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# Investigations of the temperature dependence of the electron paramagnetic resonance $g$ -factor for the MgO:Cr<sup>3+</sup> crystal

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**Abstract.** Detailed theoretical studies of the temperature dependence of EPR  $g$ -factor for the MgO:Cr<sup>3+</sup> crystal have been made by considering both the static contribution due to the thermal expansion of crystal and the vibrational contributions due to the electron–phonon (including the acoustic and optical phonons) interaction. The static contribution is calculated from the macroscopic thermodynamic method and the microscopic crystal-field method. The results from both methods are close to each other, suggesting that the two methods are applicable to studies of temperature dependence of the  $g$ -factor. The vibrational contribution due to acoustic phonons is obtained by using a Debye model for the lattice vibrations, and that due to optical phonons is calculated by use of a single-frequency model. The calculated results show that, for the  $g(T)$ -factors at various temperatures, the static contribution is dominant; however, for the temperature dependence of the  $g$ -factor, i.e.  $dg/dT$ , the vibrational contributions are large and should be taken into account.

## 1. Introduction

The EPR  $g$ -factors of paramagnetic ions bound in cubic crystals change with temperature. The change results from both the implicit or static contribution related to the lattice thermal expansion and the explicit or vibrational contribution due to the electron–phonon (including the acoustic and optical phonons) interaction [1–3]. Thus, according to the general thermodynamic relation, the change in  $g$  produced by a change in temperature may be written as [1]

$$(dg/dT)_P = [\partial g/\partial(\ln R)]_T [\partial(\ln R)/\partial T]_P + (\partial g/\partial T)_R. \quad (1)$$

The first and second terms on the right of equation (1) are the implicit and explicit contributions, respectively.  $R$  is the metal–ligand distance and  $[\partial(\ln R)/\partial T]_P = \alpha_{loc}$  is the local thermal expansion coefficient in the vicinity of paramagnetic ion. If the isothermal pressure dependence of  $g$  and the local linear compressibility  $\beta_{loc}$  and the coefficient  $\alpha_{loc}$  are known, the static contribution can be evaluated as

$$\begin{aligned} (dg/dT)_{stat} &\approx (\partial g/\partial P)_T [\partial P/\partial(\ln R)]_T [\partial(\ln R)/\partial T]_P \\ &\approx (-\alpha_{loc}/\beta_{loc})(\partial g/\partial P)_T. \end{aligned} \quad (2)$$

For MgO:Cr<sup>3+</sup>, Walsh *et al* [1] evaluated the static contribution to the  $g$ -factor from the experimental pressure dependence of the  $g$ -factor [4] and from the compressibility  $\beta_h$  and

thermal expansion coefficient  $\alpha_h$  of the host MgO crystal. They found that the static contributions are different from the observed values in the high-temperature zone and so the vibrational contributions should be considered. However, no further detailed theoretical studies were made; in particular, quantitative calculations of various contributions based on the theoretical models were not carried out. In this paper, we shall make a detailed theoretical study of the  $g(T)$ -factors at various temperatures and the temperature dependence of the  $g$ -factor, i.e.  $dg/dT$ , of a MgO:Cr<sup>3+</sup> crystal by taking all the contributions into account.

## 2. Vibrational contributions

The vibrational contributions to  $g(T)$  and  $dg/dT$  consist of two parts: the contribution of acoustic phonons and that of optical phonons. As is known, both the vibrational contributions to the  $g$ -factor (or other spin-Hamiltonian parameters) are proportional to the mean value  $\langle Q^2 \rangle$  of the square of the amplitudes of vibrations (an average over the different normal modes) [2, 3, 5–8]. For vibrations related to the acoustic phonons, by using a Debye model for the lattice vibrations, we have [3, 8]

$$\begin{aligned} \langle Q^2 \rangle &\propto T^4 \int_0^{T_D/T} x^3 [\frac{1}{2} + (\exp x - 1)^{-1}] dx \\ &\approx \frac{1}{8} T_D^4 + T^4 \int_0^{T_D/T} x^3 (\exp x - 1)^{-1} dx. \end{aligned} \quad (3)$$

Thus, the vibrational contribution from acoustic phonons to the  $g$ -factor can be written as

$$g_{ac} \approx \frac{1}{8} K_g T_D^4 + K_g T^4 \int_0^{T_D/T} x^3 (\exp x - 1)^{-1} dx \quad (4)$$

where the first term is the zero-point vibrational contribution and  $T_D$  is the Debye temperature.  $K_g$  depends on the strength of electron–phonon interaction and also on the vibrational properties of crystal. Usually,  $K_g$  is treated as an adjustable parameter.

