

## Zircon EPR revisited: 10 K EPR of three low-symmetry centres in irradiated zircon (zircon silicate)

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1994 J. Phys.: Condens. Matter 6 3429

(<http://iopscience.iop.org/0953-8984/6/18/019>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.147

The article was downloaded on 12/05/2010 at 18:20

Please note that [terms and conditions apply](#).

## Zircon EPR revisited: 10 K EPR of three low-symmetry centres in irradiated zircon (zircon silicate)

R F C Claridge, K M Mackle, G L A Sutton and W C Tennant

Chemistry Department, University of Canterbury, Private Bag 4800, Christchurch, New Zealand

Received 31 December 1993

**Abstract.** 8.9 GHz 10 K EPR studies of three low-symmetry centres in x-irradiated zircon are reported. Precise spin-Hamiltonian parameters are given for a  $Zr^{3+}$  centre, including  $^{91}Zr$  hyperfine and  $^{89}Y$  superhyperfine matrices, where the ideal tetragonal symmetry of the Zr site is lowered by charge compensator(s) to Laue class  $\bar{1}$ . Precise  $g$ -values are given for two previously unreported electron-hole centres shown to be located respectively at short- and long-bonded O-ligand sites, each of Laue class  $2/m$ , monoclinic.

### 1. Introduction

There is currently considerable interest in precise parameters of paramagnetic species in single crystals as determined by electron paramagnetic resonance (EPR). Such measurements have been greatly facilitated by the development of an extended (maximally reduced) spin Hamiltonian (SH) containing all terms under the usual symmetry constraints of the site of the paramagnetic ion and its spin,  $S$  (McGavin *et al* 1990), and the use of full matrix least-squares refinement (McGavin *et al* 1989) together with precise crystal-alignment procedures to determine the parameter principal values and their corresponding principal directions with a precision close to that obtained for bond-direction determination in single-crystal x-ray crystallography. EPR thus allows one to measure with high precision the parameter matrix (tensor) properties in the microregion surrounding a paramagnetic ion. Such measurements are exemplified by measurement of a large variety of paramagnetic centres in  $\alpha$ -quartz (Weil 1984 and references therein) and are now being extended to other crystals of practical importance, e.g.,  $CaWO_4$  (McGavin and Tennant 1985) and the current work on  $ZrSiO_4$ .

Our interest in zircon arose in the first instance from the quality of EPR information obtained for  $\alpha$ -quartz and the possibility of extending this to other crystalline materials of technological importance. There is a keen interest in zircon as a 'high-tech' material because of its high refractive index, its hardness and resistance to chemical attack. High-purity synthetic zircon may be used in laser components, in which case it is important to be aware of the impurities, often at trace levels, which may be associated with unpaired electrons, and their consequent amenability to study by EPR.

In this paper we present detailed EPR studies of three low-symmetry paramagnetic species: a triclinic  $Zr^{3+}$  centre (previously observed and reported by Solntsev and Shcherbakova (1973)) and two previously unreported monoclinic species thought to be hole centres trapped at ligand O atoms. We group these three because of their symmetry characteristics; the  $Zr^{3+}$  centre is only slightly lower than monoclinic symmetry and the other two are, within the accuracy of the measurements, exactly monoclinic.

## 2. Experimental details

The crystal of zircon chosen for study was grown from molten  $\text{Li}_2\text{MoO}_4\text{-MoO}_3$  as described by Chase and Osmer (1966) and supplied by Aerospace Corporation, CA. The crystal was cut to 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.

All measurements were carried out at X band at around 10 K using a Varian E12 spectrometer. The crystal was irradiated under liquid nitrogen using x-rays from a W tube and the sample transferred cold to the Displex head of the EPR cavity system. The cavity system is similar to that previously described by Isoya *et al* (1987). The crystal is mounted on a Cu holder attached to the reflux head inside a modified Varian E235 wide-access cavity, and is rotated about an axis precisely perpendicular to the magnetic field. The angle of rotation in the plane containing the static field can be determined to about 1 minute of arc and in the plane vertical to this accurately using EPR degeneracies of the symmetry-related sites in particular crystal orientations. All measurements described herein were performed in the  $bc$ - and  $ab$ -planes of the crystal. Use of the technique of symmetry-related sites as described by Weil *et al* (1973) meant that all parameter matrices were then well determined.

