Theoretical Studies of the *g* Factors for Co^{2+} in MgO and CaO Crystals

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This paper presents a cluster approach to the calculation of the *g* factors for $3d^7$ ions in cubic octahedral crystals, in which the parameters related to the configuration interaction and the covalency reduction effects are obtained from optical spectra of the studied crystals, and so no adjustable parameters are applied. From the approach, the *g* factors for MgO:Co^{2+} and CaO:Co^{2+} are calculated. The calculated results show good agreement with the observed values. The experimental values of $g < 4.333$ (the first order value in absence of configuration and covalency interactions) for MgO:Co^{2+} and $g > 4.333$ for CaO:Co^{2+} are also explained.

Key words: Electron Paramagnetic Resonance (EPR); Crystal-field Theory; Co^{2+} Ion; MgO; CaO.

1. Introduction

Theoretical studies of EPR *g* factors for $3d^7$ ions in cubic octahedral crystals, such as Co^{2+} in MgO and CaO crystals, have attracted interest for a long time [1 - 4]. In these crystals, the ground state of the $3d^7$ ion is an orbital triplet $^4T_1$ (F). From the eigenfunctions $|M_Z\rangle = |\pm\frac{1}{2}\rangle$ of the spin degenerate ground states, the isotropic *g* factor can be written as [1]

$$g = 2\langle \pm\frac{1}{2}|L_Z + 2S_Z|\pm\frac{1}{2}\rangle \approx \frac{10}{3} + \frac{2}{3}\alpha - \frac{15\lambda}{2\Delta} \approx \frac{10}{3} + \frac{2}{3}\alpha - \frac{5\zeta_d}{2\Delta} \qquad (1)$$

where α is the effective Lande factor, ζ_d (or λ) the spin-orbit coupling coefficient of the $3d^7$ ion, and Δ the energy separation between the $^4T_2$(F) and $^4T_1$(F) states. In the absence of any admixture of $^4T_1$(F) with $^4T_1$ (P) states, α would have the value $\frac{3}{2}$ and so (1) becomes

$$g \approx \frac{13}{3} + \frac{5\zeta_d}{2\Delta}. \qquad (2)$$

Since the signs of ζ_d and Δ are positive the value of *g* should be greater than $\frac{13}{3}$ (= 4.333). This is consistent with the observed value *g* (≈ 4.3747(2) [5]) for Co^{2+} in CaO, but opposite to the observed value *g* (≈ 4.2785(10) [6]) for Co^{2+} in MgO. In order to understand the *g* factors for $3d^7$ ions in octahedral crystals, and also Co^{2+} in MgO and CaO, the configuration interaction due to the admixture of $^4T_1$(F) to $^4T_1$(P) states and the orbitals reduction effect due to the admixture of the orbitals of $3d^7$ ion and ligands were considered by many authors [1 - 4]. Thus we have

$$g \approx \frac{10}{3} + \frac{2}{3}k\alpha - \frac{5k\zeta_d\varepsilon^2}{2\Delta} \qquad (3)$$

with

$$\alpha = \frac{3}{2}\varepsilon^2 - \tau^2, \qquad (4)$$

where ε and τ are the configuration interaction coefficients and k is the orbital reduction factor. ε and τ can be estimated from the optical spectra of the studied crystals, but k was used as an adjustable parameter in the previous studies [1 - 4]. So, the *g* factors of $3d^7$ ions in crystals can not be calculated and explained quantitatively. In this paper we present a cluster approach to the calculation of the *g* factor for $3d^7$ ions in cubic octahedral crystals. In the approach, the k factor and also the covalency reduction of the spin-orbit coupling coefficient in crystals can be estimated from the optical spectra of the studied crystals, and so no adjustable parameter is applied. Based on this, the *g* factors of MgO:Co^{2+} and CaO:Co^{2+} are reasonably explained and the difficulty related to the explana-

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Table 1. The parameters related to the configuration interaction and the covalency reduction effects for $MgO:Co^{2+}$ and $CaO:Co^{2+}$ crystals.

	$S_{dp}(t_{2g})$	$S_{dp}(e_g)$	N_t	N_e	λ_t	λ_e	ϵ	τ	k'	$\zeta'(cm^{-1})$
$MgO:Co^{2+}$	0.00891	0.03087	0.919	0.925	0.306	0.317	0.978	0.207	0.877	484
$CaO:Co^{2+}$	0.00538	0.02027	0.919	0.923	0.302	0.309	0.988	0.152	0.878	485

tions of $g < 4.333$ for $MgO:Co^{2+}$ and $g > 4.333$ for $CaO:Co^{2+}$ is also removed.

