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# Theoretical investigations of the temperature dependence of zero-field splitting for $\text{Fe}^{3+}$ in $\text{Al}_2\text{O}_3$ crystals

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**Abstract.** In this paper, we carry out a detailed theoretical investigation of the temperature dependence of zero-field splitting (characterized by  $\Delta D(T) = D(T) - D(0)$ ) of  $\text{Al}_2\text{O}_3:\text{Fe}^{3+}$  crystals by taking into account both the static contributions due to the thermal expansion of crystal and the vibrational contributions due to the electron–phonon interaction. The static contributions are calculated from the spin–orbit coupling mechanism, the relativistic mechanism, the covalency and overlap mechanism and the spin–spin interaction mechanism. Similar to the studies on the specific heat of crystals, the vibrational contribution of phonons of acoustic branches is given using the long-wavelength approximation and that of phonons of optical branches is calculated using a single-frequency model. The calculated results show that the contribution coming from the coupling with optical phonons is comparable with that due to the thermal expansion and that, to reach good fits between the theoretical and experimental  $\Delta D(T)$ , all the contributions from the thermal expansion and the electron–phonon (including the optical and acoustic phonons) interaction should be taken into account.

## 1. Introduction

The temperature dependence of the EPR spectrum for  $\text{Fe}^{3+}$  ions in  $\text{Al}_2\text{O}_3$  crystals was measured decades ago (Geifman and Glinchuk 1971). It was found that the zero-field splitting  $D$  decreased with increasing temperature. By comparing the temperature dependence of the relative change in the splitting  $D$  (i.e.  $\Delta D(T)/D_0$ ) with that of the relative change in the linear dimensions of  $\text{Al}_2\text{O}_3$  (i.e.  $\Delta L(T)/L_0$ ), Geifman and Glinchuk (1971) assumed that the thermal expansion of a crystal makes the main contribution to the temperature dependence of zero-field splitting (note that, usually, this temperature dependence can be characterized by  $\Delta D(T) = D(T) - D(0)$  or  $\Delta D(T)/\Delta T \approx dD/dT$ ; we use  $\Delta D(T)$  in this paper). However, they did not make a theoretical investigation to support this assumption. As is known, the temperature dependence of the zero-field splitting  $\Delta D(T)$  results from both the implicit, or static, contribution related to the lattice thermal expansion and the explicit, or vibrational, contribution due to electron–phonon interaction (Walsh 1959, Shrivastava 1975). The implicit part comes not only from the changes in bond lengths (which is related to the linear dimension  $L$ ) but also from the changes in bond angles with the temperature. The explicit part includes the contribution from acoustic phonons and that from optical phonons. So, a reasonable and thorough theoretical investigation of the temperature dependence of the zero-field splitting  $\Delta D(T)$  should consider all these contributions and, from the investigation, the relative importance

of various contributions can therefore be determined. In the previous theoretical work on the temperature dependence of zero-field splitting for paramagnetic ions in crystals, few studies which included all these contributions were carried out because of the complexity of the problem. In this paper, we shall make detailed studies of the temperature dependence of zero-field splitting  $\Delta D(T)$  for  $\text{Al}_2\text{O}_3:\text{Fe}^{3+}$  crystals by taking all these contributions into account. On this basis, the above assumption is checked.

## 2. Static contribution to $\Delta D(T)$

The static contributions to the zero-field splitting  $D$  of  $d^5$  ions can be calculated from the microscopic mechanisms. As is known, there are many mechanisms which contribute to zero-field splitting, such as the spin-orbit (SO) coupling mechanism (Sharma 1968, Yu *et al* 1985, Yu and Zhao 1988), the spin-spin (SS) interaction mechanism (Pryce 1950), the relativistic (RE) mechanism (Heuvelen 1967, Dreybrodt and Silber 1969), the covalency and overlap (CO) mechanism (Novak and Veltrusky 1967, Emery *et al* 1981), the Orbach-Das-Sharma (ODS) (1965) mechanism and the Watanabe (WC) (Watanabe 1957) mechanism. The contributions due to the ODS and WC mechanisms are known to be negligible (Sharma 1968) and so we do not consider them here. For the SO coupling mechanism, the fourth- and sixth-order perturbation formulae of the splitting  $D$  for  $d^5$  ions in trigonal symmetry are as follows (Yu *et al* 1985, Yu and Zhao 1988):