## 3. Results

After irradiation, a number of paramagnetic species was observed and identified as illustrated in figure 1. Here we shall report the centres labelled A (otherwise known as  $\text{Zr}^{3+}(\alpha)$  after Solntsev and Shcherbakova (1973)), D and a room-temperature (RT) centre not shown in the figure. The B ( $\text{Ti}^{3+}$ ), C ( $\text{Sn}^{3+?}$ ) and E ( $\text{AlO}_4^0$ ) centres were also measured and analysed but will not be reported herein.

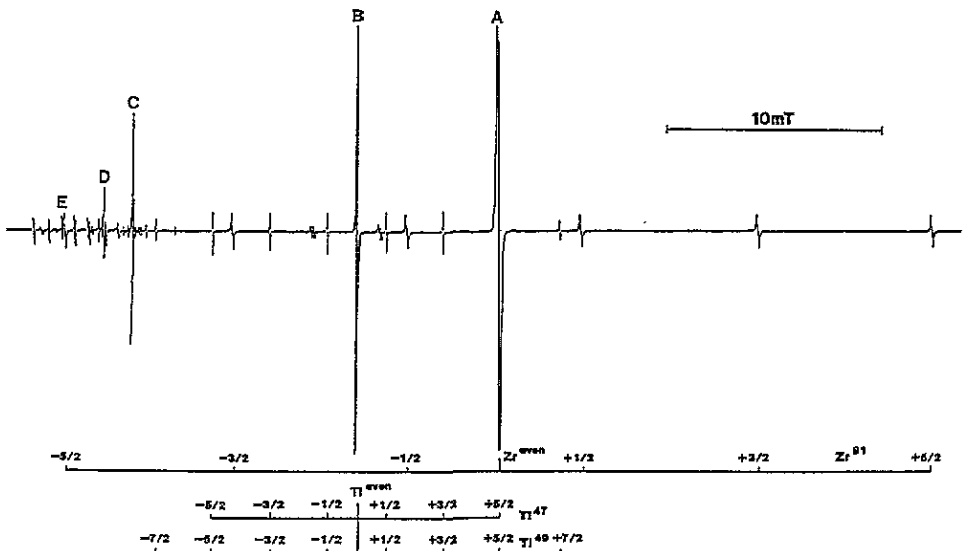


Figure 1. The  $c$ -axis spectrum at 10 K showing A ( $\text{Zr}^{3+}(\alpha)$ ) and D centres in relation to B ( $\text{Ti}^{3+}$ ), E ( $\text{AlO}_4^0$ ) and C ( $\text{Sn}^{3+?}$ ) centres (see the text for details).

The three centres A, D and RT were observed only after irradiation at 77 K. Under the conditions used to measure spectra of the A centre (0.2 mW microwave power) the D and RT centres were saturated. These could only be observed satisfactorily at low power (0.05 mW). The A and D centres disappeared on warming to above 100 K. The RT centre is so named because it was the first, but not the only centre to be found to be stable after warming to room temperature. As shown later, the similar power saturation behaviour suggests that the A and RT centres are related.

### 3.1. The A centre

Distinct  $S = \frac{1}{2}$  spectra from the abundant even zirconium isotopes ( $^{90}\text{Zr}$  (5.1.5%),  $^{92}\text{Zr}$  (17.1%),  $^{94}\text{Zr}$  (17.4%),  $^{96}\text{Zr}$  (2.83%)) and  $^{91}\text{Zr}$  ( $I = \frac{5}{2}$ , natural abundance, 11.2%) were observed. Each were split in some crystal orientations by interaction with a further 100% abundant isotope with  $I = \frac{1}{2}$ . Splittings varied from less than the linewidth to around 0.17 mT and are thought to arise from a nearby  $^{89}\text{Y}$  nucleus. At some orientations a pair of satellites (intensity ratios, 4.6%) were observed flanking the even Zr and  $^{91}\text{Zr}$  lines. These were thought to arise from hyperfine interaction with the  $^{29}\text{Si}$  nucleus (natural abundance, 4.62%). Observed peak-to-peak linewidths were between 0.06 and 0.08 mT for both sets of spectra.

