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1989 J. Phys.: Condens. Matter 1 7661

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Temperature dependence and hyperfine structure of Fe^{3+} centres in synthetic quartz

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Received 17 October 1988, in final form 17 April 1989

Abstract. The temperature dependence of spin Hamiltonian parameters of Fe^{3+} centres in synthetic quartz has been investigated with an X-band EPR spectrometer. The fine-structure parameters D and E of Fe^{3+} centres are found to be linearly increasing with decreasing temperature from 300 K to 90 K. The variations of D are in the descending order of S'_1 , S''_1 and S_1 centres, but the changes of E are in the reverse sequence. The hyperfine structure of these centres reveals that the nuclear spin of compensating ions for S_1 , S'_1 , and S''_1 is $\frac{3}{2}$, $\frac{1}{2}$ and $\frac{3}{2}$, respectively. By comparing these centres with the established Al centres, it is tentatively proposed that S_1 , S'_1 , and S''_1 centres are compensated with Na^+ , H^+ , and Li^+ , respectively.

1. Introduction

Recently, through the electron paramagnetic resonance study of synthetic quartz, grown by the hydro-thermal method at the Korea Research Institute of Chemical Technology (Park 1980), we reported three Fe^{3+} centres, namely S_1 , S'_1 , and S''_1 (Choi and Choh 1986, 1988). These three centres have the same magnetic principal axes, related to the crystallographic a and c axes in the following way: the x axis is equal to the a axis, the y axis is perpendicular to the a axis and -31.6° to the c axis, and the z axis is perpendicular to the a axis and 58.4° to the c axis. These centres are identified as substitutional Fe^{3+} ions for Si^{4+} , but slightly different spin Hamiltonian parameters imply that their charge-compensating ions are different from one another.

In order to investigate the relationship between these centres and their charge-compensating ions, the temperature dependence of spin Hamiltonian parameters and the hyperfine structure of these centres are measured and discussed in this paper.

2. Temperature dependence of spin Hamiltonian parameters

2.1. Experimental results

The resonance fields for the three centres were measured in the temperature range from 90 K to 300 K at intervals of about 20 K. The results are tabulated in table 1 for three directions of the applied magnetic field along the principal axes. When the magnetic field is parallel to the x axis, all detected resonance transitions are included in table 1. On the other hand, for the magnetic field parallel to the y axis or the z axis, some weaker

Table 1. Temperature dependence of the resonance fields of centres S_1 , S'_1 and S''_1 measured in synthetic quartz at 9.273 ± 0.002 GHz with the applied magnetic field along the principal axes.

Fe ³⁺ centres		S_1			S'_1			S''_1		
		Resonance field (mT)			Resonance field (mT)			Resonance field (mT)		
Principal axis	Transition	90 K	300 K	ΔB_{res}	90 K	300 K	ΔB_{res}	90 K	300 K	ΔB_{res}
x	$\frac{3}{2} \leftrightarrow -\frac{3}{2}$	190.2	191.5	+1.3	202.9	203.5	+0.6	182.4	183.4	+1.0
	$-\frac{1}{2} \leftrightarrow \frac{1}{2}$	294.6	291.9	-2.7	271.1	270.4	-0.7	318.5	316.3	-2.2
	$-\frac{5}{2} \leftrightarrow \frac{5}{2}$	706.0	703.3	-2.7	680.4	674.6	-5.8	651.3	647.8	-3.5
y	$-\frac{1}{2} \leftrightarrow \frac{1}{2}$	73.7	73.8	+0.1	75.3	75.4	+0.1	72.5	72.6	+0.1
	$\frac{3}{2} \leftrightarrow -\frac{3}{2}$	625.9	615.6	-10.3	542.9	534.7	-8.2	612.2	602.0	-10.2
z	$-\frac{3}{2} \leftrightarrow \frac{3}{2}$	129.9	129.5	-0.4	127.5	127.4	-0.1	133.4	133.2	-0.2
	$-\frac{5}{2} \leftrightarrow \frac{5}{2}$	537.6	525.3	-12.3	443.8	432.0	-11.8			
	$\frac{3}{2} \leftrightarrow -\frac{3}{2}$	787.9	776.4	-11.5	691.6	679.7	-11.9			

signals are observed but omitted in table 1. The resonance points change almost linearly up or down with increasing temperature from 90 K. ΔB_{res} indicates the amount of the field change when the temperature increases from 90 K to 300 K. The resonance fields in the low-field range shift minutely upward or downward but those in the high-field region change largely downward with increasing temperature. In addition, the three centres S_1 , S'_1 , and S''_1 are slightly different from one another in the degree of the resonance field changes. This fact means that the three centres differ in the temperature dependency of their spin Hamiltonian parameters.

