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# Pressure and temperature shifts of the zero-field splitting for $\text{Mn}^{2+}$ and $\text{Fe}^{3+}$ ions in MgO

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**Abstract.** The relationship between the EPR cubic parameter  $a$ -value and the local structure of  $3d^5$  ions in crystals has been established by utilizing the crystal-field-like model. A general method for calculating both the local compressibility and local thermal expansion coefficient of the  $3d^5$  impurities in crystals has been proposed. Results show that the EPR cubic parameter  $a$ -value and its pressure and temperature shifts for  $\text{MgO}:\text{Mn}^{2+}$  and  $\text{MgO}:\text{Fe}^{3+}$  can be interpreted uniformly. It is also shown that: (a) the local compressibility and local thermal expansion coefficients of  $\text{MgO}:\text{Mn}^{2+}$  and  $\text{MgO}:\text{Fe}^{3+}$  crystals deduced are close to those of the host lattice, within experimental errors, and that the local bond lengths deduced are quite close to those of the shell model calculation values; and (b) the  $Dq \propto R^{-5}$  relation is a good approximation.

## 1. Introduction

As either  $\text{Fe}^{3+}$  or  $\text{Mn}^{2+}$  is in  $3d^5$  configuration with the ground state  ${}^6\text{S}$ , one may expect that zero-field splitting (ZFS) of the  $\text{Fe}^{3+}$  ion does not markedly differ in magnitude from that of  $\text{Mn}^{2+}$  when they are doped into the same host crystal. However, this is not the case. A large number of experimental observations have shown that the ZFS of  $\text{Fe}^{3+}$  is much larger than that of  $\text{Mn}^{2+}$  [1–5].

This behaviour is difficult to understand, and so Low and Rosengarten [2] reached the conclusion that crystal-field theory is not capable of proving a unified explanation for the ZFS parameters and optical spectra of  $3d^5$  ions. Such a difficulty with the S-state ZFS continued until 1985, although many works have been published which provide good numerical estimates for  $\text{Mn}^{2+}$  ions in crystals. In 1986, this difficulty was analysed in some detail by Zhao *et al* [6]. They calculated the ZFS of  $\text{Fe}^{3+}$  doped into corundum and four kinds of garnets (YAG, YGG, LuAG, and LuGG) together with that of  $\alpha\text{-Al}_2\text{O}_3:\text{Mn}^{2+}$  and considered various mechanisms using a high-order perturbation formula of ZFS. Good agreement between the experiments and theory was obtained. However, the high-order perturbation formula is not a good approximation. In 1995, the rigorous expressions for calculating the EPR parameters  $D$ ,  $a$ , and  $F$  were developed using a complete diagonalization procedure for  $3d^5$  ions in a low-symmetry field [7]. The formulae have been applied to  $\text{RbCdF}_3:\text{Mn}^{2+}$ ,  $\text{RbMnF}_3$ ,  $\text{Rb}_2\text{CdF}_4:\text{Mn}^{2+}$ , and  $\alpha\text{-Al}_2\text{O}_3:\text{Fe}^{3+}$ . Results indicate that the optical and EPR spectra for  $\text{Mn}^{2+}$  ions in  $\text{RbCdF}_3$ ,  $\text{RbMnF}_3$ ,  $\text{Rb}_2\text{CdF}_4$ , and  $\text{Fe}^{3+}$  ions in  $\alpha\text{-Al}_2\text{O}_3$  can be interpreted uniformly. We expect it to also work well in the  $\text{MnO}:\text{Mn}^{2+}$  and  $\text{MgO}:\text{Fe}^{3+}$  problem.

In this work, the relationship between the EPR cubic parameter  $a$ -value and the local structure of  $3d^5$  ions in crystals has been established by utilizing the crystal-field-like

model proposed by Zhao *et al* [7–9]. A general method for calculating both the local compressibility and local thermal expansion coefficient of the 3d<sup>5</sup> impurities in crystals has been proposed. Results show that the EPR cubic parameter *a*-value and its pressure and temperature shifts for MgO:Mn<sup>2+</sup> and MgO:Fe<sup>3+</sup> can be interpreted uniformly.