$$D_{\text{stat}}^{(SO)} = D^{(4)} + D^{(6)} \quad (1)$$

with

$$D^{(4)} = -5\zeta^2(B_{40}^2 - 7B_{43}^2/10)/63P^2G - 3\zeta^2B_{20}(B_{20} + 21\zeta)/70P^2D \quad (2)$$

$$\begin{aligned} D^{(6)} = & -\zeta^2B_{20}^2[175B_{43}^2 + (24B_{20} - 25B_{40})^2]/(360150P^2D^2F) - 9\zeta^2B_{20}^4/2450P^3D^2 \\ & - \zeta^2B_{20}^2(11B_{43}^2 + 10B_{40}^2)/735P^3DG + \zeta^2[7B_{20}B_{43}^2(25B_{40} - 68B_{20}) \\ & + 10B_{20}B_{40}(B_{20} + B_{40})(24B_{20} - 25B_{40})]/(36015P^2DFG) \\ & - 5\zeta^2(B_{40}^2 - 7B_{43}^2/10)(29B_{43}^2 + 10B_{40}^2)/3969P^3G^2 \\ & + \zeta^2[-5(B_{43}^2 - 7B_{40}^2/10)(15B_{40}^2 - 14B_{43}^2) + 7B_{20}B_{43}^2(57B_{20} - 120B_{40}) \\ & - 75B_{20}B_{40}^2(B_{20} + 2B_{40})]/(21609P^2G^2F) \end{aligned} \quad (3)$$

where  $\zeta$  is the SO coupling coefficient. For  $\text{Fe}^{3+}:\text{Al}_2\text{O}_3$ ;  $\zeta = 400 \text{ cm}^{-1}$  was obtained from the optical data (Krebs and Maisch 1971).  $P$ ,  $D$ ,  $F$  and  $G$  are the energy separations between the excited quarters and the ground sextet of the free ion. The optical spectrum of a  $3d^n$  impurity  $M$  in an ionic lattice can be understood to a great extent only on the basis of an  $\text{MX}_n$  group formed by the impurity and the  $n$ th-nearest neighbours or ligands (Lucas *et al* 1994). So, from the nearest-neighbour point-charge-dipole model, we can write the trigonal field parameters  $B_{kl}$  as

$$\begin{aligned} B_{20} &= -\frac{3}{2} \sum_{i=1}^2 (3 \cos^2 \theta_i - 1) e q \left( \frac{1 + 3p}{eR} \right) \frac{\langle r^2 \rangle}{R_i^3} \\ B_{40} &= -\frac{3}{8} \sum_{i=1}^2 (35 \cos^4 \theta_i - 30 \cos^2 \theta_i + 3) e q \left( \frac{1 + 5p}{eR} \right) \frac{\langle r^4 \rangle}{R_i^5} \\ B_{60} &= \frac{3\sqrt{35}}{4} \sum_{i=1}^2 (\sin^3 \theta_i \cos \theta_i) e q \left( \frac{1 + 5p}{eR} \right) \frac{\langle r^4 \rangle}{R_i^5} \end{aligned} \quad (4)$$

where  $q(= -2e)$  is the ligand charge and  $p$  is the dipole, an adjustable parameter.  $R_i$  are the metal–ligand distances and  $\theta_i$  are the angles between the  $R_i$  directions and the  $C_3$  axis.

For  $Fe^{3+}$  ions, from the empirical d orbital and by introducing a parameter  $N$  to denote the average covalency reduction effect (Zhao *et al* 1986), we have

$$\begin{aligned} B &= 1130.22N^4 \text{ cm}^{-1} & C &= 4111.45N^4 \text{ cm}^{-1} \\ \langle r^2 \rangle &= 1.89039N^2 \text{ au}^2 & \langle r^4 \rangle &= 11.46485N^2 \text{ au}^4. \end{aligned} \quad (5)$$

The parameter  $N$ , dipole  $p$  and Trees correction  $\alpha$  can be obtained by fitting the observed optical spectra of the studied crystal. For  $Al_2O_3:Fe^{3+}$ , from the optical spectra (Sherman 1985), we have

$$N \approx 0.902 \quad p \approx 0.0545eR \quad \alpha \approx 38 \text{ cm}^{-1}. \quad (6)$$

The comparison between the optical spectrum bands obtained by calculation and in experiment is shown in table 1.

