Theoretical studies of the EPR parameters for Ni^{2+} and Co^{+} in MgO

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The electron paramagnetic resonance (EPR) parameters (g factors and the hyperfine structure constants) for Ni^{2+} and Co^{+} in MgO are theoretically studied from the perturbation formulas of these parameters for a $3d^8$ ion in octahedral crystal-fields. In the computations, the ligand orbital and spin-orbit coupling contributions are taken into account using the cluster approach. The calculated EPR parameters are in good agreement with the experimental data. The larger g factor and the smaller magnitude of the hyperfine structure constant for Ni^{2+} as compared with those for Co^{+} can be attributed to the higher spin-orbit coupling coefficient and the lower dipolar hyperfine structure parameter of the former, respectively.

Keywords: Impurity and defects; Electron paramagnetic resonance; Ni^{2+}; Co^{+}; MgO.

1. INTRODUCTION

Magnesium oxide (MgO) is usually regarded as a model system to investigate magnetic [1,2], adsorption [3,4], structure [5,6] and optical properties [7] of doped transition-metal impurities. Particularly, MgO containing Ni^{2+} and Co^{+} can exhibit unique catalytic [8-10] and tunable laser properties [11,12]. Normally, these properties are closely correlated with the electronic states of the transition-metal ions in the hosts, which can be investigated by means of electron paramagnetic resonance (EPR) technique. For example, EPR experiments were carried out for Ni^{2+} and Co^{2+} doped MgO, and the EPR parameters (i.e., the isotropic g factors and the hyperfine structure constants) were also measured for the cubic Ni^{2+} and Co^{+} centers [13,14].

Up to now, however, the above EPR experimental results have not been satisfactorily explained. On the other hand, the EPR spectra and magnetic properties have been extensively investigated for Ni^{2+} in various chlorides by considering only the central ion orbital and spin-orbit coupling contributions [15]. Nevertheless, the contributions to the EPR parameters from the ligand orbital and spin-orbit coupling interactions were not taken into account in the previous studies. In fact, for the $3d^8$ ions in oxides, the systems may still show some covalency and impurity-ligand orbital admixtures. In addition, the EPR spectra for MgO:Co^{+} have not been interpreted until now. Considering that (i) investigations on the EPR parameters for Ni^{2+} and Co^{+} in MgO can reveal useful information about electronic structures which would be helpful to understand the properties of these systems and that (ii) $3d^8$ ions can be treated as model systems containing only two unpaired holes, further quantitative studies on the EPR spectra for the Ni^{2+} and Co^{+} centers are of scientific and practical significance. In this work, the improved perturbation formulas of the EPR parameters based on the cluster approach are applied to the theoretical analysis of the Ni^{2+} and Co^{+} centers in MgO. In the calculations, the ligand orbital and spin-orbit coupling contributions are considered in a uniform way. The results are discussed.

2. CALCULATIONS

Judging from the observed isotropic g factors and the hyperfine structure constants, the experimental EPR signals [13,14] can be assigned to the substitutional cubic Ni^{2+} and Co^{+} centers in MgO. When a $3d^8$ ion locates on an octahedral (O_h) site, the free-ion configuration ^3F would be separated into two orbital doublets $^3T_{1g}$ and $^3T_{2g}$ and one singlet $^3A_{2g}$, with the latter lying lowest corresponding to the isotropic g and A signals [16]. As for the g factor of a $3d^8$ ion in octahedra, the perturbation formula was established using the conventional crystal-field model [17,18], by including only the contributions from the central ion orbital and spin-orbit coupling interactions. In order to study the EPR spectra of the $3d^8$ centers more exactly, the ligand orbital and spin-orbit contributions may be taken into account. Thus, the improved g formula based on the cluster approach is applied here. Meanwhile, the perturbation formula of the hyperfine structure constant for a $3d^8$ ion in regular octahedra can be similarly derived. Thus, we have [19]:

$$\begin{aligned} g &= g_s + 4k'\zeta'/E_1 - k'\zeta\zeta'[1/(E_1E_2) + \\ &\quad +1/E_1^2] + (k/2 - g_s)\zeta'^2(1/E_1^2 + 1/E_3^2) \ , \\ A &= P'\{4k'\zeta'/E_1 - k'\zeta\zeta'[1/(E_1E_2) + 1/E_1^2] + \\ &\quad +(k/2 - g_s)\zeta'^2(1/E_1^2 + 1/E_3^2)\} - P'\kappa \ . \end{aligned} \qquad (1)$$

