

Studies on the Local Angular Distortion and Spin Hamiltonian Parameters for the Trigonal Co^{2+} Center in MgCl_2

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The local angular distortion and spin Hamiltonian parameters (g factors g_{\parallel} , g_{\perp} and the hyperfine structure constants) for the trigonal Co^{2+} center in MgCl_2 are theoretically studied by diagonalizing the 6×6 energy matrix of ground 4T_1 state for a trigonally distorted octahedral $3d^7$ cluster. Based on the cluster approach, the contributions from the admixtures of various J ($= 1/2, 3/2, 5/2$) states and the ligand orbital and spin–orbit coupling interactions are taken into account in a uniform way. The local impurity–ligand bond angle in the Co^{2+} center is found to be about 3.44° larger than the host metal–ligand bond angle in the pure crystal due to substitution of smaller Mg^{2+} by bigger Co^{2+} , inducing a further compressed ligand octahedron. The calculated spin Hamiltonian parameters using the above local angular distortion are in good agreement with the experimental data. The present studies on the local structure and the spin Hamiltonian parameters for Co^{2+} in MgCl_2 are tentatively extended to a more general case by comparing the relevant impurity behaviours for Co^{2+} in various trigonal environments.

Key words: Electron Paramagnetic Resonance; Crystal and Ligand Fields; Co^{2+} ; MgCl_2 .

1. Introduction

MgCl_2 can be adopted as widely used catalysts when doped with some transition-metal elements [1, 2]. Particularly, MgCl_2 containing Co^{2+} shows interesting structural, energetic [3], and catalyzing properties [4–6] and biological activity in some issues [7, 8]. Usually, these properties are closely related to the electronic states and local structure around Co^{2+} in MgCl_2 , which can be conveniently investigated with electron paramagnetic resonance (EPR) technique. For example, EPR studies were performed on $\text{MgCl}_2:\text{Co}^{2+}$, and the spin Hamiltonian parameters (anisotropic g factors g_{\parallel} , g_{\perp} and the hyperfine structure constants A_{\parallel} and A_{\perp}) were also measured for the trigonal Co^{2+} center decades ago [9]. Up to now, however, the above experimental results have not been theoretically interpreted, and the local structure (e.g., angular distortion) around the impurity has not been obtained as yet.

Since the microscopic mechanisms of EPR spectra and information about defect structures would be helpful to understand properties of this material with Co^{2+} (or other transition-metal) dopants, studies on the EPR spectra for the trigonal Co^{2+} center in MgCl_2 are of fundamental and practical significance. As regards the studies of the spin Hamiltonian parameters for Co^{2+} in trigonally distorted octahedra, the previous treatments [10, 11] were usually based on the lowest Kramers doublet ($J = 1/2$), whereas the admixtures among different J ($= 1/2, 3/2$, and $5/2$) states within the ground ${}^4T_1(F)$ configuration were not taken into account. Secondly, the conventional crystal-field model was adopted by considering merely the central ion $3d$ orbital and spin–orbit coupling contributions. The above treatments may only be suitable for the systems (e.g., Fe^+ and Co^{2+} in oxides) with weak covalency and ligand spin–orbit coupling interactions. For the present $\text{MgCl}_2:\text{Co}^{2+}$ system, however, moderate covalency and large spin–orbit coupling coefficient of

Cl^- may bring forward significant ligand orbital and spin-orbit coupling contributions which should be included in the EPR analysis. Thirdly, the previous calculations were largely based on the impurity Co^{2+} occupying ideal cation sites in the hosts, and the local lattice distortions due to size mismatch were not taken into account [10, 11]. In fact, the local structures around impurities are usually dissimilar to those of the host cation sites in pure crystals because of the lattice deformations. For example, the local angular distortions were reported for the trigonal Co^{2+} (and some other divalent impurities V^{2+} , Mn^{2+} , Ni^{2+}) centers on Mg^{2+} sites in CsMgCl_3 based on the EPR analysis [12]. Therefore, the investigations of the spin Hamiltonian parameters should be correlated to the local structures (lattice distortions) of the impurity centers. In order to provide satisfactory explanations to the experimental EPR spectra and to obtain information about the local structure of $\text{MgCl}_2:\text{Co}^{2+}$, in this work, the spin Hamiltonian parameters for this Co^{2+} center are theoretically calculated by diagonalizing the 6×6 energy matrix of the ground ${}^4T_1(F)$ state for a trigonally distorted octahedral $3d^7$ cluster. In the calculations, the contributions from the J -admixture, the ligand orbital and spin-orbit coupling interactions as well as the local angular distortion are quantitatively taken into account in a uniform way.