**Table 1.** Optical absorption spectra of  $Al_2O_3:Fe^{3+}$  crystals.

	Calculated value ( $\text{cm}^{-1}$ )	Observed value <sup>a</sup> ( $\text{cm}^{-1}$ )
${}^6A_1 \rightarrow {}^4T_1^a$	9770	9450
${}^4T_2^a$	14 863	14 350
${}^4A_1, {}^4E^a$	22 250	22 270
${}^4T_2^b$	24 430	25 510
${}^4E^b$	26 674	26 800
${}^4T_1^b$	32 300	32 500

<sup>a</sup> From Sherman (1985).

For the RE mechanism, the zero-field splitting in axial symmetry is (Dreybrodt and Silber 1969)

$$D_{RE} = 6\zeta A_2^0 \langle b_2(11) \rangle / 125P \quad (7)$$

where  $A_2^0 = B_2^0 / \langle r^2 \rangle$  and

$$\langle b_2(11) \rangle = -(R_{++}^2 - 3R_{+-}^2 - R_{--}^2) \approx -2.5(R_{++}^2 - R_{--}^2) \quad (8)$$

because  $R_{+-}^2$  is approximately the mean of  $R_{++}^2$  and  $R_{--}^2$  (Wybourne 1965, Heuvelen 1967). For  $Mn^{2+}$  ions,  $\langle b_2(11) \rangle = -0.0485 \text{ au}^2$  (Heuvelen 1967, Dreybrodt and Silber 1969); unfortunately, the value of  $\langle b_2(11) \rangle$  for  $Fe^{3+}$  ions has not been reported. However, a reasonable estimate for the value can be made from that of the isoelectronic  $Mn^{2+}$  ion. Starting from a comparison for the values of rare-earth ions of different valences, Karthe (1977) found that the constant  $R_{++}^2 - R_{--}^2$  turns out to be nearly independent of the elements in the constant valence state and is reduced by a factor of 2 when going from divalent to trivalent ions. So, he estimated that the value of  $R_{++}^2 - R_{--}^2$  for  $Fe^{3+}$  is approximately half that for  $Mn^{2+}$ . So, for  $Fe^{3+}$  ions, we have

$$\langle b_2(11) \rangle \approx -0.0243 \text{ au}^2. \quad (9)$$

The contribution of the CO mechanism to zero-field splitting in trigonal symmetry can be written as (Novak and Veltrusky 1976, Emery *et al* 1981).

$$D_{CO} = \frac{9}{2} \sum_{i=1}^2 d(R_i)(3 \cos^2 \theta_i - 1). \quad (10)$$

The  $R$  dependence of  $d(R)$  was calculated theoretically for  $(\text{FeO}_6)^{9-}$  groups and can be expressed approximately as (Novak and Veltrusky 1976)

$$d(R) \approx 2.29/R^5 \text{ cm}^{-1} \quad (11)$$

where  $R$  is in ångströms.

The zero-field splitting due to the SS interaction mechanism for  $(\text{FeO}_6)^{9-}$  groups is (Sharma 1968)

$$D_{SS}(0) \approx 0.4815A_2^0 \text{ cm}^{-1} \quad (12)$$

where  $A_2^0$  is in units of  $e^2/a_0^3$ ,  $a_0$  being the Bohr radius.

