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 $g_{||}$, $g_{\perp}$ and the hyperfine structure constants) for the trigonal Co$^{2+}$ center in MgCl$_2$ are theoretically studied by diagonalizing the $6 \times 6$ 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 $3.44^\circ$ 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 MgCl$_2$:Co$^{2+}$, and the spin Hamiltonian parameters (anisotropic $g$ factors $g_{||}$, $g_{\perp}$ and the hyperfine structure constants $A_{||}$ 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 $J (=1/2, 3/2, 5/2)$ 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$^{3+}$ and Co$^{2+}$ in oxides) with weak covalency and ligand spin–orbit coupling interactions. For the present MgCl$_2$: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 largely based on the impurity Co\(^{2+}\) centers on MgCl\(_2\) 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 MgCl\(_2\), the spin Hamiltonian parameters for this Co\(^{2+}\) center are theoretically calculated by diagonalizing the \(6 \times 6\) energy matrix of the ground \(^4T_1(F)\) state for a trigonally distorted octahedral \(3d^7\) cluster. In the calculations, the contributions from the \(J\)-admixtures, 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 layer-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 \(R_{\text{H}} (\approx 2.541 \text{ Å})\) [13] and bond angle \(\beta_1 (\approx 54.78^\circ)\) [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., \(J\)-admixtures) and the modifications of the electronic states and the spin Hamiltonian parameters. Therefore, the \(J\)-admixtures 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 \(J\)-admixtures and the ligand orbital and spin–orbit coupling contributions are included uniformly from the cluster approach.

Applying Abragam’s fictitious angular momentum theory [14, 15], the energy matrix \(W\) containing \(\ket{1 - \frac{1}{2}}, \ket{0 \frac{1}{2}}, \ket{-1 \frac{1}{2}}, \ket{1 \frac{1}{2}}, \ket{0 \frac{3}{2}},\) and \(\ket{1 \frac{3}{2}}\) bases of the ground state \(^4T_1\) is established in terms of the cubic field parameter \(D_q\), the trigonal field parameters \(D\sigma\) and \(D\tau\), the spin–orbit coupling coefficients \(\zeta\), \(\zeta'\) and the effective Landé factors \(\alpha_0\) and \(\alpha_1\) parallel with and perpendicular to the \(C_3\) axis. Thus, one can obtain:

\[
\begin{align*}
W_{11} &= 3D\sigma/5 - D\tau - 2Dq/3 + 3\alpha_1 \zeta/2, \\
W_{12} &= 6D\sigma + 8D\tau, \\
W_{13} &= 0, \\
W_{14} &= 7D\sigma 20D\tau/3, \\
W_{15} &= -\sqrt{6}\alpha_\perp \zeta'/2, \\
W_{16} &= 0, \\
W_{22} &= 3D\sigma/5 - D\tau - 2Dq/3 - \alpha_0 \zeta/2, \\
W_{23} &= 0, \\
W_{24} &= 0, \\
W_{25} &= 0, \\
W_{26} &= -\sqrt{6}\alpha_\perp \zeta'/2, \\
W_{33} &= 3D\sigma/5 - D\tau - 2Dq/3 - 3\alpha_1 \zeta/2, \\
W_{34} &= 0, \\
W_{35} &= 0, \\
W_{36} &= 0, \\
W_{44} &= 3D\sigma/5 - D\tau - 2Dq/3 + \alpha_0 \zeta/2, \\
W_{45} &= -\sqrt{2}\alpha_\perp \zeta', \\
W_{46} &= 0, \\
W_{55} &= -D\sigma - 3D\tau - 2Dq, \\
W_{56} &= 0, \\
W_{66} &= -D\sigma - 3D\tau - 2Dq.
\end{align*}
\]