## 2. The determination of the local structure of MgO:Mn<sup>2+</sup> and MgO:Fe<sup>3+</sup>

Some transition metal impurities play an important role in the physical properties of the crystals. A proper microscopic understanding of such properties requires a knowledge of the local structure around the impurity. It is currently accepted that for impurities in solids the bond lengths can be determined through the extended x-ray absorption fine-structure splitting (EXAFS) technique. The bond lengths can also be determined through the superhyperfine splitting (SHF) measurement [10, 11]. However, they are not suitable for the determination of the bond angles of impurity. The ENDOR technique can give direct information on the identity and the superhyperfine and quadrupole interactions of the neighbouring nuclei except those with zero nuclear spin (e.g., <sup>16</sup>O, the only abundant oxygen isotope). Zhao *et al* [7–9] have shown that the bond lengths and bond angles of transition metal impurities in solids can be determined through the optical and EPR spectra. We expect it to also work well in the case of MgO:Mn<sup>2+</sup> and MgO:Fe<sup>3+</sup> crystals.

According to the crystal-field-like model proposed by Zhao *et al* [7–9], we have

$$\begin{aligned} B &= N^4 B_0 & C &= N^4 C_0 & \alpha &= N^4 \alpha_0 \\ \beta &= N^4 \beta_0 & \zeta_d &= N^2 \zeta_d^0 & \langle r^2 \rangle &= N^2 \langle r^2 \rangle_0 \\ \langle r^4 \rangle &= N^2 \langle r^4 \rangle_0 & Dq &= \frac{qe \langle r^4 \rangle}{6R^5} \end{aligned} \quad (1)$$

where *B*, *C*,  $\alpha$ ,  $\beta$ ,  $\zeta_d$ ,  $\langle r^n \rangle$ , *q*, *N*, and *R* denote the electrostatic parameters, the Trees correction constant, the Racah correction constant, the spin-orbit coupling constant, the expectation values of  $r^n$ , the effective charge of ligands, the average covalency reduction factor and the bond length, respectively. For Mn<sup>2+</sup> and Fe<sup>3+</sup> ions, we have

Mn<sup>2+</sup> [7, 8, 12]

$$\begin{aligned} B_0 &= 911 \text{ cm}^{-1} & C_0 &= 3273 \text{ cm}^{-1} & \alpha_0 &= 65 \text{ cm}^{-1} \\ \beta_0 &= -131 \text{ cm}^{-1} & \zeta_d^0 &= 336.6 \text{ cm}^{-1} & \langle r^2 \rangle_0 &= 2.7755 \text{ au} \\ \langle r^4 \rangle_0 &= 23.2594 \text{ au} \end{aligned} \quad (2)$$

Fe<sup>3+</sup> [6, 7]

$$\begin{aligned} B_0 &= 1130.22 \text{ cm}^{-1} & C_0 &= 4111.45 \text{ cm}^{-1} & \alpha_0 &= 40 \text{ cm}^{-1} \\ \beta_0 &= -131 \text{ cm}^{-1} & \zeta_d^0 &= 588.946 \text{ cm}^{-1} & \langle r^2 \rangle_0 &= 1.89039 \text{ au} \\ \langle r^4 \rangle_0 &= 11.46485 \text{ au} \end{aligned} \quad (3)$$

As can be seen, this model leaves at most two model parameters *N* and *q*, which remain to be determined from two theoretically or experimentally known energy levels. By diagonalizing the complete energy matrix (252 × 252), and using equation (1) to (3), we find that (a) *N* = 0.903262, *q* = 1.8071*e*, and *R* = 1.88 Å fitted from the optical spectrum and the EPR *a*-value for MgO:Fe<sup>3+</sup>, and *N* = 0.9679, *q* = 1.49*e*, and *R* = 2.1655 Å fitted from the optical spectrum and the EPR *a*-value for MgO:Mn<sup>2+</sup>. The result is listed in table 1. A good agreement between the calculation and experiments shows that the results are reasonable and safe. It is interesting to note that the bond lengths obtained are close to those of the shell (and breathing shell) model calculation values by Sangster *et al* [13] and by Yeung [14].

