mT in other crystal orientations. In general orientations, as observed in the 60° plane, four pairs of lines were observed, collapsing to three pairs in the *b*–*c* plane and to a single pair along the *c* axis. These observations are consistent with monoclinic site symmetry for the Ti^{3+} ion with the monoclinic axis parallel to *a*. The observed superhyperfine structure is accounted for by interaction with a nearby Y^{3+} ion (^{89}Y ; $I = \frac{1}{2}$; 100% abundance) which lowers the site symmetry of the Ti^{3+} impurity ion from uniaxial to monoclinic. Similar small superhyperfine splittings in the spectra of $\text{Zr}^{3+}(\alpha)$ had been attributed earlier (Claridge *et al* 1994) to ^{89}Y hyperfine structure. The Ti^{3+} assignment was confirmed unequivocally by observing along the *c* axis the ^{47}Ti and ^{49}Ti hyperfine structure corresponding to the nuclear spins $I = \frac{5}{2}$ and $\frac{7}{2}$, respectively, and with intensities corresponding to the known abundances of the two isotopes.

Data from the two planes of observation were fitted simultaneously using the program EPR–NMR (McGavin *et al* 1995) and the spin Hamiltonian

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

where the subscript *i* refers to the four symmetry-related sites of the C_4 rotation group (Weil *et al* 1973). The matrix \bar{g}_N in (1) was held constant at the assumed isotropic value for ^{89}Y , i.e. $-0.528\mathbf{U}$ where \mathbf{U} is the 3×3 unit matrix. Initially all off-diagonal elements in the *g* and *A* parameter matrices were allowed to vary in the fittings but, within error, only the Y_{23} elements were non-zero. This was of course expected from the observed site splittings and is in accord with the assumed monoclinic site symmetry.

During the early stages of data refinement the matrix \bar{g} was well determined, to within 1 part in 10^5 – 10^6 . The elements of the matrix \bar{A} (^{89}Y) were, however, poorly determined and, from the computed intensities, it was clear that some level labels for one or more of the symmetry-related sites were not correct. This arises because the energies due to hyperfine and nuclear Zeeman interactions are comparable and one cannot assume a simple labelling scheme. The procedure was then as follows. Good initial estimates of the ^{89}Y hyperfine matrix elements were obtained by fitting the observed hyperfine splittings from the *b*–*c* plane to the equation

$$Y = A + B \cos(2\theta) + C \sin(2\theta)$$

where *A*, *B* and *C* are linear combinations of the hyperfine matrix elements A_{ij} . These elements were then used as new (constant) starting values in the EPR–NMR fitting procedure, with both planes of data included, and new intensities computed. From these intensities the level labels were allocated so that all hyperfine lines corresponded to the ‘allowed’ (most intense) transitions. The final fittings allowed all *g* and *A* matrix elements to vary freely. The results of this analysis are listed in table 1.

Unfortunately it was not possible to obtain the ^{47}Ti and ^{49}Ti hyperfine parameter matrices because the intensities of the Ti hyperfine lines were too weak. Along the crystal *c* axis, at high instrumental gain, pairs of very weak lines were identified unequivocally as ^{47}Ti and ^{49}Ti lines. The average measured splittings were 3.14 mT which can be taken as a first-order approximation to ‘ A_{\parallel} ’ for both isotopes. This compares with $A_{\parallel} = 2.97$ mT found for the ^{47}Ti and ^{49}Ti isotopes in the $\text{B}(\text{Ti}^{3+})$ centre.

4. Discussion

From table 1 the *g* and *A* (^{89}Y) interaction matrices are, within error, coaxial. On crystal symmetry grounds there is no requirement for this to be so. In both cases, one principal

Table 1. Spin-Hamiltonian parameters for the $[\text{TiO}_8/\text{Y}]^-$ centre^a. (248 unit-weighted data points; root mean square deviation, 0.011 mT).

	Matrix \bar{Y}			k	Principal value Y_k	Principal direction θ_k (deg)	Principal direction ϕ_k (deg)
\bar{g}	1.954 636(7)	0	0	1	1.954 636(7)	90	0
		1.940 504(9)	-0.011 840(6)	2	1.945 894(9)	65.52(1)	90
			1.919 885(4)	3	1.914 495(5)	24.48(1)	270
$\bar{A}/g_e\beta_e(^{89}\text{Y})$ (mT)	0.045(4)	0	0	1	0.106(2)	21.9(2.8)	270
		0.057(5)	0.020(3)	2	0.049(5)	90	0
			0.098(2)	3	0.045(4)	68.1(2.8)	90
$A_{\parallel}/g_e\beta_e(\text{Ti})$ (mT)					3.14(1)	c axis	

^a Error estimates in parentheses.

axis lies along a as demanded by crystal symmetry and the other two principal directions lie in the b - c plane with the major axis making an angle of 24.48° (g tensor) with the tetragonal crystal axis. In comparison with $\text{B}(\text{Ti}^{3+})$ (Claridge *et al* 1995) the g tensor is only slightly distorted from uniaxial symmetry and the principal values of the two centres are closely similar. It is reasonable to suppose therefore that in both cases the impurity Ti^{3+} ion occupies the same tetragonal Zr^{4+} site. The difference in alignment and the lower monoclinic site symmetry arise from the interaction with the nearby ^{89}Y nucleus.