2. Calculations

MgCl_2 has the layered-type structure (space group D_{3d}^5) with anion-cation-anion sandwich layers [13]. Significant chemical bonding occurs inside the sandwich layer, whereas the interaction between the sandwich layers is of weak van der Waals nature. A divalent Mg^{2+} ion is surrounded by a trigonally (D_{3d}) distorted chlorine octahedron, characterized by the host metal-ligand bond length R_H ($\approx 2.541 \text{ \AA}$) [13] and bond angle β_H ($\approx 54.78^\circ$) [13] related to the C_3 axis. When a Co^{2+} ion is doped into MgCl_2 , it may occupy host Mg^{2+} site and conserve original trigonal point symmetry, since no charge compensation is needed.

The ground ${}^4T_1(F)$ state for a $3d^7(\text{Co}^{2+})$ ion under trigonally distorted octahedra can be separated into six Kramers doublets (belonging to $J = 1/2, 3/2$, and $5/2$ states, respectively) by the spin-orbit coupling and crystal-field interactions, with $J = 1/2$ state lying lowest [14, 15]. The energy separation between $J = 1/2$

and $3/2$ states is usually a few hundred wave numbers based on the theoretical expectations from the cubic crystal-field scheme [14, 15]. However, the trigonal distortion and the weak Jahn-Teller effect in the $[\text{CoCl}_6]^{4-}$ cluster may somewhat decrease the above energy differences between various J states [10, 11]. Consequently, the excited $J = 3/2$ and $5/2$ states can be close to the lowest $J = 1/2$ state and thus lead to the admixtures of the various J states (i.e., J -admixture) and the modifications of the electronic states and the spin Hamiltonian parameters. Therefore, the J -admixture should be taken into account in the EPR analysis for Co^{2+} in some octahedral environments. In order to make more reasonable and complete investigations, the J -admixture and the ligand orbital and spin-orbit coupling contributions are included uniformly from the cluster approach.

Applying Abragam's fiction angular momentum theory [14, 15], the energy matrix \mathbf{W} containing $|1 - \frac{1}{2}\rangle, |0 \frac{1}{2}\rangle, |-1 \frac{3}{2}\rangle, |1 \frac{1}{2}\rangle, |0 \frac{3}{2}\rangle$, and $|1 \frac{3}{2}\rangle$ bases of the ground state 4T_1 is established in terms of the cubic field parameter Dq , the trigonal field parameters $D\sigma$ and $D\tau$, the spin-orbit coupling coefficients ζ, ζ' and the effective Landé factors α_{\parallel} and α_{\perp} parallel with and perpendicular to the C_3 axis. Thus, one can obtain:

$$\begin{aligned} W_{11} &= 3D\sigma/5 - D\tau - 2Dq/3 + 3\alpha_{\parallel}\zeta/2, \\ W_{12} &= 6D\sigma + 8D\tau, \quad W_{13} = 0, \quad W_{14} = 7D\sigma 20D\tau/3, \\ W_{15} &= -\sqrt{6}\alpha_{\perp}\zeta'/2, \quad W_{16} = 0, \\ W_{22} &= 3D\sigma/5 - D\tau - 2Dq/3 - \alpha_{\parallel}\zeta/2, \\ W_{23} &= 0, \quad W_{24} = 0, \quad W_{25} = 0, \\ W_{26} &= -\sqrt{6}\alpha_{\perp}\zeta'/2, \\ W_{33} &= 3D\sigma/5 - D\tau - 2Dq/3 - 3\alpha_{\parallel}\zeta/2, \\ W_{34} &= 0, \quad W_{35} = 0, \quad W_{36} = 0, \\ W_{44} &= 3D\sigma/5 - D\tau - 2Dq/3 + \alpha_{\parallel}\zeta/2, \\ W_{45} &= -\sqrt{2}\alpha_{\perp}\zeta', \quad W_{46} = 0, \\ W_{55} &= -D\sigma - 3D\tau - 2Dq, \quad W_{56} = 0, \\ W_{66} &= -D\sigma - 3D\tau - 2Dq. \end{aligned} \quad (1)$$