The appropriate SH for the analysis is

$$(\mathcal{H}_S)_i = \beta_e S \cdot \mathbf{g}_i \cdot \mathbf{B} + \sum_j \{ S \cdot (\mathbf{A}_j)_i \cdot \mathbf{I}_j - \beta_N I_j \cdot (\mathbf{g}_{N_j})_i \cdot \mathbf{B} + I_j \cdot (\mathbf{Q}_j)_i \cdot \mathbf{I}_j \} \quad (1)$$

where the terms have their normal meanings and the subscripts refer to the  $i = 1-4$  symmetry-related species and the  $j = 2$  nuclei,  $^{91}\text{Zr}$  and  $^{89}\text{Y}$  ( $^{29}\text{Si}$  was not included in the fittings). The nuclear  $g_N$  matrices for  $^{91}\text{Zr}$  and  $^{89}\text{Y}$  were taken as the respective isotropic matrices  $-0.521448\mathbf{U}$  and  $-0.274835\mathbf{U}$  ( $\mathbf{U}$  is the  $3 \times 3$  unit matrix). Even Zr and  $^{91}\text{Zr}$  data were fitted separately, including the  $^{89}\text{Y}$  hyperfine data in the former, but not in the latter. The even Zr isotope spectra were fitted to within the inherent scatter in the data (root mean squared deviation, RMSD over 329 unit weighted lines, 0.025 mT) but the  $^{91}\text{Zr}$  fit was rather poorer (RMSD over 307 unit weighted lines, 0.077 mT). This is thought to be due to imprecision in measuring some very weak hyperfine lines and neglect of further  $^{89}\text{Y}$  hyperfine splittings for this isotope.

The SH parameters so obtained are listed in table 1.

### 3.2. D and RT centres

The D-centre and RT-centre spectra were each characteristic of an  $S = \frac{1}{2}$  paramagnetic species and displayed symmetry requirements of a site of Laue class  $2/m$  (monoclinic). There was a maximum of four symmetry-related species in a general crystal orientation collapsing to three in the  $bc$ -plane and to two in the  $ab$ -plane (see figure 2 for the D centre). The data in each centre were fitted to the first term of (1) and the results are given in table 2. For the D centre the RMSD between calculated and measured resonant fields was 0.013 mT over 148 unit weighted lines and for the RT centre it was 0.011 mT over 144 unit weighted lines. The fits were therefore to within the inherent scatter in the data (i.e., RMSD  $\leq \frac{1}{3}$  (peak-to-peak linewidth)).

Table 1. SH parameters for the A centre ( $Zr^{3+}$ ): site 1 at around 10 K<sup>a</sup>.