**Table 1.** Optical spectrum and EPR  $a$ -value (293 K, zero pressure). All energies are in units of  $cm^{-1}$ .

Transition	Calculated		Observed			
	MgO:Fe <sup>3+</sup> $N = 0.903262$ $q = 1.8071e$ $R = 1.88 \text{ \AA}^a$	MgO:Mn <sup>2+</sup> $N = 0.9679$ $q = 1.49e$ $R = 2.1655 \text{ \AA}^b$	MgO:Fe <sup>3+</sup>		MgO:Mn <sup>2+</sup>	
<sup>6</sup> A <sub>1</sub>			[18]	[19]	[3]	[20]
<sup>4</sup> T <sub>1</sub> (G)	12 191	14 598				
	12 441	14 653	12 100	10 000	15 200	
	12 614	14 733		-13 500		
	12 711	14 786				
<sup>4</sup> T <sub>2</sub> (G)	17 215	19 527				
	17 278	19 573	18 000			
	17 285	19 577				
	17 301	19 595				
<sup>4</sup> A <sub>1</sub> (G), <sup>4</sup> E(G)	21 565	23 464				
	21 667	23 481		21 740	23 500	23 474
	21 699	23 494				
	21 742	23 503				
<sup>4</sup> T <sub>2</sub> (D)	24 187	26 055				
	24 254	26 061	25 500	25 120		25 710
	24 470	26 274				
	24 481	26 459				
<sup>4</sup> E(D)	26 657	28 317				
	26 663	28 323	25 500	27 500	28 100	28 090
	26 677	28 327				
<sup>4</sup> T <sub>1</sub> (P)	31 015	32 291				
	31 241	32 208	32 500	30 970	33 200	33 220
	31 321	32 346				
	31 994	32 488				
$a$ ( $10^{-4} cm^{-1}$ )	203.9	18.55	[16] 203.8		[16] 19	18.3(3)

<sup>a</sup>  $R = 1.888 \text{ \AA}$  [13],  $R = 1.879 \text{ \AA}$  [14].

<sup>b</sup>  $R = 2.153 \text{ \AA}$  [13],  $R = 2.184 \text{ \AA}$  [14].

### 3. Pressure and temperature shifts of MgO:Mn<sup>2+</sup> and MgO:Fe<sup>3+</sup>

The cubic ZFS of  $Mn^{2+}$  and  $Fe^{3+}$  ions doped as impurities in  $MgO$  crystals has been observed by Walsh [1] at different hydrostatic pressures. It has been found that  $a$  increases linearly with increasing pressure  $P$ , with processing variation coefficient  $da/a dP = 4.03 \times 10^{-3} \text{ kbar}^{-1}$  for both crystals at room temperature, and in the range  $P \leq 10 \text{ kbar}$ . The effect of temperature on the EPR spectra for  $Mn^{2+}$  and  $Fe^{3+}$  in  $MgO$  had been measured by Rubio and Medrano [15], and Walsh *et al* [16],  $da/a dT = -2.2(3) \times 10^{-4} \text{ K}^{-1}$  for  $MgO:Fe^{3+}$ , and  $da/a dT = -1.6(3) \times 10^{-4} \text{ K}$  for  $MgO:Mn^{2+}$ . Rubio and Medrano indicated that the temperature-dependent EPR parameter  $a$  for  $Fe^{3+}$  in  $MgO$  is quite different from that of  $MgO:Mn^{2+}$ , and they believed that this result was very difficult to understand. We report here our theoretical interpretation.