2. Calculations

For $3d^n$ ions in many crystals, the role of covalency in explaining the EPR parameters is often considered. So we should apply a cluster approach and take the LCAO molecular orbital [7, 8]

$$|\gamma\rangle = N_\gamma^{1/2}\left(|d_\gamma\rangle - \lambda_\gamma |p_\gamma\rangle\right) \tag{5}$$

as a one-electron orbital, where $|d\rangle$ is the d orbital of the central $3d^n$ ion and $|p\rangle$ the p orbital of the ligand. $\gamma = t_{2g}$ or e_g denotes the irreducible representation of the O_h group. N_γ is the normalization factor and λ_γ the orbital mixing coefficient. From the one-electron orbital and the features of the spin-orbit coupling operator H_{SO} [9] and the orbital angular momentum L [9] we can express the spin-orbit coupling coefficients and orbital reduction factors as [7, 8]

$$\begin{aligned} \zeta &= N_t\left(\zeta_d{}^0 + \lambda_t{}^2\zeta_p{}^0/2\right), \\ \zeta' &= \left(N_t N_e\right)^{1/2}\left(\zeta_d{}^0 - \lambda_t\lambda_e\zeta_p{}^0/2\right), \\ k &= N_t\left(1 + \lambda_t{}^2/2\right), \\ k' &= \left(N_t N_e\right)^{1/2}\left(1 - \lambda_t\lambda_e/2\right). \end{aligned} \tag{6}$$

where $\zeta_d{}^0$ and $\zeta_p{}^0$ are, respectively, the spin-orbit coupling coefficients of the free $3d^n$ ion and the ligand. By using the perturbation method similar to that in [1, 2] we obtain for $3d^7$ ion in octahedral crystals

$$g \approx \frac{10}{3} + \frac{2}{3}k'\alpha - \frac{5k\zeta'\varepsilon^2}{2\Delta}. \tag{7}$$

In the conventional crystal-field theory, the admixture of the spin-orbit coupling coefficients between central ion and its ligand via the covalency effects is not considered, i. e, $\lambda_t = \lambda_e = 0$, $N_t = N_e = N$ and so $\zeta' = \zeta_d$, $k' = k$. Then, (7) becomes (3).

Now we apply (7) to calculate the g factors for $MgO:Co^{2+}$ and $CaO:Co^{2+}$ crystals. Considering the admixture of $^4T_1(F)$ to $^4T_1(P)$ states in crystals, we have [2, 10]

$$\psi = \varepsilon\phi + \tau\pi, \tag{8}$$

where ϕ and π are, respectively, the wave functions of $^4T_1(F)$ and $^4T_1(P)$ in the absence of configuration interaction. So, we have the normalization relationship [2, 10]

$$\varepsilon^2 + \tau^2 = 1. \tag{9}$$

A modified perturbation procedure is used to determine the configuration interaction coefficients ε and τ. The ground state ψ may be expressed to first order:

$$\begin{aligned} \psi &\approx \psi^{(0)} + \psi^{(0)} \approx \varepsilon\phi + \frac{H_{FP'}}{E[^4T_1(P)] - E[^4T_1(F)]}\varepsilon\pi \\ &\approx \varepsilon\phi + \frac{-4D_q}{15B - 6D_q}\varepsilon\pi. \end{aligned} \tag{10}$$

So we have

$$\tau/\varepsilon = \frac{-4D_q}{15B - 6D_q}, \tag{11}$$

where B (and C) are the Racah parameters and D_q is the cubic field parameter. Thus ε and τ can be estimated from the optical spectra of the studied crystal by using (9) and (11). From the optical spectra [10, 11] we obtain for $MgO:Co^{2+}$

$$B \approx 811\,cm^{-1},\ C \approx 4155\,cm^{-1},\ D_q \approx -940\,cm^{-1} \tag{12}$$

and for $CaO:Co^{2+}$

$$B \approx 815\,cm^{-1},\ C \approx 4158\,cm^{-1},\ D_q \approx -610\,cm^{-1} \tag{13}$$

Thus the parameters ε and τ for both crystals can be calculated and are shown in Table 1.

Table 2. g factors for $MgO{:}Co^{2+}$ and $CaO{:}Co^{2+}$ crystals.

	Cal [a]	Cal [b]	Cal [c]	Expt.
$MgO{:}Co^{2+}$	4.3392	4.4162	4.2713	4.2785(10) [5]
$CaO{:}Co^{2+}$	4.4142	4.5431	4.3758	4.3747(2) [6]

[a] Calculated by neglecting the configuration interaction (i. e., $\varepsilon = 1$, $\tau = 0$, $\alpha = 3/2$). [b] Calculated by neglecting the covalency reduction effects (i. e., $k' = 1$, $\zeta' = \zeta_d{}^0$). [c] Calculated by considering both effects.