The wave functions of the lowest Kramers doublet can be given as:

$$\Phi_{\pm} = \sum_{j=1}^6 D_{1j} \zeta_j^{\pm}, \quad (2)$$

where ζ_j^+ (or ζ_j^-) and D_{1j} are the j th component and the corresponding coefficient of the lowest Kramers

doublet in the matrix \mathbf{W} . Applying the angular momentum and hyperfine interaction operators [14, 15] to the wave functions in (2), the formulas of the spin Hamiltonian parameters for a trigonally distorted octahedral $3d^7$ cluster can be obtained from the perturbation procedure as follows:

$$\begin{aligned} g_{\parallel} &= 2[(D_{11}^2 + D_{12}^2 - D_{13}^2 - D_{14}^2)\alpha_{\parallel} \\ &\quad + 3(D_{11}^2 + D_{13}^2 - D_{16}^2) - D_{12}^2 - D_{14}^2 + D_{15}^2], \\ g_{\perp} &= 2\sqrt{2}\alpha_{\perp}(D_{11}D_{16} + D_{12}D_{15} - D_{13}D_{16} - D_{14}D_{15}) \\ &\quad + 4\sqrt{3}(D_{11}D_{14} + D_{12}D_{13} - D_{15}D_{16}) \\ &\quad - 8D_{12}D_{14} + 4D_{15}^2, \\ A_{\parallel} &= 2P'\alpha_{\parallel}(D_{11}^2 + D_{12}^2 - D_{13}^2 - D_{14}^2) \\ &\quad - \kappa P g_s [3(D_{11}^2 + D_{13}^2 - D_{16}^2) - D_{12}^2 - D_{14}^2 + D_{15}^2]/2, \\ A_{\perp} &= 2\sqrt{2}P'\alpha_{\perp}(D_{11}D_{16} + D_{12}D_{15} - D_{13}D_{16} \\ &\quad - D_{14}D_{15}) - \kappa P g_s [2\sqrt{3}(D_{11}D_{14} + D_{12}D_{13} - D_{15}D_{16}) \\ &\quad - 4D_{12}D_{14} + 2D_{15}^2]. \end{aligned} \quad (3)$$

Here g_s ($= 2.0023$) is the spin-only value. P (or P') and κ are the dipolar hyperfine structure parameter and the core polarization constant, denoting the anisotropic and isotropic contributions to the hyperfine structure constants, respectively. The effective Landé factors α_{\parallel} and α_{\perp} can be determined from the related configuration interaction coefficients in terms of the cubic and trigonal field parameters and the Racah parameters B and C for a $3d^7$ ion in crystals [12].

From the cluster approach [12], 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 obtained:

$$\begin{aligned} \zeta &= N_t(\zeta_d^0 + \lambda_t^2 \zeta_p^0/2), \\ \zeta' &= (N_t N_e)^{1/2}(\zeta_d^0 - \lambda_t \lambda_e \zeta_p^0/2), \\ k &= N_t(1 + \lambda_t^2/2), \\ k' &= (N_t N_e)^{1/2}[1 - \lambda_t(\lambda_e + \lambda_s A)/2], \\ P &= N_t P_0, \quad P' = (N_t N_e)^{1/2} P_0. \end{aligned} \quad (4)$$

Here ζ_d^0 and ζ_p^0 are the spin-orbit coupling coefficients of the free $3d^7$ and ligand ions, respectively. P_0 is the dipolar hyperfine structure parameter for a $3d^7$ ion in a free state. A denotes the integral $R\langle ns|\partial/\partial y|np_y\rangle$, with the reference impurity-ligand bond length R . λ_{γ} and N_{γ} ($\gamma = e$ and t stand for the irreducible representations E and T_{2g} of group O_h) are, respectively, the orbital admixture coefficients and the normalization fac-

tors. They satisfy the approximate relationships [12]

$$\begin{aligned} N^2 &= N_t^2[1 + \lambda_t^2 S_{dpt}^2 - 2\lambda_t S_{dpt}], \\ N^2 &= N_e^2[1 + \lambda_e^2 S_{dpe}^2 + \lambda_s^2 S_{ds}^2 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds}], \end{aligned} \quad (5)$$

and the normalization conditions [12]

$$\begin{aligned} N_t(1 - 2\lambda_t S_{dpt} + \lambda_t^2) &= 1, \\ N_e(1 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds} + \lambda_e^2 + \lambda_s^2) &= 1. \end{aligned} \quad (6)$$