By diagonalizing the complete energy matrix ( $252 \times 252$ ) and using equations (1) to (3), we find that: (a) the local compressibility  $dR/R dP = -1.9 \times 10^{-4} \text{ kbar}^{-1}$  for  $MgO:Fe^{3+}$ , and  $dR/R dP = -2.0 \times 10^{-4} \text{ kbar}^{-1}$  for  $MgO:Mn^{2+}$ ; and (b) the local thermal expansion

coefficient  $dR/R dT = 10.4 \times 10^{-6} \text{ K}^{-1}$  for both crystals of  $\text{MgO:Fe}^{3+}$  and  $\text{MgO:Mn}^{2+}$ . The result is listed in table 2. It can be seen from table 2 that the local compressibilities and local thermal expansion coefficients obtained are in good agreement with the experimental data for the host MgO [17, 21], within experimental errors.

**Table 2.** Pressure and temperature shifts of EPR  $a$ -values.

	Calculated		Observed	
	MgO:Fe <sup>3+</sup>	MgO:Mn <sup>2+</sup>	MgO:Fe <sup>3+</sup>	MgO:Mn <sup>2+</sup>
$(dR/R dT)_p$ ( $10^{-6} \text{ K}^{-1}$ )	10.4	10.4	10.4 (MgO) [17]	10.4 (MgO) [17]
$(dR/R dP)_T$ ( $10^{-4} \text{ kbar}^{-1}$ )	-1.9	-2.0	-1.9 (MgO) [21]	-1.9 (MgO) [21]
$(da/a dT)_p$ ( $10^{-4} \text{ K}^{-1}$ )	-2.16	-1.44	-2.2 (3) [15]	-1.6 (3) [15]
$(da/a dP)_T$ ( $10^{-3} \text{ kbar}^{-1}$ )	4.06	4.00	4.03 ([1], 1961)	4.03 ([1], 1961)

#### 4. Summary

An excellent agreement between the calculations and experiments shows that:

(a) the optical and EPR spectra of  $\text{MgO:Fe}^{3+}$  and  $\text{MgO:Mn}^{2+}$  can be interpreted uniformly, based on both the crystal-field-like model and the rigorous energy matrix diagonalization procedure;

(b) the effect of temperature on the EPR parameter  $a$ -value for  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  in magnesium oxide ( $T \geq 293 \text{ K}$ ) is associated with the local linear thermal expansion coefficient [16, 17], and the electron-phonon interaction will not contribute directly to the ZFS, because  $a_v = a(\text{obsd}) - a(\text{calc}) < 0.3 \times 10^{-4} \text{ cm}^{-1}$  and  $-da_v/a_v dT < 10^{-5} \text{ K}^{-1}$ , here  $a_v$  denotes the  $a$ -value arising from the electron-phonon coupling. However, the indirect electron-phonon contribution is important because of the importance of phonon coupling to produce changes in both the equilibrium geometry and the local force constants [13];

(c) the local compressibilities and local thermal expansion coefficients of  $\text{MgO:Fe}^{3+}$  and  $\text{MgO:Mn}^{2+}$  are close to those of the host lattice, within experimental error;

(d) the  $Dq \propto R^{-5}$  relation is a good approximation, because the good agreements between the pressure and temperature experiments and equation (1) (i.e.  $Dq = eq\langle r^4 \rangle / 6R^5$ ) are achieved;

(e) the calculated bond lengths at room temperature and room pressure for  $\text{MgO:Fe}^{3+}$  and  $\text{MgO:Mn}^{2+}$  are quite close to those of the shell (and breathing shell) model calculation values by Sangster *et al* [13] and by Yeung [14]; and

(f) the present result shows again that the local structures and transition metal impurities in solids can be determined through the optical and EPR measurements, based on the crystal-field model proposed by Zhao *et al*.

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