The vibrational contribution of optical phonons is due to all the optical modes. However, since the spectrum of optical phonons is confined to a very narrow frequency region, the single-frequency model may be taken as a good approximation. Thus, similar to the Einstein model in the study of specific heat, only one mode of vibration with frequency  $\omega_{eff}$  is considered here. So, we have [5, 6]

$$\langle Q^2 \rangle \propto \left\{ \frac{1}{2} + [\exp(\hbar\omega_{eff}/kT) - 1]^{-1} \right\} = \frac{1}{2} \coth(\hbar\omega_{eff}/2kT). \quad (5)$$

Thus, the vibrational contribution to the  $g$ -factor from optical phonons is

$$g_{op}(T) = g_\tau \coth(\hbar\omega_{eff}/2kT) \quad (6)$$

where  $g_\tau$  is also an adjustable parameter that depends on the strength of the electron–phonon interaction and also on the vibrational properties of the crystal. At  $T = 0$  K,  $g_{op}(0) = g_\tau$ . So, the zero-point vibrational contribution is included in equation (6).

## 3. Static contributions

The static contributions to  $g(T)$  and  $dg/dT$  can be calculated from the macroscopic thermodynamic method and microscopic crystal-field method. The former is related to equation (2). So, if the local thermal expansion coefficients  $\alpha_{loc}(T)$  and compressibilities  $\beta_{loc}(T)$  at various temperatures are known, the temperature dependence  $(dg/dT)_{stat}$  at these

temperatures can be calculated from the pressure dependence of the  $g$ -factor. From this,  $g(T)$  at various temperatures can be calculated.

The microscopic method is based on the perturbation formula for the  $g$ -factor. For the  $MgO:Cr^{3+}$  crystal, because the spin-orbit coupling coefficient  $\zeta_p^0$  ( $\approx 150 \text{ cm}^{-1}$ ) of the free  $O^{2-}$  ion is smaller than that of the  $Cr^{3+}$  ion ( $\zeta_p^0 \approx 240 \text{ cm}^{-1}$ ), the contributions of the spin-orbit coupling of the ligand (i.e.  $O^{2-}$ ) to the  $g$ -factor (and other spin-Hamiltonian parameters) can be neglected [9] and so the classical crystal-field theory can be used here. According to the theory, the high-order perturbation formulae for  $g_{\parallel}$  and  $g_{\perp}$  for  $d^3$  ions in trigonal symmetry based on the strong-field coupling scheme were established by Macfarlane [10]. By letting the trigonal field parameters  $V = V' = 0$  and correcting a few misprints in these formulae, we obtain for  $d^3$  ions in cubic symmetry

$$g = g_s - 8k\zeta/3D_1 - 2\zeta^2(k + 2g_s)/9D_1^2 + 4\zeta^2(k - 2g_s)/9D_3^2 - 2\zeta^2(k + g_s)/3D_2^2 + 4k\zeta^2[\frac{1}{9}D_1D_3 - \frac{1}{3}D_1D_2 + \frac{1}{3}D_2D_3] \quad (7)$$

where  $g_s (= 2.0023)$  is the spin-only value,  $\zeta$  is the spin-orbit coupling coefficient of central metal ion in crystal and  $k$  is the orbital reduction factor. The zero-order energy separations are [10]

$$D_1 = \Delta = 10Dq \quad D_2 = 15B + 5C + 2\alpha' \quad D_3 = \Delta + 9B + 3C + 6\alpha' \quad (8)$$

where  $B$  and  $C$  are the Racah parameters,  $\alpha'$  is the Trees correct,  $\Delta$  (or  $Dq$ ) is the cubic field parameter which is related to the metal-ligand distance  $R$ . So, when the distance  $R$  is changed by temperature variations, the change in the parameter  $\Delta$  and then in the static contribution to the  $g$ -factor due to thermal expansion can be calculated.