Here g_s (≈ 2.0023) is the spin-only value. ζ and ζ' are the spin-orbit coupling coefficients, k and k' are the orbital reduction factors, and P and P' are the dipolar hyperfine structure parameters for a $3d^8$ ion in crystals. κ is the core polarization constant. The energy denominators $E_i (i = 1 \sim 3)$ denote the energy separations between the excited $^3T_2$, $^1T_{2a}$ and $^1T_{2b}$ and the ground $^3A_2$ states [17-19]. They can be described in terms of the cubic field parameter Dq and the Racah parameters B and C for the $3d^8$ ion in crystals: $E_1 \approx 10\ Dq$, $E_2 \approx 10\ Dq + 12\ B$ and $E_3 \approx 8\ B + 2C + 10Dq$ [17-19]. From the cluster approach containing the ligand $p-$ and s-orbital contributions [20], the spin-orbit coupling coefficients ζ and ζ', the orbital reduction factors k and k' and the dipolar hyperfine structure parameters P and P' can be

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expressed as

$$\begin{aligned} \zeta &= N_t(\zeta_d^0 + \lambda_t^2\zeta_p^0/2), & \zeta' &= (N_tN_e)^{1/2}(\zeta_d^0 - \lambda_t\lambda_e\zeta_p^0/2) \ , \\ k &= N_t(1+\lambda_t^2/2), & k' &= (N_tN_e)^{1/2}[1-\lambda_t(\lambda_e+\lambda_s A)/2] \ , \\ P &= N_tP_0, & P' &= (N_tN_e)^{1/2}P_0 \ . \end{aligned} \quad (2)$$

Here ζ_d^0 and ζ_p^0 are the spin-orbit coupling coefficients of the free $3d^8$ and the ligand ions, respectively. A denotes the integral $R\left\langle ns|\frac{\partial}{\partial y}|np_y\right\rangle$, where R is the impurity-ligand distance of the studied systems. N_γ and λ_γ (here the subscripts $\gamma = t$ and e denote the irreducible representations T_{2g} and E_g of O_h group, respectively) are the normalization factors and the orbital admixture coefficients. They are determined from the approximation relationships [20]

$$\begin{aligned} N^2 &= N_t^2[1+\lambda_t^2 {S_{dpt}}^2 - 2\lambda_t S_{dpt}] \ , \\ N^2 &= N_e^2[1+\lambda_e^2 {S_{dpe}}^2 + \lambda_s^2 {S_{ds}}^2 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds}] \end{aligned} \quad (3)$$

and the normalization conditions [20]

$$\begin{aligned} N_t(1-2\lambda_t S_{dpt} + \lambda_t^2) &= 1 \ , \\ N_e(1-2\lambda_e S_{dpe} - 2\lambda_s S_{ds} + \lambda_e^2 + \lambda_s^2) &= 1 \ . \end{aligned} \quad (4)$$

Here N is the average covalency factor, characteristic of the covalency of the studied systems. $S_{dp\gamma}$ (and S_{ds}) are the group overlap integrals. In general, the orbital admixture coefficients increase with increasing the group overlap integrals, and one can approximately adopt the proportional relationship $\lambda_s/\lambda_e \approx S_{ds}/S_{dpe}$ between the orbital admixture coefficients and the related group overlap integrals within the same irreducible representation Eg. Obviously, omission of the ligand contributions (i.e., $\zeta' = \zeta = N\zeta_d^0$, $k' = k = N$, $P' = P = P_0N$), the above g formula returns to that of the previous work based on the conventional crystal-field model [17,18].