To account for the monoclinic symmetry of both g and A (^{89}Y) tensors the Y atom has to be situated in one of the mirror planes of the zircon structure. It is noted from table 1 that the two extreme principal values of both the g and the A tensors lie in the b - c plane, one of the mirror planes of the zircon unit cell. If one takes the $\text{Ti}^{3+}/\text{Zr}^{4+}$ lattice position, fractional coordinates $[\frac{1}{2}\frac{1}{2}\frac{1}{2}]$ as origin, then g_2 (and A_3 approximately) lies in the b - c plane, making an angle of 65.52° with the c axis. This is only about 0.1° away from a Zr - Zr direction. There is strong evidence therefore that the ^{89}Y nucleus is situated in a nearest-neighbour Zr^{4+} lattice position at fractional coordinates $[11\frac{5}{8}]$. Figure 2 depicts the relative positions and principal axis orientations of the two Ti^{3+} centres in the zircon unit cell.

Assuming coaxiality of the g and A (^{47}Ti and ^{49}Ti) matrices the maximum hyperfine splitting might be expected to lie along a direction making an angle of 24.5° with c . Hyperfine structure was sought along this orientation but the intensity was such that no pairs of lines could be assigned unequivocally to ^{47}Ti and ^{49}Ti . In the absence of any estimate of the other principal values of the hyperfine tensor, it is not possible to attempt a ligand field analysis as was done for $\text{B}(\text{Ti}^{3+})$ (Claridge *et al* 1995). Using tables from Morton and Preston (1978) it is found that the ^{89}Y superhyperfine interaction matrix from table 1 could arise because about 3% of the spin density is associated with the d orbitals of the ^{89}Y nucleus. In view of the similar magnitudes of the ' A_{\parallel} ' ^{47}Ti and ^{49}Ti values for $\text{B}(\text{Ti}^{3+})$ and the present centre, it is reasonable to assume that the spin density on Ti is around 97% and is associated predominantly with the d orbitals as was found for $\text{B}(\text{Ti}^{3+})$.

It appears that, as for $\text{B}(\text{Ti}^{3+})$, the ground-state wavefunction for the new centre is predominantly $^2\text{B}_1$. Expressions similar to equations (2) and (3) of Claridge *et al* (1995) can be obtained for the g -values in terms of ligand-field splittings. From the observed g -values (table 1) and assuming the free-ion value of 154 cm^{-1} for the spin-orbit coupling constant, the orbital states $B_2(xy)$, $E_a(yz)$ and $E_b(xz)$ lie $14\,031$, 6511 and 5470 cm^{-1} ,

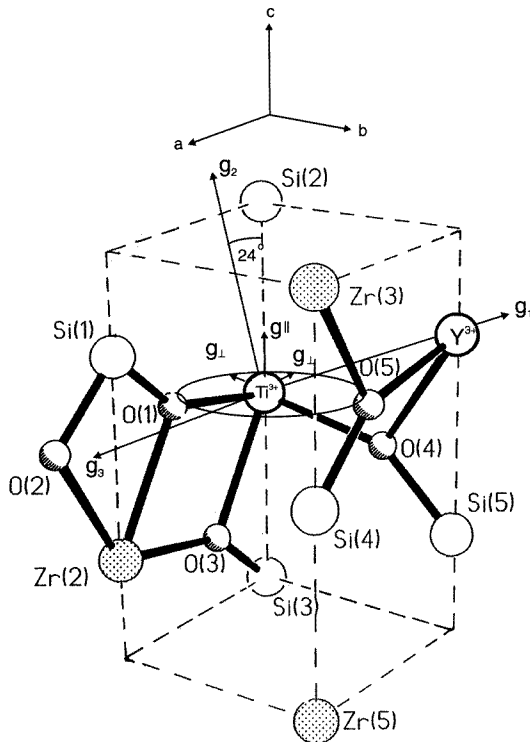


Figure 2. A portion of the unit cell of zircon showing the relative orientations of the g tensors of the $B(\text{Ti}^{3+})$ and $[\text{TiO}_8/\text{Y}]^-$ centres. $g_{||}$, g_{\perp} refer to $B(\text{Ti}^{3+})$ and g_1 , g_2 , g_3 refer to $[\text{TiO}_8/\text{Y}]^-$.

respectively, above the ground state. The 2E orbital states, unsplit under D_{2d} point-group symmetry, are here calculated to be split by 1041 cm^{-1} . In comparison the B_2 and E orbital states in $B(\text{Ti}^{3+})$ are calculated to lie 16324 and 4997 cm^{-1} , respectively, above the ground state. The relative splittings of the orbital states in the two centres are expected to be little affected by orbital reduction.

The designation $[\text{TiO}_8/\text{Y}]^-$ is suggested for the new centre where, as with $B(\text{Ti}^{3+})$, the Ti^{3+} ion, occupying a Zr^{4+} lattice site, is formed following capture of an electron during cold x-irradiation; a remote unobserved $+1$ compensator is required.

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