Obviously, the total values of  $g(T)$  and the temperature dependence  $dg/dT$  can be written as

$$g_{tot}(T) = g_{stat}(T) + g_{ac}(T) + g_{op}(T) \quad (9)$$

$$(dg/dT)_{tot} = (dg/dT)_{stat} + (dg/dT)_{ac} + (dg/dT)_{op}. \quad (10)$$

#### 4. Calculations and results

Now let us calculate numerically  $g(T)$  and  $dg/dT$  for the  $MgO:Cr^{3+}$  crystal by considering all the above contributions. From the peak of the acoustic phonon branches, the strong optical branch peak in the phonon density of states for  $MgO$  and the vibrational side band of the optical spectrum of the  ${}^2E \rightarrow {}^4A_2$  transition of  $MgO:Cr^{3+}$  [11, 12], we obtain  $T_D \approx 390 \text{ K}$  and  $\hbar\omega_{eff} \approx 422.5 \text{ cm}^{-1}$ . These values are very close to those used in the theoretical explanation of the thermal shift of the R line of the  $MgO:Cr^{3+}$  crystal [13] and can be regarded as reasonable. In the calculation of  $g_{stat}(T)$  by the macroscopic method (i.e. from equation (2)), the pressure dependence of the  $g$ -factor is taken as the observed value [4]

$$dg/dP \approx (0.26 \pm 0.01) \times 10^{-4} \text{ kbar}^{-1}. \quad (11)$$

The local thermal expansion coefficients  $\alpha_{loc}(T)$  and compressibilities  $\beta_{loc}(T)$  for  $MgO:Cr^{3+}$  are difficult to determine; however, some workers [14, 15] suggested that the relative change in coefficient  $\alpha$  (i.e.  $\alpha_{loc}/\alpha_h$ ) is the same as that in compressibility  $\beta$  and thus the ratio of  $\alpha/\beta$  would be unchanged for the doped crystals. This point can be understood in physics from the Grüneisen law [16]  $\alpha \approx \gamma C_v \beta / V$  and the fact that both the thermal expansion coefficient and the compressibility depend upon the bonding strength [17]. So, we can use the coefficients  $\alpha_h(T)$  and compressibilities  $\beta_h(T)$  of the host  $MgO$  crystal here. These

coefficients and compressibilities at various temperatures were calculated in [18] using the thermodynamic formulae. The calculated results are in good agreement with the observed values [19–21]. The values of  $\alpha_h(T)$  and  $\beta_h(T)$  are shown in table 1. The  $g_{stat}(0)$ -value at 0 K is treated as an adjustable parameter. Thus, by fitting the total calculated values of  $g(T)$  to the observed values at all temperatures, we obtain

$$\begin{aligned} g_{stat}(0) &\approx 1.9801 & \text{or } \Delta g_{stat}(0) &\approx g_{stat}(0) - g_s \approx -222 \times 10^{-4} \\ K_g &\approx 4.38 \times 10^{-14} \text{ K}^{-4} & g_\tau &\approx -1.1 \times 10^{-4}. \end{aligned} \quad (12)$$

The various contributions to the  $g$ -factor and the comparison between the calculated and observed  $\Delta g_{tot}(T)$  are shown in table 2.