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

\[
\Phi_\pm = \frac{1}{\sqrt{6}} \sum_{j=1}^6 D_{1j} \zeta_{j}^\pm, \tag{2}
\]

where \(\zeta_{j}^\pm\) (or \(\zeta_{j}'^\pm\)) and \(D_{1j}\) are the \(j\)th component and the corresponding coefficient of the lowest Kramers
doublet in the matrix $W$. 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 3$d^7$ cluster can be obtained from the perturbation procedure as follows:

\[
g_\parallel = 2[(D_{11}^2 + D_{13}^2 - D_{12}^2)\alpha_\parallel + 3(D_{11}^2 + D_{13}^2 - D_{12}^2 - D_{14}^2 + D_{15}^2)],
\]

\[
g_\perp = 2\sqrt{2}\alpha_\perp(D_{11}D_{16} + D_{12}D_{15} - D_{13}D_{16} - D_{14}D_{15}) + 4\sqrt{3}(D_{11}D_{14} + D_{12}D_{13} - D_{15}D_{16}) - 8D_{12}D_{14} + 4D_{15}^2,
\]

\[
A_\parallel = 2\alpha_\parallel^2(D_{11}^2 + D_{12}^2 - D_{13}^2 - D_{14}^2)
\]

\[
- \kappa P_h[3(D_{11}^2 + D_{13}^2 - D_{15}^2) - D_{12}^2 - D_{14}^2 + D_{15}^2]/2,
\]

\[
A_\perp = 2\sqrt{2}\alpha_\perp(D_{11}D_{16} + D_{12}D_{15} - D_{13}D_{16} - D_{14}D_{15}) - \kappa P_h[2\sqrt{3}(D_{11}D_{14} + D_{12}D_{13} - D_{15}D_{16}) - 4D_{12}D_{14} + 2D_{15}^2].
\]

Here $g_\parallel (= 2.0023)$ is the spin-only value. $P$ (or $P'$) and $\kappa$ 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 $\alpha_\parallel$ and $\alpha_\perp$ 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 3$d^7$ ion in crystals \([12]\).

From the cluster approach \([12]\), the spin–orbit coupling coefficients $\zeta$ and $\zeta'$, the orbital reduction factors $k$ and $k'$ and the dipolar hyperfine structure parameters $P$ and $P'$ can be obtained:

\[
\zeta = N_\zeta(\zeta_\parallel^2 + \lambda_\zeta^2 \zeta_\parallel^0/2),
\]

\[
\zeta' = (N_\zeta N_e)^{1/2}(\zeta_\perp^2 - \lambda_\zeta \lambda_e \zeta_\parallel^0/2),
\]

\[
k = N_\zeta(1 + \lambda_\zeta^2/2),
\]

\[
k' = (N_\zeta N_e)^{1/2}[1 - \lambda_\zeta(\lambda_e + \lambda_\Lambda)/2],
\]

\[
P = N_\zeta P_0, P' = (N_\zeta N_e)^{1/2} P_0.
\]

Here $\zeta_\parallel^0$ and $\zeta_\parallel^0$ are the spin–orbit coupling coefficients of the free 3$d^7$ and ligand ions, respectively. $P_0$ is the dipolar hyperfine structure parameter for a 3$d^7$ ion in a free state. $A$ denotes the integral $R(n\delta/\partial/\partial|n_p_n|)$, with the reference impurity–ligand bond length $R$, $\lambda_\gamma$ and $N_\gamma (\gamma = e$ and $\tau$ stand for the irreducible representations $E$ and $T_\gamma$ of group $O_h$) are, respectively, the orbital admixture coefficients and the normalization factors. They satisfy the approximate relationships \([12]\)

\[
N_2 = N_1^2[1 + \lambda_\epsilon^2 S_{dpr}^2 - 2\lambda_\epsilon S_{dpr}],
\]

\[
N_2 = N_1^2[1 + \lambda_\epsilon^2 S_{dpe}^2 + \lambda_\epsilon^2 S_{dpr}^2 - 2\lambda_\epsilon S_{dpe} - 2\lambda_\epsilon S_{dpr}],
\]

and the normalization conditions \([12]\)

\[
N_1(1 - 2\lambda_\epsilon S_{dpr} + \lambda_\epsilon^2) = 1,
\]

\[
N_2(1 - 2\lambda_\epsilon S_{dpe} - 2\lambda_\epsilon S_{dpr} + \lambda_\epsilon^2 + \lambda_\epsilon^2) = 1.
\]