Here N is the average covalency factor. S_{dpy} and S_{ds} are the group overlap integrals. In general, the orbital admixture coefficients increase with increasing the corresponding group overlap integrals, and one can reasonably adopt the proportionality relationship $\lambda_e/\lambda_s \approx S_{dpe}/S_{ds}$ between the orbital admixture coefficients and the related group overlap integrals within the same E_g representation.

From the superposition model [16] and the local geometrical relationship of the Co^{2+} center in MgCl_2 , the trigonal field parameters can be expressed as follows:

$$\begin{aligned} D\sigma &= -(6/7)\bar{A}_2(3\cos^2\beta - 1), \\ D\tau &= -2\bar{A}_4[5\cos^4\beta - (30/7)\cos^2\beta \\ &\quad + 3/7 + \sqrt{2}\sin^3\beta\cos\beta]. \end{aligned} \quad (7)$$

Here \bar{A}_2 and \bar{A}_4 are the intrinsic parameters. For $3d^n$ ions in octahedra, $\bar{A}_4 \approx (3/4)Dq$ and $\bar{A}_2 \approx 10.8\bar{A}_4$ [16–18] are proved valid in many crystals and reasonably adopted here. β is the angle between the impurity-ligand bond length R and the C_3 axis. Thus, the local structure of the studied Co^{2+} center is correlated to the spin Hamiltonian parameters, particularly the anisotropy Δg ($= g_{\perp} - g_{\parallel}$) or ΔA ($= A_{\perp} - A_{\parallel}$).

Since the ionic radius r_i (≈ 0.745 Å [19]) of impurity Co^{2+} is larger than the radius r_h (≈ 0.72 Å [19]) of host Mg^{2+} , the local impurity-ligand bond length R and the bond angle β would be different from the host R_H and β_H in a pure crystal. Usually, strict theoretical determination of impurity-ligand distance R (or angle β) in crystals is difficult. Fortunately, one can reasonably estimate R from the empirical formula $R \approx R_H + (r_i - r_h)/2$ [20, 21], yielding $R \approx 2.554$ Å. From this distance and the Slater-type self-consistent field (SCF) wave functions [22, 23], the integrals $S_{dpt} \approx 0.0074$, $S_{dpe} \approx 0.0252$, $S_{ds} \approx 0.0131$, and $A \approx 1.2902$ are calculated.

Since the spectral parameters for $\text{MgCl}_2:\text{Co}^{2+}$ have not been reported until now, they can be obtained from

those ($Dq \approx -680 \text{ cm}^{-1}$ and $N \approx 0.867$ [24]) determined by optical absorption measurements for a similar $[\text{CoCl}_6]^{4-}$ cluster in $\text{AgCl}:\text{Co}^{2+}$ (with slightly shorter $R \approx 2.505 \text{ \AA}$ [25]). Based on the relationship $Dq \propto R^{-5}$ [26, 27] and the fact that the covalency factor N increases slightly with increasing the distance R [28], one can approximately obtain $Dq \approx -620 \text{ cm}^{-1}$ and $N \approx 0.88$ for $\text{MgCl}_2:\text{Co}^{2+}$. From the free-ion values $B_0 \approx 1115 \text{ cm}^{-1}$ and $C_0 \approx 4366 \text{ cm}^{-1}$ [29] for Co^{2+} , the Racah parameters $B \approx B_0 N^2 \approx 863 \text{ cm}^{-1}$ and $C \approx C_0 N^2 \approx 3381 \text{ cm}^{-1}$ are calculated. Using the free-ion values $\zeta_d^0 \approx 533 \text{ cm}^{-1}$ [29] and $P_0 (\approx 254 \times 10^{-4} \text{ cm}^{-1}$ [30]) for Co^{2+} and $\zeta_p^0 \approx 587 \text{ cm}^{-1}$ [31] for Cl^- , the values in (4) can be obtained: $\zeta \approx 495 \text{ cm}^{-1}$, $\zeta' \approx 480 \text{ cm}^{-1}$, $k \approx 0.970$, $k' \approx 0.829$, $P \approx 234 \times 10^{-4} \text{ cm}^{-1}$, and $P' \approx 235 \times 10^{-4} \text{ cm}^{-1}$. In the formulas of the hyperfine structure constants, the core polarization constant is taken as $\kappa \approx 0.325$ [32].