**Table 1.** Thermal expansion coefficient  $\alpha$  and compressibility  $\beta$  of MgO [18].

Temperature (K)	$\alpha$ ( $10^{-6} \text{ K}^{-1}$ )	$\beta$ ( $10^{-4} \text{ kbar}^{-1}$ )
10	0.0013	1.955
50	0.231	1.955
75	0.965	1.955
100	2.198	1.955
150	5.097	1.961
200	7.517	1.961
250	9.23	1.972
300	10.6	2.008
400	12.15	2.026
500	13.0	2.051
600	13.6	2.083
700	14.0	2.110
800	14.44	2.134
900	14.75	2.189

The temperature dependence  $dg/dT$  changes with temperature in the low-temperature zone but is close to constant in the high-temperature ( $T > 500$  K) zone. From the above calculations, we find for MgO:Cr<sup>3+</sup> in the high-temperature zone

$$\begin{aligned} (dg/dT)_{tot} &= (dg/dT)_{stat} + (dg/dT)_{ac} + (dg/dT)_{op} \\ &\approx (-1.87 + 0.86 - 0.33) \times 10^{-6} \text{ K}^{-1} \approx -1.34 \times 10^{-6} \text{ K}^{-1}. \end{aligned} \quad (13)$$

The result shows good agreement with the observed value (about  $(-1.40 \pm 0.20) \times 10^{-6} \text{ K}^{-1}$  [1]).

For the calculations of  $g_{stat}(T)$  and  $(dg/dT)_{stat}$  by the microscopic method, the perturbation formulae (i.e. equation (7)) should be used. In the formula, the parameters  $B$ ,  $C$ ,  $\alpha'$  and  $\Delta$  can be obtained from optical spectra of the studied crystal. From the optical spectra of MgO:Cr<sup>3+</sup> [22, 23], we have

$$B \approx 665 \text{ cm}^{-1} \quad C \approx 3084 \text{ cm}^{-1} \quad \alpha' \approx 25 \text{ cm}^{-1} \quad \Delta \approx 16200 \text{ cm}^{-1}. \quad (14)$$

The orbital reduction factor  $K \approx 0.7$ , as shown in [10] for Cr<sup>3+</sup> in many oxides. The spin-orbit coupling coefficient is treated as an adjustable parameter. By fitting the observed value of  $g$  ( $\approx 1.9798 \pm 0.0001$  [1]) of MgO:Cr<sup>3+</sup> at room temperature and by considering the above vibrational contributions to the  $g$ -factor, we obtain  $\zeta \approx 193.6 \text{ cm}^{-1}$ . The value for Cr<sup>3+</sup> in MgO is smaller than that (about  $240 \text{ cm}^{-1}$  [9]) for a free Cr<sup>3+</sup> ion and can be regarded as reasonable. The parameter  $\Delta$  changes with the distance  $R$ . The dependence  $\Delta \propto R^{-5}$

**Table 2.** Various contributions to the  $g$ -factor (in  $10^{-4}$ ) of the  $\text{MgO}:\text{Cr}^{3+}$  crystal (note that  $\Delta g = g - g_s$  here).

Temperature (K)	$\Delta g_{stat}^a$	$\Delta g_{stat}^b$	$g_{ac}$	$g_{op}$	$\Delta g_{tot}^a$	$\Delta g_{tot}^b$	$\Delta g_{Expt}$ [1] <sup>c</sup>
0	-222.0	-222.4	1.3	-1.1	-221.8	-224.2	-222.7
50	-222.0	-224.4	1.3	-1.1	-221.8	-224.2	-222.7
100	-222.3	-224.6	1.4	-1.1	-222.0	-224.3	-222.8
150	-223.0	-224.9	1.7	-1.1	-222.4	-224.3	-223.2
200	-224.0	-225.3	2.0	-1.2	-223.2	-224.5	-223.5
250	-225.0	-225.8	2.4	-1.3	-223.9	-224.7	-223.9
300	-226.1	-226.4	2.8	-1.4	-224.7	-225.0	-224.9
400	-228.2	-227.8	3.6	-1.7	-226.3	-225.9	-225.8
500	-230.2	-229.4	4.5	-2.0	-227.8	-226.9	-226.9
600	-232.2	-231.0	5.3	-2.4	-229.2	-228.1	-228.4
700	-234.1	-232.8	6.2	-2.7	-230.6	-229.3	-230.1
800	-236.0	-234.6	7.0	-3.0	-232.0	-230.6	-231.0
900	-237.8	-236.6	7.9	-3.4	-233.3	-232.1	-232.6

<sup>a</sup>  $\Delta g_{stat}$  is calculated by the macroscopic thermodynamic method.