The LCAO coefficients N_γ and λ_γ can be obtained by a semiempirical method [7, 8]. We have the normalization correlation

$$N_\gamma\left(1 - 2\lambda_\gamma S_{\mathrm{dp}}(\gamma) + \lambda_\gamma^2\right) = 1 \qquad (14)$$

and the approximate relationship [7, 8]

$$f_\gamma = N_\gamma^2\left[1 + \lambda_\gamma^2 S_{\mathrm{dp}}^2(\gamma) - 2\lambda_\gamma S_{\mathrm{dp}}(\gamma)\right], \qquad (15)$$

where $S_{\mathrm{dp}}(\gamma)$ is the group overlap integral and f_γ $[\approx (B/B_0 + C/C_0)/2]$ the ratio of the Racah parameters for an ion in a crystal to those in the free ion. For the free Co^{2+} ion, $B_0 \approx 1115$ cm^{-1} and $C_0 \approx 4366$ cm^{-1} [12], thus, from the above optical spectral parameters we obtain $f_\gamma \approx 0.8395$ for $MgO{:}Co^{2+}$ and $f_\gamma \approx 0.8417$ for $CaO{:}Co^{2+}$. The integrals $S_{\mathrm{dp}}(\gamma)$ can be calculated using the Slater-type SCF functions [13, 14] and the impurity-ligand distance R. In general, $R \neq R_{\mathrm{H}}$ (where R_{H} is the cation-anion distance in the host crystal) in the doped crystal because of the different ionic radii of impurity and the replaced host ion. We can reasonably estimate R from the approximate formula [15, 16]

$$R \approx R_{\mathrm{H}} + (r_{\mathrm{i}} - r_{\mathrm{h}})/2, \qquad (16)$$

where r_{i} and r_{h} are the ionic radius of the impurity and that of the replaced host ion. For TO (T = Mg, Ca):Co^{2+} crystals, r_{i} is 0.72 Å and r_{h} are 0.66 Å, 0.99 Å [17], R_{H} are 2.105 Å, 2.405 Å [17] for T = Mg, Ca, respectively. Thus we have $R \approx 2.135$ Å for $MgO{:}Co^{2+}$ and $R \approx 2.270$ Å for $CaO{:}Co^{2+}$. The calculated integrals $S_{\mathrm{dp}}(\gamma)$ and so the coefficients N_γ and λ_γ from (14) and (15) for both crystals are shown in Table 1. From $\zeta_d{}^0(Co^{2+}) \approx 533$ cm^{-1} [12] and $\zeta_p{}^0(O^{2-}) \approx 136$ cm^{-1} [18], the parameters k' and ζ' are calculated from (6) and shown in Table 1. The values $\Delta \approx 8470$ cm^{-1} for $MgO{:}Co^{2+}$ and $\Delta \approx 5246$ cm^{-1} for $CaO{:}Co^{2+}$ can be obtained from the optical spectra. Substituting the values of ε, τ, ζ', k', and Δ in (7), the g factors for $MgO{:}Co^{2+}$ and $CaO{:}Co^{2+}$ crystals were calculated. The results are shown in Table 2. For comparison, the g factors calculated by neglecting the covalency effects (i. e., $k' = 1$, $\zeta' = \zeta_d{}^0$) and those calculated by neglecting the configuration interaction (i. e., $\varepsilon = 1$, $\tau = 0$) as well as the observed g values for both crystals are also shown in Table 2.

3. Discussion

From the above studies it can be seen that the g factors of $MgO{:}Co^{2+}$ and $CaO{:}Co^{2+}$ can be quantitatively calculated by means of the cluster approach without using adjustable parameters. The calculated results show good agreement with the observed values (see Table 2), suggesting that the cluster approach is suitable to the calculation of g factors of $3d^7$ ion in octahedral crystals. The g factor is sensitive to both the admixture of $^4T_1(F)$ and $^4T_1(P)$ states (configuration interaction) and the admixture of metal and ligand orbitals (covalency effect). If only one admixture effect is considered, from Table 2, one can find that the calculated values are not consistent with the observed values (particularly, for $MgO{:}Co^{2+}$, $g > 4.333$). Obviously, the smaller the metal-ligand distance R, the stronger are the two admixture effects and so the larger the admixture coefficients τ and λ_γ as well as the smaller the parameters k' and ζ'. For $MgO{:}Co^{2+}$, the small metal-ligand distance R results in the large τ and the small ζ' and k' and hence the small value of g. So, the experimental values of $g < 4.333$ for $MgO{:}Co^{2+}$ and $g > 4.333$ for $CaO{:}Co^{2+}$ can be understood physically.

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