Substituting the above data (and also the host bond angle β_{H} of Mg^{2+} site in MgCl_2) into (3), the spin Hamiltonian parameters are calculated and shown in Table 1. It can be found that the theoretical results (Cal. ^a) show poor agreement with the experimental results, particularly the anisotropy Δg is one order in magnitude smaller than the observed value. This reveals that the trigonal distortion based on the host structural parameters of Mg^{2+} site in MgCl_2 are significantly underestimated and unsuitable for the analysis of the impurity Co^{2+} center. Thus, an angular variation can be expected to increase the local trigonal distortion and hence the calculated Δg . Then the host angle β_{H} should be replaced by a local one β in terms

of the angular variation $\Delta\beta$ as: $\beta \approx \beta_{\text{H}} + \Delta\beta$. Matching the theoretical Δg to the observed value, one can obtain the local angle

$$\beta \approx 58.22^\circ. \quad (8)$$

The corresponding spin Hamiltonian parameters (Cal. ^c) are shown in Table 1. For comparison, the calculation results (Cal. ^b) based on the above local angle β and omission of the J -admixture (i.e., similar to the previous treatments [10, 11]) are also collected in Table 1.

3. Discussion

Table 1 reveals that the results (Cal. ^c) of the spin Hamiltonian parameters for $\text{MgCl}_2:\text{Co}^{2+}$ based on the J -admixture and the local impurity–ligand bond angle β in (8) show good agreement with the observed values. Therefore, the experimental EPR spectra for the trigonal Co^{2+} center in MgCl_2 are satisfactorily interpreted, and the information about the local structure is also obtained in this work.

(i) The increase ($\Delta\beta > 0$) of the metal–ligand bond angle from β_{H} ($\approx 54.78^\circ$) in the host to β ($\approx 58.22^\circ$) in the impurity center can be attributed to the local tension along the C_3 axis arising from the substitution of smaller host Mg^{2+} by larger Co^{2+} . The above axial tension around the impurity Co^{2+} may easily modify the distances between the neighbouring layers suffering weak van der Waals interactions [13] and thus considerably increase the impurity–ligand bond angle. For convenience, the property of trigonal distortion can be described by the trigonal distortion angle $\delta\beta$ ($= \beta - \beta_c$, where $\beta_c \approx 54.74^\circ$ is the value for an ideal octahedron). So, the chlorine octahedron changes from slight compression ($\delta\beta_{\text{H}} \approx 0.04^\circ$) in the host crystal to considerable compression ($\delta\beta \approx 3.48^\circ$) in the impurity center. As regards the relationship between the anisotropy of EPR spectra and trigonal distortion of the system, one can find that Δg (or ΔA) > 0 when $\delta\beta > 0$, as reported in the EPR studies for Co^{2+} in various trigonally compressed halide octahedra [9, 33].

(ii) The admixtures among the various J states have obvious contributions to the spin Hamiltonian parameters. Neglecting of the above J -admixture may lead to the results (Cal. ^b) of much smaller g_{\perp} (and slightly lower g_{\parallel}) and hence smaller anisotropy Δg . Although the above calculated anisotropy could be improved

Table 1. Spin Hamiltonian parameters for the trigonal Co^{2+} center in MgCl_2 .

| | g_{\parallel} | g_{\perp} | A_{\parallel} (10^{-4} cm^{-1}) | A_{\perp} (10^{-4} cm^{-1}) |
|-------------------|-----------------|-------------|--|--|
| Cal. ^a | 4.208 | 4.283 | 96 | 105 |
| Cal. ^b | 2.605 | 4.460 | 12 | 181 |
| Cal. ^c | 2.864 | 5.026 | 40 | 155 |
| Expt. [9] | 2.858 (10) | 5.032 (5) | 45 (20) | 161 |

^a Calculations based on inclusion of the J -admixture and the host angle β_{H} (i.e., omission of the local angular variation by taking $\Delta\beta = 0$).