Here $N$ is the average covalency factor. $S_{dpe}$ and $S_{dpr}$ 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 $\lambda_e/\lambda_e \approx S_{dpe}/S_{dpr}$ 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:

\[
D\sigma = -(6/7)\tilde{A}_2(3\cos^2 \beta - 1),
\]

\[
D\tau = -2\tilde{A}_4[5\cos^2 \beta - (30/7)\cos^2 \beta + 3/7 + \sqrt{2}(3/7 + \cos^2 \beta)].
\]

Here $\tilde{A}_2$ and $\tilde{A}_4$ are the intrinsic parameters. For 3$d^n$ ions in octahedra, $\tilde{A}_4 \approx (3/4)D_q$ and $\tilde{A}_2 \approx 10.8\tilde{A}_4$ \([16 - 18]\) are proved valid in many crystals and reasonably adopted here. $\beta$ 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 $\Delta g (= g_\perp - g_\parallel)$.\footnote{For example, the $\Delta g$ values for 3$d^n$ ions in octahedra, $\tilde{A}_4 \approx (3/4)D_q$ and $\tilde{A}_2 \approx 10.8\tilde{A}_4$ \([16 - 18]\) are proved valid in many crystals and}$

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

Since the spectral parameters for MgCl$_2$:Co$^{2+}$ have not been reported until now, they can be obtained from
those \((Dq \approx -680 \text{ cm}^{-1} \text{ and } N \approx 0.867 [24])\) determined by optical absorption measurements for a similar \([\text{CoCl}_6]^{4-}\) cluster in \(\text{AgCl}:\text{Co}^{2+}\) (with slightly shorter \(R \approx 2.505 \text{ Å} [25])\). Based on the relationship \(Dq \propto R^{-3} [26, 27]\) 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 \(\text{Co}^{2+}\), the Racah parameters \(B \approx B_0N^2 \approx 863 \text{ cm}^{-1}\) and \(C \approx C_0N^2 \approx 3381 \text{ cm}^{-1}\) are calculated. Using the free-ion values \(\xi_0^P \approx 533 \text{ cm}^{-1} [29]\) and \(P \approx 254 \times 10^{-4} \text{ cm}^{-1} [30]\) for \(\text{Co}^{2+}\) and \(\xi_0^P \approx 587 \text{ cm}^{-1} [31]\) for \(\text{Cl}^{-}\), the values in (4) can be obtained: \(\xi \approx 495 \text{ cm}^{-1}\), \(\xi^C \approx 480 \text{ cm}^{-1}\), \(k \approx 0.970\), \(k' \approx 0.829\), \(P \approx 234 \times 10^{-4} \text{ cm}^{-1}\), and \(P^C \approx 235 \times 10^{-4} \text{ cm}^{-1}\). 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 \(\beta_{\text{H}}\) of \(\text{Mg}^{2+}\) site in \(\text{MgCl}_2\)) 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 \(\Delta g\) is one order in magnitude smaller than the observed value. This reveals that the trigonal distortion based on the host structural parameters of \(\text{Mg}^{2+}\) site in \(\text{MgCl}_2\) are significantly underestimated and unsuitable for the analysis of the impurity \(\text{Co}^{2+}\) center. Thus, an angular variation can be expected to increase the local trigonal distortion and hence the calculated \(\Delta g\). Then the host angle \(\beta_{\text{H}}\) should be replaced by a local one \(\beta\) in terms of the angular variation \(\Delta \beta\) as: \(\beta \approx \beta_{\text{H}} + \Delta \beta\). Matching the theoretical \(\Delta g\) to the observed value, one can obtain the local angle \(\beta \approx 58.22^\circ\).