	Matrix $y$			$k$	Principal values, $Y_k$	Principal directions <sup>b</sup>	
						$\theta_k$ (°)	$\phi_k$ (°)
Even isotopes, $I = 0$							
<b>g</b>	1.935 65(1)	0.000 02(1)	-0.000 71(4)	1	1.935 66(1)	89.10(5)	180.67(10)
		1.926 27(1)	0.005 66(3)	2	1.927 05(2)	97.89(5)	90.79(10)
			1.886 27(2)	3	1.885 48(2)	7.94(5)	84.21(30)
<b>A</b> ( <sup>89</sup> Y)/ $g_c\beta_c$ (mT)	0.178(4)	0.004(7)	0.000(18)	1	0.178(4)	89.9(4.6)	181.4(2.3)
		0.003(6)	-0.002(11)	2	0.003(6)	91.6(11.6)	91.4(2.3)
			-0.053(14)	3	-0.053(4)	1.6(11.6)	(—) <sup>c</sup>
$A(^{29}\text{Si})_{\text{max}} = 0.44$ mT $A(^{29}\text{Si})_{\text{min}} = 0.26$ mT RMSD <sup>d</sup> = 0.025 mT Odd isotope, <sup>91</sup> Zr, $I = \frac{5}{2}$							
<b>g</b>	1.935 79(4)	0.000 11(5)	0.000 25(9)	1	1.935 79(5)	90.2(1)	180.5(5)
		1.926 27(6)	-0.005 61(7)	2	1.927 04(6)	97.8(1)	90.5(3)
			1.886 20(6)	3	1.885 43(7)	7.8(1)	92.2(7)
<b>A</b> ( <sup>91</sup> Zr)/ $g_c\beta_c$ (mT)	4.824(7)	-0.004(9)	0.016(10)	1	8.741(7)	1.0(1)	103.5(8.7)
		4.927(9)	0.064(9)	2	4.926(8)	91.0(1)	92.2(4.9)
			8.740(7)	3	4.824(7)	90.2(2)	182.2(4.8)
<b>Q</b> ( <sup>91</sup> Zr)/ $g_c\beta_c$	0.043(20)	-0.003(44)	-0.013(19)	1	0.046(34)	98(9)	337(177)
		0.036(18)	0.011(20)	2	0.036(35)	92(28)	246(174)
			-0.079(14)	3	-0.082(14)	8(9)	318(72)
RMSD = 0.0772 mT							

<sup>a</sup> Error estimates in parentheses.<sup>b</sup> Angle  $\theta$  measured from  $c$  and angle  $\phi$  in an anticlockwise direction from  $a$ .<sup>c</sup> Angle  $\phi$  indeterminate.<sup>d</sup> RMSD = root-mean-squared-deviation.

#### 4. Discussion

The A centre results from capture of an electron at a  $Zr^{4+}$  site in the x-irradiated zircon and has previously been recorded and reported by Solntsev and Shcherbakova (1973) as  $Zr^{3+}(\alpha)$ . Our current results correct an error in axis identification by Solntsev and Shcherbakova, more precisely determine the SH parameters and extend the measurements by including the <sup>89</sup>Y hyperfine interaction. The experiments do not establish the absolute signs of the principal values,  $A(^{91}\text{Zr})$ ; the signs of  $A(^{89}\text{Y})$  and  $Q(^{91}\text{Zr})$  principal values are known relative to those of  $A(^{91}\text{Zr})$  (assumed here to be positive).

The site symmetry of the A centre is established from the observed site splittings as Laue class  $\bar{1}$  (Rae 1969), which implies that the tetragonal ( $4\bar{2}m$ ) symmetry of the ideal  $Zr^{4+}$  site is destroyed by the presence of one or more nearby ions. Tentatively we take the  $Y^{3+}$  ion to isomorphously replace a  $Zr^{4+}$  ion next-nearest neighbour to the  $Zr^{3+}$  centre. A single positively charged compensator is also required, which, because of the lack of observable hyperfine structure, is presumably remotely located. The influence of the  $Y^{3+}$  and +1 compensator are clearly sufficient to lower the site symmetry at the  $Zr^{3+}$  centre from tetragonal to triclinic but the deviations from uniaxial symmetry are not great and the 'unique'  $g$ - and <sup>91</sup>Zr  $A$ -tensor directions lie within a few degrees of the tetragonal axis,  $c$ . (The 'unique' <sup>89</sup>Y axis however lies almost along  $a$ .) The low symmetry of the site of the