^b Calculations based on the local angular variation $\Delta\beta$ and omission of the J -admixture.

^c Calculations based on the J -admixture and the local angular variation $\Delta\beta$.

Table 2. Impurity–ligand distance R (in Å), the anisotropy Δg , size mismatch $r_i - r_h$ between impurity and host cation ions (in Å), local and host trigonal distortion angles ($\delta\beta$ and $\delta\beta_H$) and angular variation $\Delta\beta$ (in degree) as well as the variation of whole trigonal distortion Δ_{tri} related to the host cation sites based on the EPR analysis for Co^{2+} in various trigonal (D_{3d}) environments.

| Hosts | R^a | Δg | $r_i - r_h^b$ | $\delta\beta$ | $\delta\beta_H$ | $\Delta\beta$ | Δ_{tri} |
|--|-------|-------------|---------------|---------------|-----------------|---------------|-----------------------|
| CsMgCl_3 [12, 34, 35] | 2.509 | −4.860 | 0.025 | −3.71 | −3.03 | −0.68 | ↑ |
| K_4CdCl_6 [9, 36, 37] | 2.538 | −0.706(5) | −0.225 | −1.20 | 0.16 | −1.36 | ↑ |
| CdCl_2 [9, 33, 38, 40] | 2.545 | 1.907(6) | −0.225 | 3.80 | 2.05 | 1.75 | ↑ |
| MgCl_2 [present work] | 2.554 | 2.174(15) | 0.025 | 3.48 | 0.04 | 3.44 | ↑ |
| CdBr_2 [9, 33, 38, 40] | 2.674 | 0.952(7) | −0.225 | 2.09 | 0.95 | 1.14 | ↑ |
| PbI_2 [33, 39, 41] | 2.994 | −0.76(1) | −0.445 | −2.51 | 0.15 | −2.66 | ↑ |
| $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$ [42–44] | 2.081 | −2.251(8) | 0.005 | −2.08 | −0.07 | −2.01 | ↑ |
| $\text{Ca}(\text{OH})_2$ [45–47] | 2.106 | −1.0862(13) | −0.255 | −1.06 | 6.26 | −7.32 | ↓ |
| CaCO_3 [40, 48, 49] | 2.110 | 1.411(4) | −0.255 | 1.71 | −1.59 | 3.30 | ↑ |
| CdCO_3 [40, 48, 50] | 2.110 | 1.86(6) | −0.225 | 2.74 | −0.94 | 3.68 | ↑ |

^a The values are based on the relationship $R \approx R_H + (r_i - r_h)/2$ [20] for Co^{2+} in monatomic ionic crystals. Those for Co^{2+} in the molecular ionic crystals ($\text{Ca}(\text{OH})_2$, CaCO_3 and CdCO_3) are taken as the corresponding cobalt–molecule groups distances of $\text{Co}(\text{OH})_2$ and CoCO_3 crystals.

^b [19].

by increasing the local bond angle β , the average $\bar{g} [= (g_{\parallel} + 2g_{\perp})/3]$ would still be about 12% smaller than the experimental value since the increase of g_{\perp} with increasing β cannot compensate its decline without the J -admixture. Further, the calculated hyperfine structure constants in this case are not as good as those (Cal. ^c) including the J -admixture. In fact, the J -admixture can induce some modifications of the electronic states (or the wave functions of the lowest Kramers doublet) as compared with those in the absence of the above admixtures. For a Co^{2+} ion in chlorine octahedra, the energy separations between different J states are usually no more than several hundred wave numbers. As local environment is lowered to trigonal symmetry, the above energy differences will decline somewhat due to the trigonal distortion and the Jahn–Teller effect [10, 11]. Thus, the theoretical model and formulas containing the J -admixture in this work seem applicable to the systems with significant trigonal distortions.