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 \(\beta\) and omission of the \(J\)-admixtures (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 \(J\)-admixtures in the local impurity–ligand bond angle \(\beta\) in (8) show good agreement with the observed values. Therefore, the experimental EPR spectra for the trigonal \(\text{Co}^{2+}\) center in \(\text{MgCl}_2\) 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 \(\beta_{\text{H}} \approx 54.78^\circ\) in the host to \(\beta \approx 58.22^\circ\) in the impurity center can be attributed to the local tension along the \(C_3\) axis arising from the substitution of smaller host \(\text{Mg}^{2+}\) by larger \(\text{Co}^{2+}\). The above axial tension around the impurity \(\text{Co}^{2+}\) 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 \(\Delta g\) (or \(\Delta A\)) > 0 when \(\delta \beta > 0\), as reported in the EPR studies for \(\text{Co}^{2+}\) 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 \(J\)-admixtures may lead to the results (Cal. b) of much smaller \(g_{\|}\) (and slightly lower \(g_{\perp}\)) and hence smaller anisotropy \(\Delta g\). Although the above calculated anisotropy could be improved

Table 1. Spin Hamiltonian parameters for the trigonal \(\text{Co}^{2+}\) center in \(\text{MgCl}_2\).

<table>
<thead>
<tr>
<th>(g_{|})</th>
<th>(g_{\perp})</th>
<th>(A_{|}) ((10^{-4} \text{ cm}^{-1}))</th>
<th>(A_{\perp}) ((10^{-4} \text{ cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cal. a</td>
<td>4.208</td>
<td>4.235</td>
<td>96</td>
</tr>
<tr>
<td>Cal. b</td>
<td>2.605</td>
<td>4.460</td>
<td>12</td>
</tr>
<tr>
<td>Cal. c</td>
<td>2.864</td>
<td>5.026</td>
<td>40</td>
</tr>
<tr>
<td>Expt. [9]</td>
<td>2.858 (\times 10^2) (\times 5.032 \times 40.0 \times 161)</td>
<td>2.858 (\times 10^2) (\times 5.032 \times 40.0 \times 161)</td>
<td>2.858 (\times 10^2) (\times 5.032 \times 40.0 \times 161)</td>
</tr>
</tbody>
</table>

* a Calculations based on inclusion of the \(J\)-admixtures and the host angle \(\beta_{\text{H}}\) (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 \(J\)-admixtures.

* c Calculations based on the \(J\)-admixtures and the local angular variation \(\Delta \beta\).
Table 2. Impurity–ligand distance \( R \) (in Å), the anisotropy \( \Delta g \), size mismatch \( r_i - r_b \) between impurity and host cation ions (in Å), local and host trigonal distortion angles \( (\delta \beta i \) and \( \delta \beta H) \) and angular variation \( \Delta \beta \) (in degree) as well as the variation of whole trigonal distortion \( \Delta \beta i \) related to the host cation sites based on the EPR analysis for \( \text{Co}^{2+} \) in various trigonal \( (D_3d) \) environments.