2.2. Analysis

The experimental results of these resonance fields were analysed with the following spin Hamiltonian (Barry *et al* 1965).

$$\mathcal{H} = g\beta(B_z S_z + B_x S_x + B_y S_y) + D(S_z^2 - \frac{35}{12}) + E(S_x^2 - S_y^2) + \frac{7}{36}F(S_z^4 - \frac{95}{24}S_z^2 + \frac{81}{16}). \quad (1)$$

Its energy eigenvalues for the magnetic field being directed along the principal axes were calculated as discussed previously (Choi and Choh 1988).

The temperature dependences of the second-order axial field parameter D and the rhombic field parameter E for the three centres are displayed in figures 1 and 2, respectively. Both parameters for all centres increase with decreasing temperature. The parameters could be fitted linearly with temperature as indicated in these figures. The rates of variation of D/h are 8.944, 9.175, and 10.15 in units of 10^{-5} K^{-1} for the centres of S_1 , S''_1 and S'_1 , respectively. The similar rates of E/h are 11.92, 12.73, and 13.87 for the centres of S'_1 , S''_1 and S_1 , respectively. This sequence of S'_1 , S''_1 , and S_1 for E/h is just the reverse order for the variation of D/h .

According to the Watanabe theory based on a point-charge model, the temperature dependence of the cubic field-splitting parameter a might be written as

$$\frac{1}{a} \left(\frac{\partial a}{\partial T} \right) = -\frac{10}{3} \beta_v \quad (2)$$

where β_v is the volume coefficient of thermal expansion (Marshall and Reinberg 1963).

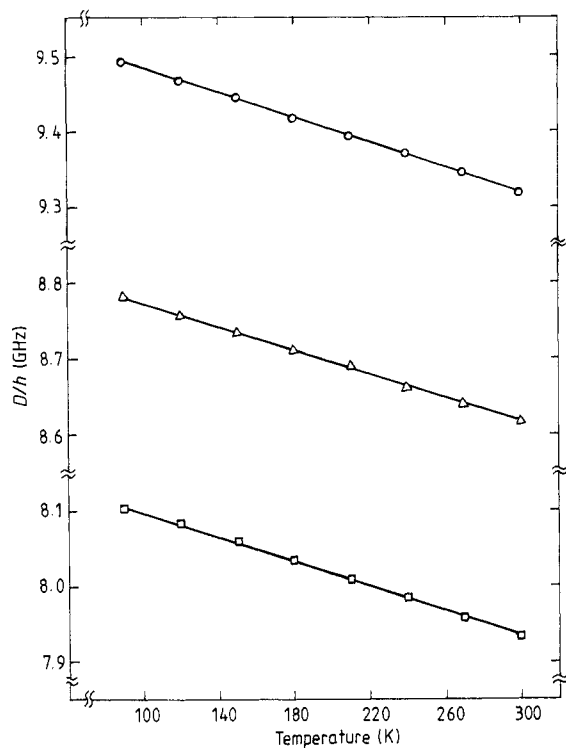


Figure 1. Temperature dependence of the second-order axial field parameter D for the centres S_1 , S_1' and S_1'' in synthetic quartz. \circ , S_1 , $9.317[1 + 8.944 \times 10^{-5}(300 - T)]$; \triangle , S_1' , $8.616[1 + 9.175 \times 10^{-5}(300 - T)]$; \square , S_1'' , $7.932[1 + 10.15 \times 10^{-5}(300 - T)]$.

