Investigations of the *g* Factors of Fe^+ in MgO and CaO

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The *g* factors of Fe^+ in MgO and CaO are theoretically investigated by the perturbation formula of the *g* factor of a $3d^7$ ion in cubic octahedral symmetry based on the cluster approach. By considering the partial quenching of the spin-orbit coupling interaction and the effective Landé factor due to the dynamic Jahn-Teller effect (DJTE), the experimental *g* factors of the studied systems are reasonably interpreted. It can be suggested that the small *g* factors of the Fe^+ centers in MgO and CaO can be likely attributed to the DJTE, rather than the covalency effect within the scheme of the static crystal-field model.

Key words: Electron Paramagnetic Resonance; Crystal- and Ligand-field Theory; Fe^+; MgO; CaO.

1. Introduction

Investigations on the *g* factors of $3d^7$ ions (e.g., Co^{2+} or Fe^+) in octahedral crystals of, e.g., MgO and CaO have been performed in [1 – 5]. As suggested in [6], the contributions from the admixture of the excited $^4T_1(P)$ states for the ground $^4T_1(F)$ state and the covalency effect should be taken into account in studies of the *g* factors of octahedral $3d^7$ clusters. Based on the above treatments, the smaller *g* factor of MgO:Co^{2+} (≈ 4.2785 [7]) compared to that of CaO:Co^{2+} (≈ 4.3747[8]) was reasonably interpreted by considering the more significant covalency and admixture of $^4T_1(P)$ states to the $^4T_1(F)$ states due to the shorter impurity-ligand distance of the latter [6]. For the isoelectronic Fe^+ centers in the same hosts, however, the even lower *g* factors (~ 4.15 [1, 2]) can hardly be attributed to the stronger covalency or admixture of energy levels in the $[FeO_6]^{11-}$ clusters than that in the $[CoO_6]^{10-}$ ones. In fact, for isoelectronic $3d^n$ clusters with the same ligand in crystals, the covalency may decrease with decreasing the valence state (e.g., $Ni^{3+} > Co^{2+} > Fe^+$) [9 – 11]. Thus, the *g* factors for the cubic Fe^+ centers in the above oxides seem difficult to be investigated on the basis of the merely static crystal-field model.

As often mentioned in works on transition-metal ions in octahedral environments [12 – 15], reduction (or quenching) of the spin-orbit (S. O.) coupling interaction and the orbital angular momentum due to the dynamic Jahn-Teller effect (DJTE) also make contributions to the *g* factors. In order to further investigate the *g* factor of Fe^+ centers, the perturbation formula for the *g* factor of a $3d^7$ ion in octahedra, based on the cluster approach, is applied in this work. Particularly, the partial quenching of the S.O. coupling interaction and the effective Landé factor due to the DJTE is considered in the analysis of the contributions to the *g* factor.

2. Calculations

For the lowest Kramers doublet ($J' = 1/2$) of a $3d^7$ ion in octahedra, the formula of the *g* factor based on the cluster approach can be written as [6]

$$g = \frac{10}{3} + \frac{2}{3}k\alpha + \frac{5k'\zeta\varepsilon^2}{16Dq}. \tag{1}$$

Here ζ' (and ζ) are the S.O. coupling coefficients, and k and k' are the orbital reduction factors. Dq is the cubic crystal-field parameter. The effective Landé factor α (related to the effective angular momentum L') can be expressed as [5, 6]

$$\alpha \approx \frac{3}{2}\varepsilon^2 - \tau^2. \tag{2}$$

The coefficients ε and τ are characteristic of the mixture between $^4T_1(F)$ and $^4T_1(P)$ states via crystal-fields and electrostatic Columbic interactions. Thus, we have [6]

$$\varepsilon^2+\tau^2=1 \quad \tau/\varepsilon=\frac{(-4Dq)}{15B-6Dq}, \tag{3}$$

where B (or C) is the Racah parameter. According to the cluster approach, the S.O. coupling coefficients and the orbital reduction factors can be expressed as [6]

$$\begin{aligned} &\zeta = N_t(\zeta_d{}^0+\lambda_t{}^2\zeta_p{}^0/2),\\ &\zeta' = (N_tN_e)^{1/2}(\zeta_d{}^0-\lambda_t\lambda_e\zeta_p{}^0/2),\\ &k=N_t(1+\lambda_t{}^2/2), \quad k'=(N_tN_e)^{1/2}(1-\lambda_t\lambda_e/2). \end{aligned} \tag{4}$$