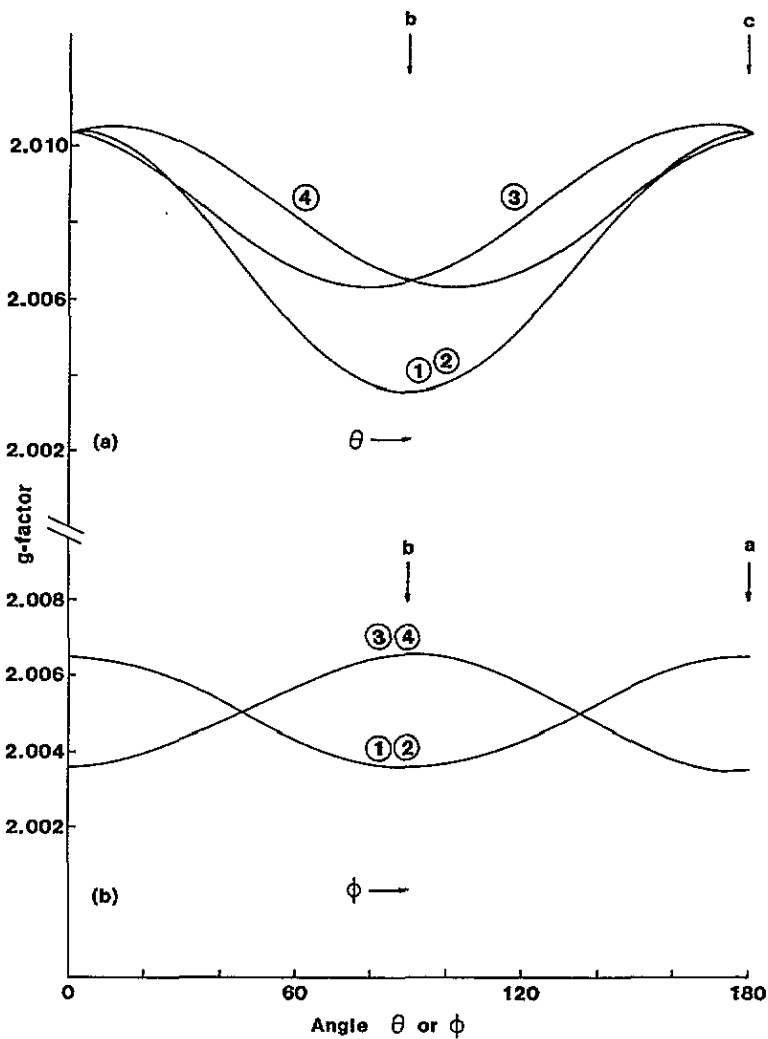


Figure 2. The angular dependence of the D-centre  $g$ -factor in the (a)  $bc$ - and (b)  $ab$ -planes of the crystal. The circled numbers represent the symmetry-related sites (1)–(4).

paramagnetic is also evidenced by the non-coincidence of the  $g$ - and  $A(^{91}\text{Zr})$ -tensor principal directions; however the degree of non-coincidence only just exceeds the combined errors in these directions (table 1). The principal directions of the  $^{91}\text{Zr}$  nuclear electric quadrupole tensor are not particularly well determined and we can only say that the 'unique' axis of the electric field gradient tensor lies close to the  $c$ -axis of the crystal.

It is useful to consider briefly the distribution of spin density in the orbitals of the  $\text{Zr}^{3+} 5s4d$  configuration and in those of the nearby interacting  $^{29}\text{Si} 3s3p$  and  $^{89}\text{Y} 5s4d$  orbitals. From the relative magnitude of the  $g$ - ( $g_z < \frac{1}{2}(g_x + g_y)$ ) and  $^{91}\text{Zr}$   $A$ -tensor ( $A_z > \frac{1}{2}(A_x + A_y)$ ) principal values in the unpaired electron can be assumed (Swalen and Ibers 1962) to be localized in the  $d_{x^2-y^2}$  orbital. The  $A$ -tensor, from table 1, converted to MHz, may be decomposed:

Table 2. Site 1 SH parameters for D and RT centres (details as in table 1).