Usually, the impurity-ligand distance R is different from the host cation-anion distance R_H in a pure crystal due to the difference between the ionic radius r_i of impurity and the radius r_h of host ions. Fortunately, studies based on experimental superhyperfine parameter and extended X-ray absorption fine structure (EXAFS) measurements have verified that the empirical formula $R \approx R_H + (r_i - r_h)/2$ is approximately valid for impurity ions in crystals [21]. From R_H ($\approx$ 2.105 Å[22]) for MgO, r_i ($\approx$ 0.69 and 0.82 Å[22]) for Ni^{2+} and Co^+ as well as r_h ($\approx$ 0.66 Å[22]) for Mg^{2+}, the distances R are obtained and listed in Table 1. From the distances R and the Slater-type self-consistent field (SCF) wave functions [23,24], the group overlap integrals are calculated and shown in Table 1. According to the optical spectra for Ni^{2+} in MgO [25,26], the cubic field parameter Dq $\approx$ 860 cm^{-1} and the covalency factor $N \approx 0.90$ can be obtained. Since the isoelectronic monovalent Co^+ suffers weaker crystal-fields (i.e., lower Dq) and covalency effect (i.e., higher N) [27] when coordinated to the same oxygen ligands, the spectral parameters $Dq \approx 780$ cm^{-1} and $N \approx 0.91$ may be estimated for Co^+ in MgO. Then the Racah parameters are determined from the relationships $B \approx N^2B_0$ and $C \approx N^2C_0$ [28], with the corresponding free-ion values $B_0 \approx 1208$ and 878 cm^{-1} and $C_0 \approx 4459$ and 3828 cm^{-1} [27] for Ni^{2+} and Co^+, respectively. Using Eqs. (3) and (4), the molecular orbital coefficients N_γ and λ_γ (and λ_s) can be calculated. From the free-ion values $\zeta_d^0 \approx 649$ and 456 cm^{-1} [27] for Ni^{2+} and Co^+ and $\zeta_p^0 \approx 151$ cm^{-1} [29] for O^{2-}, the parameters in Eq. (2) are obtained and shown in Table 1. In the formula of the hyperfine structure constant, the dipolar hyperfine structure parameters are $P_0 \approx 112 \times 10^{-4}$ cm^{-1} and 228 $\times$ 10^{-4} cm^{-1} [30] for Ni^{2+} and Co^+, respectively. The core polarization constant can be determined from the empirical relationship $\kappa \approx -2\chi/(3 < r^{-3} >)$, where χ is characteristic of the density of unpaired spins at the nucleus of the central ion and $< r^{-3} >$ the expectation value of the inverse cube of the radial wave function of the $3d^8$ orbital [30]. Applying $< r^{-3} > \approx 7.094$ and 5.388 a.u. [16] and $\chi \approx -3.15$ and -3.31 a.u. [30] for Ni^{2+} and Co^+ in oxides, one can obtain $\kappa \approx 0.3$ and 0.41 for MgO:Ni^{2+} and MgO:Co^+, respectively. Substituting the above values into the formulas of the EPR parameters, the corresponding theoretical results (Cal. b) are calculated and shown in Table 2. To clarify the importance and the tendency of the covalency and the ligand contributions for Ni^{2+} and Co^+ in MgO, the results (Cal. a) based on omission of the ligand contributions are also collected in Table 2 for comparison.

TABLE 1: The impurity-ligand distances R (in Å), the group overlap integrals S_{dpt}, S_{dpe}, S_{ds} and A, the molecular orbital coefficients N_t, N_e, λ_t, λ_e and λ_s, the spin-orbit coupling coefficients ζ and ζ' (in cm^{-1}), the orbital reduction factors k and k', the dipolar hyperfine structure parameters P and P' (in $10^{-4}cm^{-1}$) as well as the energy denominators E_1, E_2 and E_3 (in cm^{-1}) for Ni^{2+} and Co^+ in MgO.

	R	S_{dpt}	S_{dpe}	S_{ds}	A	N_t	N_e	λ_t	λ_e	λ_s
Ni^{2+}	2.120	0.0075	0.0261	0.0208	1.3802	0.908	0.916	0.326	0.264	0.210
Co^+	2.185	0.0074	0.0264	0.0210	1.4225	0.914	0.922	0.314	0.255	0.203
	ζ	ζ'	k	k'	P	P'	E_1	E_3	E_3	
Ni^{2+}	597	586	0.956	0.830	102	102	8600	20342	23651	
Co^+	424	413	0.959	0.840	208	209	7800	16525	19957	

3. DISCUSSION

Table 2 indicates that the theoretical EPR parameters (Cal. ^{b}) for Ni^{2+} and Co^+ in MgO based on the improved formulas containing the ligand contributions are in better agreement with the observed values than those (Cal. ^{a}) in the absence of the above contributions.