Here $\zeta_d{}^0$ and $\zeta_p{}^0$ are, respectively, the S. O. coupling coefficient of the d electron of the $3d^7$ ion and that of the p electron of the ligand in free states. N_γ and λ_γ (where $\gamma = t_{2g}$ or e_g denotes the irreducible representation of the O_h group.) are, respectively, the normalization factor and the orbital mixing coefficient. They can be obtained from the approximate relationship [6, 16]

$$\beta = N_\gamma{}^2[1+\lambda_\gamma{}^2S^2{}_{dp}(\gamma)-2\lambda_\gamma S_{dp}(\gamma)], \tag{5}$$

and the normalization condition [6, 16]

$$N_\gamma(1-2\lambda_\gamma S_{dp}(\gamma)+\lambda_\gamma{}^2)=1, \tag{6}$$

where β is the covalency factor. $S_{dp}(\gamma)$ is the group overlap integral, which depends on the bond length R. For the studied Fe^+ centers, $R \approx 2.105$ Å for MgO and $R \approx 2.405$ Å for CaO [17]. The integrals $S_{dp}(\gamma)$ are calculated from the distances R and the Slater-type SCF functions [18, 19].

Since no optical spectra of the octahedral Fe^+-O^{2-} clusters are reported, one must approximately estimate the parameters N_t, N_e (which are roughly related to the covalency factor β by the relationship $N_t{}^4 \approx N_e{}^4 \approx \beta \approx B/B_0 \approx C/C_0$ [9, 10]) and Dq from the empirical formulas [9, 10]

$$-10Dq \approx f(\mathrm{L})g(\mathrm{M}), \quad 1-\beta \approx h(\mathrm{L})k(\mathrm{M}), \tag{7}$$

where the parameters $f(\mathrm{L})$ or $h(\mathrm{L})$ are the characteristic parameters of the ligand, and $g(\mathrm{M})$ or $k(\mathrm{M})$ are the characteristic parameters of the central metal ion (note: the minus sign of Dq is due to the three hole $3d^7$ configuration). For the Fe^+-O^{2-} clusters in this work, the values $g(Fe^+)$ and $k(Fe^+)$ can be extrapolated from those of the isoelectronic Co^{2+} and Ni^{3+} ion. According to the data $g(Co^{2+}) \approx 9000$ cm^{-1}, $g(Ni^{3+}) \approx 18000$ cm^{-1}, $k(Co^{2+}) \approx 0.24$ and $k(Ni^{3+}) \approx 0.49$ [9, 10], we approximately obtain

$$g(Fe^+) \approx 4500\ \mathrm{cm}^{-1}, \quad k(Fe^+) \approx 0.15 \tag{8}$$

for Fe^+. So, the parameters $Dq \approx -450$ cm^{-1} and $\beta \approx 0.85$ can be calculated from the values $f(O^{2-}) \approx 1.0$ and $h(O^{2-}) \approx 1.0$ [9, 10]. Considering the small difference in the bonding lengths of both crystals, we can estimate $Dq \approx -500$ and -400 cm^{-1}, and $\beta \approx 0.845$ and 0.855 for MgO and CaO, respectively. Here, the values of Dq are smaller than those (≈ -940 and -610 cm^{-1}) in [6, 20, 21]), while the values of β are larger than those (≈ 0.840 and 0.842 cm^{-1}) in [6, 20, 21] of the isoelectronic Co^{2+}-O^{2-} clusters in the same hosts. This point is consistent with the tendency that Dq decreases and β increases with decreasing valence state of isoelectronic ions (such as $3d^2$ ions Cr^{4+}, V^{3+}, Ti^{2+}, and $3d^5$ ions Fe^{3+}, Mn^{2+}) for the same ligands [9–11]. Therefore the spectral parameters obtained for the Fe^+ centers in MgO and CaO of this work can be regarded as reasonable. Thus, the Racah parameters B and C for the studied system can be determined from the free-ion parameters $B_0 \approx 869$ cm^{-1} and $C_0 \approx 3638$ cm^{-1} for Fe^+ [11]. These parameters are shown in Table 1.