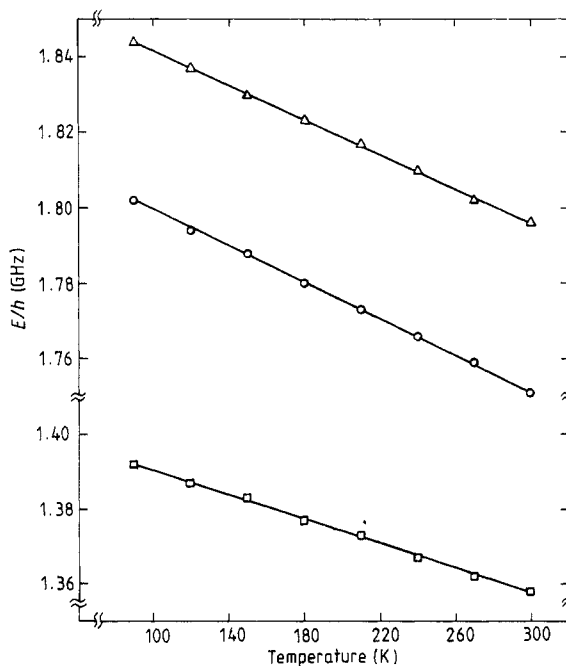


Figure 2. Temperature dependence of the rhombic field parameter E for the centres S_1 , S_1' and S_1'' in synthetic quartz. \circ , S_1 , $1.751(1 + 13.87 \times 10^{-5}(300 - T))$; \square , S_1'' , $1.358[1 + 11.92 \times 10^{-5}(300 - T)]$; \triangle , S_1' , $1.796[1 + 12.73 \times 10^{-5}(300 - T)]$.

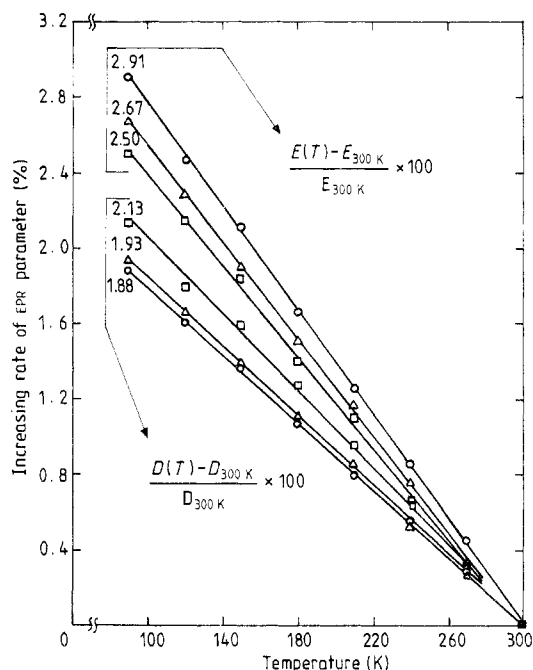


Figure 3. Temperature dependence of the variations of D and E , properly normalised with respect to the values of parameters at room temperature. Centres: \circ , S_1 ; \square , S_1' ; \triangle , S_1'' .

Applying this theory to the parameters D and E , we obtain the value of $-12.1 \times 10^{-5} \text{ K}^{-1}$ using $\beta_v = 36.4 \times 10^{-6} \text{ K}^{-1}$ for α -quartz (Bottom 1982). This value is generally in agreement with our experimental results of about $(8.944\text{--}13.87) \times 10^{-5} \text{ K}^{-1}$. The minus sign means that the parameters decrease with increasing temperature. Therefore, the temperature dependences of both D and E parameters for all centres can be understood as arising from the thermal expansion of α -quartz.

Additionally, the percentage changes of D and E are represented in figure 3 by normalising the values with respect to those at room temperature. The differences of the temperature dependence can be seen distinctly. The variations of D are in the descending order for S_1' , S_1'' and S_1 centres with increasing rates of 2.13, 1.93 and 1.88% at 90 K, respectively. The corresponding changes of E are in the reversed sequence of EPR centres with 2.91, 2.67 and 2.50% at 90 K, respectively. In other words, the more the axial field parameter D of the three centres increases, the less the asymmetric parameter E does. This fact means that the S_1' centre becomes more symmetric with decreasing temperature than the S_1'' or S_1 centres in the configuration of the Fe^{3+} ion together with O^{2-} ions and the compensating ion.

3. Hyperfine structure

3.1. Experimental results

In order to investigate the hyperfine structure of the three Fe^{3+} centres we have attempted to detect the resonance signals for the $\frac{3}{2} \leftrightarrow -\frac{3}{2}$ transitions with the orientation with the applied magnetic field parallel to the a axis (see table 1). The second derivative spectra were recorded at room temperature with a very slow scanning rate of 48 min mT^{-1} using double modulation of the field with 1 and 100 kHz simultaneously (Varian 1982). Figure 4 shows the observed hyperfine structure of each centre and ΔB