<sup>b</sup>  $\Delta g_{stat}$  is calculated by the microscopic crystal-field method.

<sup>c</sup> The experimental data are taken from figure 2 of [1]. The experimental errors of  $\Delta g(T)$  are estimated to be about  $\pm 1.0 \times 10^{-4}$ .

based on the effective point-charge model is often used in many studies; however, the  $R^{-5}$  dependence for  $\text{MgO}:\text{Cr}^{3+}$  will cause the local compressibility in the vicinity of the  $\text{Cr}^{3+}$  ion to be larger than that of the host  $\text{MgO}$  crystal from high-pressure spectroscopy, as pointed out in [22]. Considering that, when an impurity ion carries extra charge, the interionic force between the impurity ion and ligands will be larger than that in the pure lattice and hence the local compressibility decreases [24, 25], the larger local compressibility in  $\text{MgO}:\text{Cr}^{3+}$  is not reasonable from a physics viewpoint. So, as shown in [1], for  $\text{MgO}:\text{Cr}^{3+}$ , the relation  $\Delta \propto R^{-6}$  based on the effective dipole model should be used. From the relation, we obtain at room temperature the local compressibility

$$\beta_{loc} \approx 1.9 \times 10^{-4} \text{ kbar}^{-1} \quad (15)$$

by fitting the observed pressure dependences of the optical spectrum and the  $g$ -factor. The comparison between calculation and experiment is shown in table 3. Obviously, the local compressibility is smaller than the host compressibility (about  $2.008 \times 10^{-4} \text{ kbar}^{-1}$ ; see table 1) and can be regarded as reasonable.

**Table 3.** Pressure dependences of the optical spectrum and  $g$ -factor of the  $\text{MgO}:\text{Cr}^{3+}$  crystal.

	Calculation	Experiment
$d\Delta/dP$ ( $\text{cm}^{-1} \text{ kbar}^{-1}$ )	18.5	$19 \pm 1$ [22]
$dg/dP$ ( $10^{-4} \text{ kbar}^{-1}$ )	0.26	$0.26 \pm 0.01$ [4]

As has been said before,

$$\beta_{loc}/\beta_h \approx \alpha_{loc}/\alpha_h. \quad (16)$$

So, we have  $\alpha_{loc}(T) \approx 0.946\alpha_h(T)$ ; thus, according to equation (7), we can calculate the values of  $g_{stat}(T)$  and then of  $g_{tot}(T)$  (both are characterized by  $\Delta g = g - g_s$ ) from the

coefficients  $\alpha_h(T)$  of MgO at various temperatures (see table 1). The calculated results are also compared with the observed values in table 2.

In the high-temperature zone, we find that

$$(dg/dT)_{tot} \approx (-1.87 + 0.86 - 0.33) \times 10^{-6} \text{ K}^{-1} \approx -1.34 \times 10^{-6} \text{ K}^{-1}. \quad (17)$$

The result is also in good agreement with the observed value (about  $(-1.40 \pm 0.20) \times 10^{-6} \text{ K}^{-1}$ ).

## 5. Discussion

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

(i) The static contributions to  $g(T)$  (or  $dg/dT$ ) obtained from the macroscopic thermodynamic method and the microscopic crystal-field method are close to each other (see table 2), suggesting that both methods are applicable to the study of the temperature dependence of the  $g$ -factor.

(ii) The vibrational contributions to  $g(T)$  (or  $dg/dT$ ) from the acoustic and optical phonons cancel partly. The magnitude of the acoustic phonon contribution is larger than that of the optical phonon contribution.

(iii) For the  $g(T)$ -factors at various temperatures, the static contribution is dominant; however, for the temperature dependence of the  $g$ -factor, i.e.  $dg/dT$ , the vibrational contributions are large, in particular, in the high-temperature zone, and cannot be neglected. So, to explain satisfactorily the temperature dependence of the  $g$ -factor for the MgO:Cr<sup>3+</sup> crystal, all the contributions due to the thermal expansion and the electron-phonon (including the acoustic and optical phonons) interaction should be taken into account.

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