Table 1. The parameters related to the cluster approach and admixture of energy levels for Fe^+ in MgO and CaO.

	$S_{dp}(t_{2g})$	$S_{dp}(e_g)$	N_t	N_e	λ_t	λ_e	k	ζ'	ε	τ
MgO:Fe^+	0.010	0.034	0.928	0.934	0.288	0.299	0.891	487	0.968	0.176
CaO:Fe^+	0.003	0.013	0.925	0.928	0.287	0.291	0.964	326	0.984	0.180

Table 2. The g factors for Fe^+ in MgO and CaO.

	MgO:Fe^+	CaO:Fe^+
Calc.[a]	4.2478	4.2916
Calc.[b]	4.1353	4.1622
Expt.	4.15(1) [1]	4.1579(1) [2]

[a] Calculation based on the static crystal-field theory in absence of the dynamic Jahn-Teller effect (DJTE). [b] Calculation by considering the influence of the partial quenching of the spin-orbit (S. O.) coupling interaction and the effective Landé factor due to the DJTE.

Then the coefficients N_γ and λ_γ can be obtained from (5) and (6). By using the free-ion values $\zeta_d^0(Fe^+) \approx 356$ cm^{-1} [11] and $\zeta_p{}^0(O^{2-}) \approx 151$ cm^{-1} [22], the parameters ε, τ, ζ', k', etc. are calculated. These results are also shown in Table 1. Substituting these values into (1), the g factors for MgO:Fe^+ and CaO:Fe^+ are calculated and shown in Table 2.

From Table 2 one finds that the calculated g factors for both centers based on the static crystal-field model are larger than the experimental ones. As mentioned before, the contributions of the DJTE in the $[FeO_6]^{11-}$ clusters, which may lead to some reduction or quenching of the S.O. coupling interaction and the effective Landé factor, should be taken into account. Thus, an additional reduction factor γ can be introduced for ζ' and α in (2) and (4), i. e.,

$$\zeta' = \gamma(N_t N_e)^{1/2}(\zeta_d{}^0 - \lambda_t\lambda_e\zeta_p{}^0/2), \\ \alpha \approx \gamma(\frac{3}{2}\varepsilon^2 - \tau^2). \tag{9}$$

By fitting the calculated g factors to the observed values, we obtain

$$\gamma \approx 0.87 \tag{10}$$

for both crystals. The corresponding theoretical results are also shown in Table 2.

3. Discussion

Table 2 shows that, by considering the partial quenching of the S. O. coupling interaction and the effective Landé factor due to the DJTE, the calculated g factors for both crystals agree reasonably with the observed values. In addition, the larger g factor for CaO than MgO agrees with the larger bonding length and hence smaller Dq and larger β values of the former. However, the results based on the static crystal-field model do not agree, even though the contributions of the S.O. coupling coefficient and p orbitals of ligands are included in the cluster approach.

As pointed out in many works on transition-metal ions in octahedral clusters [12 – 15], reduction effect of the S. O. coupling interaction and the orbital angular momentum due to the DJTE can influence the EPR results. For Co^{2+} clusters in MgO and CaO, the S. O. coupling interaction ($\zeta_d{}^0 \approx 533$ cm^{-1} [11]) may be strong enough to depress the DJTE and then the static crystal-field theory based on the cluster approach is suitable to explain the g factors (~ 4.3) [6]. For the Fe^+ centers in the present work, however, the smaller S.O. coupling interaction ($\zeta_d{}^0 \approx 356$ cm^{-1} [11]) cannot sufficiently depress the DJTE. In view of this point, the partial reduction (by about 13%) of the S.O. coupling interaction and the effective Landeé factor and hence the small g factors (~ 4.15) can here be understood. Interestingly, if we try to obtain good agreement between theory and experiment within the scheme of the static crystal-field model (in absence of the contributions due to the DJTE), the covalency factor β has to be decreased to about 0.6. Generally, this value is somewhat too small to be regarded as reasonable, because the covalency effect can be insignificant for ions of low valence (such as Fe^+) in ionic oxides.

It seems that the small values of the experimental g factors for Fe^+ compared with those for Co^{2+} in MgO and CaO likely result from the reduction effect due to the DJTE, rather than covalency effect between the central metal and ligand ions.

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