Thus, the static contribution due to the four mechanisms is

$$D_{stat} \approx D_{SO} + D_{RE} + D_{CO} + D_{SS}. \quad (13)$$

To make the numerical calculations for the zero-field splittings due to the four mechanisms and hence for  $D_{stat}$ , the structural parameters  $R_i$  and  $\theta_i$  for  $(\text{FeO}_6)^{9-}$  groups in  $\text{Al}_2\text{O}_3$  should be known. The structural parameters of  $\text{Al}_2\text{O}_3$  at room temperature are  $R'_1 \approx 1.966 \text{ \AA}$ ,  $R'_2 \approx 1.857 \text{ \AA}$ ,  $\theta'_1 \approx 47.7^\circ$  and  $\theta'_2 \approx 63.1^\circ$  (McClure 1963). However, the structural parameters in the vicinity of a substitutional impurity ion in a crystal are often different from those of host crystal in the cases of size and/or charge mismatch. For some trivalent impurity ions in  $\text{Al}_2\text{O}_3$  crystals, from the polarized optical spectrum studies, McClure (1962) suggested that these impurities do not occupy the exact  $\text{Al}^{3+}$  position but, because of their large size, they are forced to move along the  $C_3$  axis and closer to the larger oxygen triangle. This point is supported by the following fact, i.e. from the Rutherford backscattering spectrometry–channelling techniques Lorenzo *et al* (1995) found that the rare-earth ions in  $\text{LiNbO}_3$  (note that the structure of  $\text{LiNbO}_3$  is similar to that of  $\text{Al}_2\text{O}_3$  except that the sites of cations along the  $C_3$  axis are alternately of monovalent and quinquevalent character) are incorporated in the  $\text{Li}^+$  octahedra but, owing to their large size, they are also forced to move towards the larger oxygen triangle along the  $C_3$  axis. So, for  $\text{Fe}^{3+}$  in an  $\text{Al}_2\text{O}_3$  crystal, since the ionic radius (about  $0.785 \text{ \AA}$ ) (Shannon 1976) of  $\text{Fe}^{3+}$  is larger than that (about  $0.675 \text{ \AA}$ ) (Shannon 1976) of the replaced  $\text{Al}^{3+}$ , we can expect that the  $\text{Fe}^{3+}$  ion does not occupy an exact  $\text{Al}^{3+}$  site but is displaced towards the larger oxygen triangle along the  $C_3$  axis by an amount  $\Delta Z$ . Considering that at  $T = 0 \text{ K}$  the vibrational contribution to zero-field splitting is very small, the displacement  $\Delta Z$  can be determined by fitting the calculated static part of zero-field splitting at  $0 \text{ K}$  to the observed value as follows. The local structural parameters  $R_i$  and  $\theta_i$  for the  $(\text{FeO}_6)^{9-}$  group in  $\text{Al}_2\text{O}_3$  can be calculated from the displacement  $\Delta Z$  and the host parameters  $R'_i$  and  $\theta'_i$ . From the parameters  $R'_i$  and  $\theta'_i$  and from the transverse thermal expansion coefficients  $\alpha_\perp(T)$  and longitudinal thermal expansion coefficients  $\alpha_\parallel(T)$  at various temperature (Yates *et al* 1972), we can calculate the parameters  $R_i(T)$  and  $\theta_i(T)$  (note that the data of  $\alpha_\perp(T)$  and  $\alpha_\parallel(T)$  given by Yates *et al* (1972) are only for temperatures up to  $760 \text{ K}$ ; for  $T > 760 \text{ K}$ , they are obtained by using an extrapolation) and extrapolate the parameters  $R_i(0)$  and  $\theta_i(0)$  at  $0 \text{ K}$  by using the formulae

$$R_i(T) = R_i(0) \left( 1 + \int_0^T \alpha_R(T) dT \right) \quad \theta_i(T) = \theta_i(0) \left( 1 + \int_0^T \alpha_\theta(T) dT \right) \quad (14)$$

where  $\alpha_R$  and  $\alpha_\theta$  are the thermal expansion coefficients of the bond length  $R_i$  and the bond angle  $\theta_i$ , respectively. For trigonal symmetry, from the geometric relations, we have

$$\alpha_R = \alpha_\perp \sin^2 \theta_i + \alpha_\parallel \cos^2 \theta_i \quad \alpha_\theta = \{[\sin(2\theta_i)]/2\theta_i\}(\alpha_\perp - \alpha_\parallel). \quad (15)$$

Thus, by fitting the calculated  $D_{stat}$  at 0 K to the observed value (about  $1719 \times 10^{-4} \text{ cm}^{-1}$ ) (Bogel and Symmons 1959), we obtain  $\Delta Z \approx 0.02 \text{ \AA}$ . The local structural parameters at 0 K are  $R_1(0) \approx 1.978 \text{ \AA}$ ,  $R_2(0) \approx 1.847 \text{ \AA}$ ,  $\theta_1(0) \approx 47.239^\circ$  and  $\theta_2(0) \approx 63.657^\circ$  and at room temperature are  $R_1(\text{RT}) \approx 1.979 \text{ \AA}$ ,  $R_2(\text{RT}) \approx 1.848 \text{ \AA}$ ,  $\theta_1(\text{RT}) \approx 47.236^\circ$  and  $\theta_2(\text{RT}) \approx 63.654^\circ$ . The displacement direction of Fe<sup>3+</sup> ions is consistent with the above expectation and can be regarded as reasonable. The calculated static part of zero-field splitting at 0 K is

$$D_{stat}(0) \approx D_{SO}(0) + D_{RE}(0) + D_{CO}(0) + D_{SS}(0) \approx (2084 + 336 - 658 - 38) \approx 1724 \times 10^{-4} \text{ cm}^{-1}. \quad (16)$$

It can be seen that the contributions due to the RE, CO and SS mechanisms cancel partly and the magnitude of  $D_{SO}(0)$  is much greater than those of other mechanisms; so the opinion suggested by some workers (Yu and Zhao 1988, Sharma 1968) that the SO mechanism is dominant can be understood.