1) The experimental isotropic g and A factors are attributed to the cubic Ni^{2+} and Co^+ centers on the substitutional Mg^{2+} site in MgO. It is noted that there are some low symmetrical $3d^8$ centers in other oxides, e.g., the trigonal Ni^{2+} and Cu^{3+} centers in $\alpha - Al_2O_3$ [31]. The anisotropic g factors $g_{//}$ and $g_\perp$ [31] for the trigonal centers may be similarly analyzed from the perturbation formulas [32] for a trigonally distorted octahedral $3d^8$ cluster, and the contributions from the trigonal distortion can be quantitatively considered in the calculations of the trigonal crystal-field parameters from the superposition model [33] and the local geometrical relation-

TABLE 2: The *g* factors and the hyperfine structure constants (in 10^{-4} cm^{-1}) for the Ni^{2+} and Co^{+} centers in MgO.

	Ni^{2+}		Co^{+}	
	g	A	*g*	A
Cal. [a]	2.234	−6.5	2.188	−50.6
Cal. [b]	2.215	−8.3	2.172	−53.5
Expt. [13,14]	2.215	−8.3 (4)	2.173	−54.0 (2)

[a] Calculations based on omission of the ligand orbital and spin-orbit coupling contributions.

[b] Calculations based on inclusion of the ligand contributions.

ship of the impurity centers. Interestingly, the larger g factors [31] for Cu^{3+} than those for Ni^{2+} are attributable to the higher spin-orbit coupling coefficient ($\approx$ 876 cm^{-1} [16]) of the former than that ($\approx$ 649 cm^{-1} [27]) of the latter. In addition, Co^{+} replacing the host Mg^{2+} in MgO may induce some means of charge compensation due to the fewer charge of the impurity. On the other hand, larger size of Co^{+} than Mg^{2+} can lead to enhancement of the local metal-ligand interactions around the impurity and thus make Co^{+} stable on Mg^{2+} site. Further, local charge compensation (e.g., oxygen vacancy nearby) would break the original cubic symmetry of the ideal Mg^{2+} site and yield anisotropic EPR parameters. In view of the observed isotropic EPR signals [13,14], the charge compensation may occur in the outer ligand spheres far away from the impurity Co^{+}, and the possible disturbance of the local structure of this center can be regarded as very small and negligible for simplicity. Of course, further experimental investigations of possible charge compensation for Co^{+} in MgO seem necessary and meaningful.

2) From Eqs. (1) and (2), the *g* factor largely depends upon the spin-orbit coupling coefficient ζ' (related to the central ion spin-orbit coupling coefficient). Thus, the larger g factor for MgO:Ni^{2+} than that for MgO:Co^{+} can be illustrated by the higher spin-orbit coupling coefficient ζ_d^0 ($\approx$ 649 cm^{-1}) of the former than that ($\approx$ 456 cm^{-1}) of the latter. On the other hand, the hyperfine structure constant is sensitively related to the dipolar hyperfine structure parameter P_0 and the dominant contribution proportional to the core polarization constant κ. So, the larger magnitude of the hyperfine structure constant for MgO:Co^{+} than that for MgO:Ni^{2+} can be understood in view of the higher values of P_0 and κ in the former.

3) The average covalency factors N ($\approx$ 0.90 and 0.91 for Ni^{2+} and Co^{+}) in this work still show some influences of the covalency on the EPR parameters, although the spin-orbit coupling coefficient ($\approx$ 151 cm^{-1} [28]) of the oxygen ligand is much smaller than that ($\approx$ 649 or 456 cm^{-1} [26]) of the impurity Ni^{2+} or Co^{+}. Thus, omission of the ligand contributions yields larger *g* factors and slightly lower hyperfine structure constants in magnitude (Cal. ^{a}). It seems that the improved formulas of the EPR parameters adopted in this work are superior to the previous ones [17,18] based on the conventional crystal-field model. Further, the covalency and the strength of the crystal-fields exhibit the decreasing tendency from Ni^{2+} to Co^{+} in the same MgO host, i.e., $N\ (Ni^{2+}) \leq N\ (Co^{+})$ and $Dq(Ni^{2+}) < Dq(Co^{+})$. This point is consistent with the lower valence state and hence weaker covalency and impurity-ligand interactions of the latter.

4. CONCLUSION

The EPR parameters for Ni^{2+} and Co^{+} in MgO are satisfactorily explained from the perturbation formulas based on the cluster approach. Inclusion of the ligand contributions yields better theoretical results as compared with those in the absence of these contributions. The larger g factor and the smaller magnitude of the hyperfine structure constant for Ni^{2+} than those for Co^{+} can be attributed to the higher spin-orbit coupling coefficient and the lower dipolar hyperfine structure parameter of the former.

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