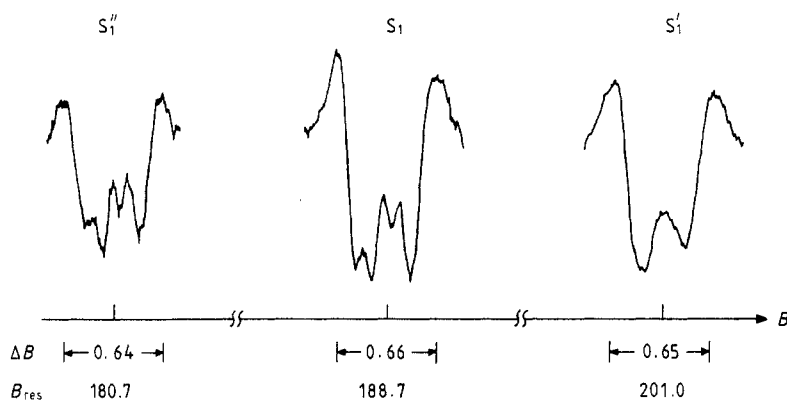


Figure 4. Hyperfine structure of the centres S_1 , S_1' and S_1'' , recorded at 9.160 ± 0.001 GHz with the second derivative mode. B_{res} indicates the resonance field and ΔB is the maximum peak-to-peak linewidth of the second derivative signals. All values are in mT.

Table 2. Properties of some monovalent ions.

Atomic no	Ion	Ionic radius (Å)	Isotope	Nuclear spin	Magnetic moment (β_N)	Nuclear g -factor	Natural abundance (%)
1	H ⁺	10^{-5}	¹ H	$\frac{1}{2}$	2.79268	5.5854	99.985
3	Li ⁺	0.68	⁷ Li	$\frac{3}{2}$	3.2560	2.1707	92.58
11	Na ⁺	0.98	²³ Na	$\frac{3}{2}$	2.2161	1.4774	100

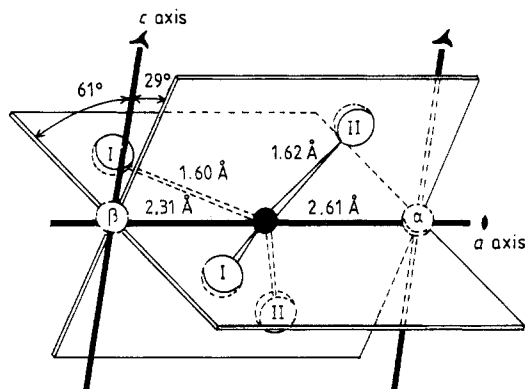
is the maximum peak-to-peak linewidth of the second derivative signals. The S_1'' and S_1 centres reveal four hyperfine lines, respectively, but the S_1' centre has only two lines. These structures indicate that the S_1'' and S_1 centres are associated with the nucleus having a nuclear spin of $\frac{3}{2}$, whereas S_1' is related to the nucleus of spin $\frac{1}{2}$. However, the hyperfine structure of S_1' does not seem to arise from the ⁵⁷Fe nucleus, because although its nuclear spin is $\frac{1}{2}$, its natural abundance is only 2.19% and the hyperfine splitting of ⁵⁷Fe in the ferric ion is usually not less than about 1.0 mT (Denison *et al* 1967, Mombourquette *et al* 1989).

3.2. Discussion

When a Si^{4+} ion is substituted by a Fe^{3+} ion, a positively monovalent compensating ion is required for charge neutrality. The compensating ions H⁺, Li⁺ and Na⁺ are probable candidates which can be introduced interstitially into α -quartz (Weil 1984). Their ionic radii, nuclear spins, nuclear magnetic moments, nuclear g -factors, and natural abundances are tabulated in table 2. Mackey (1963) investigated the hyperfine structure of ²⁷Al for the $[Al_{e^+}/M^+]^{1+}$ centre, where M^+ represents an interstitial cation such as Li⁺, Na⁺ or H⁺. Although the hyperfine lines in the first row in table 3 could not be separated by M^+ ions at 77 K, the differences in hyperfine splitting parameters of ²⁷Al are distinguished due to the attribution of M^+ ions. H⁺ affects the parameter most strongly, Na⁺ less and Li⁺ the least. However, the order of Na⁺ and Li⁺ does not agree with the sequence of their magnitudes of nuclear g -factor, as tabulated in table 2. This result means that the distances between the hole-bearing oxygen ion and Na⁺ and Li⁺, respectively, are slightly different (Mombourquette and Weil 1985).

Table 3. Hyperfine parameters of some EPR centres in α -quartz.