(iii) When the ligand orbital and spin–orbit coupling contributions are neglected, the theoretical results are not as good as those including these contributions. Particularly, the calculated g_{\parallel} is larger than the experimental value and thus leads to a lower anisotropy. Since the system has strong ligand spin–orbit coupling interaction ($\zeta_p^0 \approx 587 \text{ cm}^{-1}$) and moderate covalency ($N \approx 0.88 < 1$), omission of the ligand contributions would somewhat conceal the anisotropic influences of the spin–orbit coupling ($\zeta/\zeta' \approx 1.03$) and the orbital angular momentum ($k/k' \approx 1.17$) inter-

actions and thus result in smaller anisotropy. Therefore, in order to study the spin Hamiltonian parameters for Co^{2+} in MgCl_2 (or other trigonally distorted octahedra) more exactly, the ligand contributions should be taken into account from the cluster approach.

(iv) Table 2 provides the anisotropy Δg , the local and host trigonal distortion angles ($\delta\beta$ and $\delta\beta_H$) related to the ideal value β_c and the angular variation $\Delta\beta$ related to host β_H based on EPR analysis for Co^{2+} in various trigonally (D_{3d}) distorted octahedral systems. For comparison and clearness, the impurity–ligand bond (reference) distance R , the size mismatch $r_i - r_h$ between impurity Co^{2+} and host cation and the variation Δ_{tri} in the whole trigonal distortion related to the host cation site are also supplied in Table 2. First, the anisotropy Δg has the same sign as $\delta\beta$, i.e., Δg is positive (or negative) for Co^{2+} in trigonally compressed (or elongated) octahedra. Second, the variation Δ_{tri} generally shows increasing rule ($|\delta\beta| > |\delta\beta_H|$) for most systems except $\text{Ca}(\text{OH})_2$. The increasing tendency of the whole trigonal distortion in the impurity centers may be ascribed to the lattice modification arising from impurity substitution which may possibly lower the total energies of the systems and release the local disturbance around the dopants. Third, the magnitude of the angular variation $|\Delta\beta|$ roughly increases with increasing the distance R for the same impurity–ligand combinations, e.g., the $[\text{CoCl}_6]^{4-}$ clusters in the chlorides and the $[\text{CoO}_6]^{10-}$ clusters in $\text{Ca}(\text{OH})_2$ and $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$. This point can be attributed to

the impurity–ligand bonding (or force constant) declining with the increase of R , inducing larger probability of the variations of impurity–ligand bond angles and hence larger $|\Delta\beta|$. Fourth, interchangeability of trigonal distortion property (elongation or compression) from host cation sites to impurity centers depends largely upon size mismatch $r_i - r_h$. In detail, the Co²⁺ centers prefer to maintain the host trigonal distortion properties ($\delta\beta \cdot \delta\beta_H > 0$) for small size mismatch ($|r_i - r_h| < 0.225 \text{ \AA}$) and exchange the host trigonal distortion properties ($\delta\beta \cdot \delta\beta_H < 0$) for large size mismatch ($|r_i - r_h| \geq 0.225 \text{ \AA}$), corresponding to small and large lattice modifications, respectively. As regards the moderate $|r_i - r_h|$ ($\approx 0.225 \text{ \AA}$) for Co²⁺ in CdCl₂ and CdBr₂, the local lattice modifications seem not strong enough to reverse the large host compression distortions and thus the same positive $\delta\beta$ are obtained. Therefore, the present investigations on the local structure and the spin Hamiltonian parameters for Co²⁺ in MgCl₂ are tentatively extended to a more general case by comparing the relevant impurity behaviours for Co²⁺ in various trigonal environments. Of course, determination of local structures (e.g., angular variations) for a transition-metal impurity in crystals is actually a complicated and difficult problem, which involves various physical and chemical properties of

the impurity and host materials. So, further theoretical calculations and experimental measurements would be helpful.

4. Conclusion

The spin Hamiltonian parameters for the trigonal Co²⁺ center in MgCl₂ are theoretically studied by considering the contributions from the J -admixture, the ligand orbital and spin–orbit coupling interactions, and the local angular variation. The impurity–ligand bond angle shows an increase of 3.44° related to that in the host Mg²⁺ site due to size mismatch, resulting in a more significantly compressed ligand octahedron. The present investigations on the local structure and the spin Hamiltonian parameters for Co²⁺ in MgCl₂ are tentatively extended to a more general case by comparing the relevant impurity behaviours for Co²⁺ in various trigonal environments.

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