	Matrix $y$	$k$	Principal values, $Y_k$	Principal directions			
				$\theta_k$ ( $^\circ$ )	$\phi_k$ ( $^\circ$ )		
D centre							
<b>g</b>	2.006 49(1)	0.000 00(3)	0.000 78(2)	1	2.010 56(1)	10.8(2)	180.0(7)
		2.003 60(1)	0.000 00(1)	2	2.006 34(1)	100.8(2)	180.0(6)
			2.010 41(1)	3	2.003 60(1)	90.0	90.0
RMSD = 0.013 mT							
RT centre							
<b>g</b>	2.008 11(2)	0.000 00(1)	-0.002 87(2)	1	2.013 40(2)	28.4(1)	180.0(3)
		2.005 09(1)	0.000 00(2)	2	2.006 56(2)	118.4(1)	180.0(6)
			2.011 85(1)	3	2.005 09(1)	90.0	90.0
RMSD = 0.011 mT							

$$\begin{pmatrix} 135.20 & & \\ & 138.06 & \\ & & 244.98 \end{pmatrix} = 172.75 \begin{pmatrix} 1 & & \\ & 1 & \\ & & 1 \end{pmatrix} + \begin{pmatrix} -37.55 & & \\ & -34.69 & \\ & & 72.23 \end{pmatrix}$$

from which we obtain the isotropic parameter  $a = 172.75$  MHz and anisotropic parameter  $b = -\frac{1}{2}(37.55 + 34.69) = -36.12$  MHz.  $a$  and  $b$  are compared to the atomic parameters  $A^c$  and  $p^d$  respectively from table 1 of Morton and Preston (1978) giving for the  $^{91}\text{Zr}$  contributions Zr 5s,  $172.75/2753 = 0.063$  (6.3%) and Zr 4d,  $36.12/(\frac{2}{7} \times 155.6) = 0.812$  (81.2%). Of the remaining 12.5%, around 6% can be associated with  $^{29}\text{Si}$  3s3p orbitals, using the observed hyperfine splittings from table 1. If the remaining 6.5% is associated with  $^{89}\text{Y}$ , principally 4d orbitals, then an anisotropic parameter  $b = -0.04$  mT is predicted, in reasonable agreement with the observed value (table 1) of  $-0.05$  mT.

The D-centre and RT-centre spectra exhibit very similar characteristics and it is convenient to discuss the two together. From the site-splitting patterns (see figure 2 for the D centre), which are identical for the two, the site of the paramagnetic centre is of Laue class  $2/m$  ( $2/m^2$  in the nomenclature of Rae (1969)). Sites 1 and 2 must have a principal direction along  $b$  and sites 3 and 4 must have a principal direction along  $a$ ; the remaining principal directions are located in the  $ac$  or  $bc$  planes respectively (see table 2 for site 1). Both centres are relatively easily power saturated but differ in that D is only observable at temperatures below 77 K while RT, as the naming implies, is observable at room temperatures. All data used here were however recorded at around 10 K and usually at low microwave power ( $\sim 0.05$  mW), which effectively isolated the signals from other interfering centres, which were no longer visible. Both D and RT centres are thought to be hole centres with the hole trapped near to an O anion because (i) the  $g$  values are all greater than the free electron value, (ii) the O atoms, at positions 16h in the  $I4_1/amd$  tetragonal space group, all display point group symmetry  $m$ , or  $2/m$  Laue class, as observed in the site-splitting patterns and (iii) some principal directions can be well correlated with O-Zr or O-Si bond directions as detailed below.

The eight O atoms about a given Zr atom form two distorted tetrahedra of short (2.13 Å) and long (2.27 Å) bonds. (Each short- and long-bonded O is respectively long and short bonded to a next-nearest-neighbour Zr.) Crystallographic data were taken from the book by Wyckoff (1965). With respect to the Zr position there are then two possible types of O site for trapping the proposed paramagnetic hole. We propose that the D centre arises from

Table 3. D- and RT-centre *g*-tensor orientations in relation to crystal bond directions<sup>a</sup>.