According to the thermal expansion coefficients  $\alpha_{\perp}(T)$  and  $\alpha_{\parallel}(T)$ , the temperature dependence of zero-field splitting  $\Delta D_{stat}(T)(= D_{stat}(T) - D_{stat}(0))$  due to the thermal expansion can be calculated. The results are compared with the observed values in table 2.

**Table 2.** Temperature dependence of the zero-field splitting  $\Delta D(T)(= D(T) - D(0))$  for Al<sub>2</sub>O<sub>3</sub>:Fe<sup>3+</sup> crystals and various contributions (i.e. the static contribution  $\Delta D_{stat}$ , the vibrational contributions  $\Delta D_{ac}$  and  $\Delta D_{op}$  due to the acoustic and optical phonons, respectively) to it.

T (K)	$\Delta D_{stat}$ ( $10^{-4} \text{ cm}^{-1}$ )	$\Delta D_{ac}$ ( $10^{-4} \text{ cm}^{-1}$ )	$\Delta D_{op}$ ( $10^{-4} \text{ cm}^{-1}$ )	$\Delta D_{tot}^a$ ( $10^{-4} \text{ cm}^{-1}$ )	$\Delta D_{exp}^b$ ( $10^{-4} \text{ cm}^{-1}$ )
100	-1	0	-4	-5	-7
200	-5	1	-14	-18	-21
300	-16	2	-24	-38	-40
400	-31	5	-35	-61	-62
500	-47	7	-46	-86	-86
600	-65	10	-57	-122	-111
700	-84	13	-68	-139	-138
800	-103	15	-79	-166	-166
900	-122	18	-90	-194	-194
1000	-142	21	-101	-222	-222

<sup>a</sup> The theoretical value  $\Delta D_{tot} = \Delta D_{stat} + \Delta D_{ac} + \Delta D_{op}$ .

<sup>b</sup> The experimental data are taken from figure 1 of the paper by Geifman and Glinchuk (1971) with  $D(0) \approx 1719 \times 10^{-4} \text{ cm}^{-1}$  (Bogel and Symmons 1959). The experimental errors of  $\Delta D(T)$  are estimated to be about  $\pm 5 \times 10^{-4} \text{ cm}^{-1}$ .

From table 2, one can see that the temperature dependence of zero-field splitting  $\Delta D_{stat}(T)$  is identical in sign but too small in magnitude in comparison with the observed value. So, the static contribution due to thermal expansion cannot be regarded as the main contribution. The assumption made by Geifman and Glinchuk (1971) seems doubtful. Obviously, to explain satisfactorily the temperature dependence of zero-field splitting  $\Delta D(T)$ , the vibrational contributions due to the electron-phonon interaction should be taken into account.

### 3. Vibrational contributions to $\Delta D(T)$

The vibrational part of  $\Delta D(T)$  includes the contribution from acoustic phonons and that from optical phonons. In the case of acoustic phonons, similar to the Debye model in the

studies of the specific heat of crystal, Shrivastava (1973, 1975) used the long-wavelength approximation and obtained that the zero-field splitting induced by the acoustic phonons is

$$D_{ac}(T) = \frac{1}{8} K_D \Theta_D^4 + K_D T^4 \int_0^{\Theta_D/T} x^3 (e^x - 1)^{-1} dx \quad (17)$$

where the first term is the zero-point vibration contribution,  $\Theta_D$  is the Debye temperature and  $K_D$  is an adjustable parameter which depends on the strength of the electron-phonon interaction and the value of  $D_{stat}(0)$  in the crystal. So, the sign of  $D_{ac}(T)$  is the same as that of  $D_{stat}(0)$ . Obviously, we have

$$\Delta D_{ac}(T) = D_{ac}(T) - D_{ac}(0) = K_D T^4 \int_0^{\Theta_D/T} x^3 (e^x - 1)^{-1} dx. \quad (18)$$

To study the contribution due to optical phonons, only one mode of vibration with frequency  $\omega$  is considered because the dispersion of optical branch is often small. This point is similar to the Einstein model in the studies of specific heat. Thus, Walsh (1959) obtained that the contribution of optical phonons to the zero-field splitting is

$$D_{op}(T) = D_\tau \coth(\hbar\omega/2kT) \quad (19)$$

where  $D_\tau$  is also an adjustable parameter which describes the strength of the electron-phonon interaction. At  $T = 0$  K,  $D_{op}(0) = D_\tau$ . So, the zero-point vibrational contribution is included in  $D_{op}(T)$ , and

$$\Delta D_{op}(T) = D_\tau [\coth(\hbar\omega/2kT) - 1] \quad T \neq 0 \text{ K}. \quad (20)$$