EPR centre	Isotope	Nuclear spin	Hyperfine splitting parameter (10^{-4} cm^{-1})	Observed temperature (reference)
$[\text{Al}_{\text{c}}/\text{Li}^+]^{1+}$	^{27}Al	$\frac{5}{2}$	$A_{\text{c}} = 7.3$	77 K (Mackey 1963)
$[\text{Al}_{\text{c}}/\text{Na}^+]^{1+}$			$A_{\text{c}} = 7.8$	
$[\text{Al}_{\text{c}}/\text{H}^-]^{1-}$			$A_{\text{c}} = 8.7$	
$[\text{AlO}_4/\text{H}^+]^{1-}$	^1H	$\frac{1}{2}$	$A_1 = -0.59$ $A_2 = -0.47 \bar{A} = 0.76$ $A_3 = +1.21$	35 K (Nuttall and Weil 1981)
$[\text{AlO}_4/\text{Li}^+]^{1+}$	^7Li	$\frac{3}{2}$	$A_1 = -0.30$ $A_2 = -0.22 \bar{A} = 0.26$ $A_3 = +0.26$	35 K (Nuttall and Weil 1981)
S_1	^{23}Na	$\frac{3}{2}$	$A_{\text{a}} = 1.03 \pm 0.05$	300 K
S'_1	^1H	$\frac{1}{2}$	$A_{\text{a}} = 2.62 \pm 0.05$	(present work)
S''_1	^7Li	$\frac{3}{2}$	$A_{\text{a}} = 0.93 \pm 0.05$	

**Figure 5.** The tetrahedron of oxygen atoms (open circles) surrounding a silicon atom (full circle) in right-handed α -quartz. α and β are interstitial sites.

At 35 K Nuttall and Weil (1981) observed the hyperfine structures of ^1H and ^7Li for $[\text{AlO}_4/\text{M}^+]^{1+}$ centres, where M^+ is H^+ or Li^+ . Their hyperfine splitting parameters are tabulated in the second and third row, respectively, of table 3. $[\text{AlO}_4/\text{M}^+]^{1+}$ centres are merely another representation of $[\text{Al}_{\text{c}}/\text{M}^+]^{1+}$ centres. Comparing the hyperfine splitting parameters of S'_1 and S''_1 centres with the average values of hyperfine parameters of ^1H and ^7Li for $[\text{AlO}_4/\text{M}^+]^{1+}$ centres, respectively, we can observe that those of S'_1 and S''_1 centres are 3.4 and 3.6 times as large as those of ^1H and ^7Li for $[\text{AlO}_4/\text{M}^+]^{1+}$ centres, respectively. Hyperfine parameters are proportional to the magnetic field splittings of the resonance signal and the splitting is produced by a nuclear magnetic moment at the site of a magnetic ion. In addition, the superhyperfine field is inversely proportional to the cube of the distance between the nucleus and the magnetic ion, if the interaction is assumed to be dipolar. Considering the distances of the substitutional Fe^{3+} ion and the hole-trapped O^- ion, respectively, from the interstitial M^+ ion of the above centres, we can qualitatively compare the magnitude of hyperfine parameters. The distance between the Fe^{3+} ion, substituted for Si^{4+} , and the site α of an interstitial M^+ ion as shown in figure 5 is 2.61 Å, but the distance between the hole-bearing $\text{O}(\text{I})$ and the site α is approximately 4.0 Å. From the ratio of $(2.61/4.0)^{-3}$, we can evaluate that the hyperfine splitting parameters of S'_1 and S''_1 must be 3.6 times as large as those of ^1H and ^7Li for

[AlO₄/M⁺]¹⁺ centres. This multiplicative factor is in good agreement with the values of 3.4 and 3.6 times as previously discussed.

In addition, the variations of D with temperature are in the descending order for S₁', S₁'' and S₁ centres. This sequence of EPR centres turns out to correspond to the ascending order of ionic radii and masses of H⁺, Li⁺ and Na⁺ ions. It is reasonable to argue that the lighter and smaller the ion, the more sensitive it is to the temperature variation and the more it contributes to the change of the axial field parameters.

4. Conclusions

The second-order axial field parameter D increases linearly with decreasing temperature from 300 K to 90 K owing to thermal contraction. The hyperfine structures of the three Fe³⁺ centres, recorded with the second derivative mode, indicate that S₁ and S₁'' centres are associated with the nuclei having nuclear spin of $\frac{3}{2}$, whereas the S₁' centre is related to the nucleus of spin $\frac{1}{2}$. By comparing the hyperfine splitting parameters of S₁' and S₁'' centres with those of ¹H and ⁷Li for [AlO₄/M⁺]¹⁺ centres, respectively, and from the temperature dependences of D and E for the three Fe³⁺ centres, we tentatively propose that S₁, S₁', and S₁'' centres are compensated with the interstitial Na⁺, H⁺ and Li⁺ ions, respectively, as Fe³⁺ substitutes for Si⁴⁺.

Acknowledgment

The research grant received from the Korea Science and Engineering Foundation (1985–1988) is gratefully acknowledged.

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