D centre						
<i>g</i> -matrix			Hole-centre (1) at O (0.32, 0, 0.07)			
<i>g<sub>k</sub></i>	$\theta_k$	$\phi_k$	direction to:	<i>r</i> (Å)	$\theta$	$\phi$
2.010 56	10.8	180	O(0.18, 0, 0.67)	3.75	13.5	180
2.006 34	100.8	180	Zr(0, 0, 0)	2.13	101.4	180
2.003 60	90	90	O(0.31, $\frac{1}{2}$ , 0.18)	3.36	78.8	90
RT centre						
<i>g</i> -matrix			Hole-centre (2) at O (0.32, 0, 0.07)			
<i>g<sub>k</sub></i>	$\theta_k$	$\phi_k$	direction to:	<i>r</i> (Å)	$\theta$	$\phi$
2.013 40	28.4	180	Zr( $\frac{1}{2}$ , 0, $-\frac{1}{4}$ )	2.27	32.4	180
2.006 56	118.4	180	Si( $\frac{1}{2}$ , 0, $\frac{1}{4}$ )	1.61	131.5	180
2.005 09	90	90	O(0.32, $\frac{1}{2}$ , 0.18)	3.36	78.8	90

<sup>a</sup> Fractional coordinates of atoms in parentheses.

a hole trapped at a short-bonded O when the two *g*-tensor principal directions of species 1 contained in the *ac*-plane lie 0.6° and 2.7° respectively away from the Zr–O and O–O direction as indicated in table 3; the third principal direction, along *b*, lies 11.2° away from another O–O direction. The RT centre seems sensibly to be related to a hole trapped at a long-bonded O site or, alternatively and equivalently, trapped at the short-bonded O as above but with a different orientation of the *g*-tensor principal directions. In this case, as outlined in table 3, the *g*-tensor principal directions of species 1 in the *ac*-plane lie 4° away from an O–Zr direction (this is a next-nearest-neighbour Zr to which the O-trapping centre is long bonded) and 13.1° away from an O–Si direction. The two sets of principal directions are related by a 17.6° rotation about *b*. The close proximity of this proposed position to an Si atom might lead to the expectation of <sup>29</sup>Si hyperfine structure being observed. Weak hyperfine lines were indeed observed for the RT centre but it could not be definitively established as <sup>29</sup>Si hyperfine structure.

This portrayal of two differently oriented paramagnetic hole centres existing on the same trapping O centre raises an interesting possibility. We have noted above that the D centre is irreversibly destroyed as the temperature is raised. Does it convert to the second, more stable RT orientation, leading to an increased EPR signal for the latter? Unfortunately it is not easy to carry out an unambiguous experiment to check the decay of the D centre and possible growth of the RT centre so this intriguing possibility remains for further experiment. The irreversible destruction of the D centre with increasing temperature precludes the sort of dynamical interchange between the two centres that was obtained for Ge centres in  $\alpha$ -quartz (Isoya *et al.* 1978).

## References

- Chase A B and Osmer J A 1966 *J. Electrochem. Soc.* **113** 198–9  
 Isoya J, Weil J A and Claridge R F C 1978 *J. Chem. Phys.* **69** 4876–84  
 McGavin D G, Mombourquette M J and Weil J A 1989 *Computer Program EPR* University of Saskatchewan  
 McGavin D G and Tennant W C 1985 *J. Magn. Reson.* **61** 321–32  
 McGavin D G, Tennant W C and Weil J A 1990 *J. Magn. Reson.* **87** 92–109



- Morton J R and Preston K F 1978 *J. Magn. Reson.* **30** 577-82  
Rae A D 1969 *J. Chem. Phys.* **50** 2672-85  
Solntsev V P and Shcherbakova M Ya 1973 *Dok. Akad. Nauk SSSR* **1** 156-8  
Swalen J D and Ibers J A 1962 *J. Chem. Phys.* **37** 17-20  
Weil J A 1984 *Phys. Chem. Minerals* **10** 149-65  
Weil J A, Buch T and Clapp J E 1973 *Adv. Magn. Reson.* **6** 183-257  
Wyckoff R W G 1965 *Crystal Struct.* vol 3 (New York: Wiley) pp 157-9