Thus, we have the total theoretical value including all contributions as follows:

$$\Delta D_{tot}(T) = \Delta D_{stat}(T) + \Delta D_{ac}(T) + \Delta D_{op}(T). \quad (21)$$

For  $\text{Al}_2\text{O}_3$ , using a Debye-model phonon spectrum to fit the specific heat of this crystal, one would find that  $\Theta_D \approx 935$  K (McCumber and Sturge 1963). From the maximum phonon frequency obtained by the Raman measurement, the single optical phonon frequency can be taken as  $\omega \approx 2.3 \times 10^{13} \text{ s}^{-1}$  (Klein *et al* 1977). Thus, we find that, to give the best fit of the observed temperature dependence of zero-field splitting, the parameters

$$K_D \approx 1.12 \times 10^{-14} \text{ cm}^{-1} \text{ K}^{-4} \quad D_\tau \approx -9.68 \times 10^{-4} \text{ cm}^{-1}. \quad (22)$$

So, at  $T = 0$  K, we have

$$\begin{aligned} D_{tot}(0) &= D_{stat}(0) + D_{ac}(0) + D_{op}(0) \approx (1724 + 10.7 - 9.68) \times 10^{-4} \text{ cm}^{-1} \\ &\approx 1725 \times 10^{-4} \text{ cm}^{-1}. \end{aligned} \quad (23)$$

The result is also close to the observed value (about  $1719 \times 10^{-4} \text{ cm}^{-1}$ ). The calculated and observed  $\Delta D(T)$  and the static and vibrational contributions to the values of  $\Delta D(T)$  are compared in table 2.

#### 4. Discussion and conclusions

From the above calculations, several points should be stressed here.

- (1) The contributions to  $\Delta D(T)$  from the acoustic and optical phonons cancel partly.
- (2) The zero-field splittings  $D(T)$  at various temperatures are related mainly to the static trigonal distortion of crystal; however, for the temperature dependence of zero-field splitting  $\Delta D(T)$ , the static contribution due to thermal expansion cannot be regarded as the main contribution because the vibrational contribution due to the optical phonons is comparable with it. The assumption obtained by comparing the values of  $\Delta D(T)/D_0$  with  $\Delta L(T)/L_0$

(Geifman and Glinchuk 1971) is not reasonable. The reason is, in our opinion, that the zero-field splitting  $D$  is related not only to the linear dimension  $L$  but also to the distortion of the oxygen octahedron of Al<sub>2</sub>O<sub>3</sub>. In fact, although the increase in the linear dimension  $L$  with increasing temperature will result in a reduction in the crystal-field strength and hence in the zero-field splitting, the anisotropy of the thermal expansion coefficient (characterized by  $\alpha_{\perp} - \alpha_{\parallel}$ ) increases with increasing temperature, which will result in an increase in the trigonal distortion of oxygen octahedron and hence an increase in the zero-field splitting of Al<sub>2</sub>O<sub>3</sub>:Fe<sup>3+</sup>. The effects of the two phenomena on the value of  $\Delta D(T)$  cancel partly and so the assumption obtained by considering only the change in  $\Delta L(T)/L_0$  is not correct.

(3) In the previous theoretical work on the temperature dependence of zero-field splitting, only some of the contributions were included. For example, Shrivastava (1973, 1975, 1988) studied the temperature dependence of the zero-field splitting for d<sup>n</sup> ions in many crystals by taking into account only the vibrational contribution from acoustic phonons, and Sharma (1970) studied the temperature dependence of the zero-field splitting for CdCl<sub>2</sub>:Mn<sup>2+</sup> in terms of only the effect due to lattice thermal expansion. These studies should not be regarded as satisfactory because they did not confirm that the contributions from other causes can be neglected. Our present study shows that, to explain satisfactorily the temperature dependence of the zero-field splitting  $\Delta D(T)$  of Al<sub>2</sub>O<sub>3</sub>:Fe<sup>3+</sup>, all the contributions to  $\Delta D(T)$  from the thermal expansion and the electron-phonon (including the acoustic and optical phonons) interaction should be taken into account.

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