<table>
<thead>
<tr>
<th>Hosts</th>
<th>( R )</th>
<th>( \Delta g )</th>
<th>( r_i - r_b )</th>
<th>( \delta \beta i )</th>
<th>( \delta \beta H )</th>
<th>( \Delta \beta )</th>
<th>( \Delta \beta i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CaMgCl}_2 ) [12, 34, 35]</td>
<td>2.509</td>
<td>-4.860</td>
<td>0.025</td>
<td>-3.71</td>
<td>-3.03</td>
<td>-0.68</td>
<td>↓</td>
</tr>
<tr>
<td>( \text{K}_2\text{CdCl}_3 ) [9, 36, 37]</td>
<td>2.538</td>
<td>-0.706(5)</td>
<td>-0.225</td>
<td>-1.20</td>
<td>0.16</td>
<td>-1.36</td>
<td>↑</td>
</tr>
<tr>
<td>( \text{CdCl}_2 ) [9, 33, 38, 40]</td>
<td>2.545</td>
<td>1.907(6)</td>
<td>-0.225</td>
<td>3.80</td>
<td>2.05</td>
<td>1.75</td>
<td>↑</td>
</tr>
<tr>
<td>( \text{MgCl}_2 ) [present work]</td>
<td>2.554</td>
<td>2.174(15)</td>
<td>0.025</td>
<td>3.48</td>
<td>0.04</td>
<td>3.44</td>
<td>↑</td>
</tr>
<tr>
<td>( \text{CdBr}_2 ) [9, 33, 38, 40]</td>
<td>2.674</td>
<td>0.952(7)</td>
<td>-0.225</td>
<td>2.09</td>
<td>0.95</td>
<td>1.14</td>
<td>↑</td>
</tr>
<tr>
<td>( \text{PbI}_2 ) [33, 39, 41]</td>
<td>2.994</td>
<td>-0.76(1)</td>
<td>-0.445</td>
<td>-2.51</td>
<td>0.15</td>
<td>-2.66</td>
<td>↑</td>
</tr>
<tr>
<td>( \text{ZnSiF}_6 \cdot \text{H}_2\text{O} ) [42–44]</td>
<td>2.081</td>
<td>-2.251(3)</td>
<td>0.005</td>
<td>-2.08</td>
<td>-0.07</td>
<td>-2.01</td>
<td>↑</td>
</tr>
<tr>
<td>( \text{Co(OH)}_2 ) [45–47]</td>
<td>2.106</td>
<td>-1.086(13)</td>
<td>-0.255</td>
<td>-1.06</td>
<td>6.26</td>
<td>-7.32</td>
<td>↓</td>
</tr>
<tr>
<td>( \text{CaCO}_3 ) [40, 48, 49]</td>
<td>2.110</td>
<td>1.411(4)</td>
<td>-0.255</td>
<td>1.71</td>
<td>-1.59</td>
<td>3.30</td>
<td>↑</td>
</tr>
<tr>
<td>( \text{CdCO}_3 ) [40, 48, 50]</td>
<td>2.110</td>
<td>1.86(6)</td>
<td>-0.225</td>
<td>2.74</td>
<td>-0.94</td>
<td>3.68</td>
<td>↑</td>
</tr>
</tbody>
</table>

\( \delta \beta i = (g_1 + 2g_\perp)/3 \) would still be about 12% smaller than the experimental value since the increase of \( g_\perp \) with increasing \( \beta \) cannot compensate its decline without the \( J \)-admixtures. Further, the calculated hyperfine structure constants in this case are not as good as those (Cal. \( ^{a} \)) including the \( J \)-admixtures. In fact, the \( J \)-admixtures 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 \( \text{Co}^{2+} \) 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 \( J \)-admixtures 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 \( g_1 \) is larger than the experimental value and thus leads to a lower anisotropy. Since the system has strong ligand spin–orbit coupling \( (\zeta_0 \approx 587 \text{ cm}^{-1}) \) and moderate covalency \( (N \approx 0.88 < 1) \), omission of the ligand contributions would somewhat conceal the anisotropic influences of the spin–orbit coupling \( (\zeta/\zeta_0 \approx 1.03) \) and the orbital angular momentum \( (k/k' \approx 1.17) \) interactions and thus result in smaller anisotropy. Therefore, in order to study the spin Hamiltonian parameters for \( \text{Co}^{2+} \) in \( \text{MgCl}_2 \) (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 \( \Delta g \), the local and host trigonal distortion angles \( (\delta \beta i \) and \( \delta \beta H) \) related to the ideal value \( \beta \), and the angular variation \( \Delta \beta \) related to \( \beta H \) based on EPR analysis for \( \text{Co}^{2+} \) in various trigonally \( (D_3d) \) distorted octahedral systems. For comparison and clearness, the impurity–ligand bond (reference) distance \( R \), the size mismatch \( r_i - r_b \) between impurity \( \text{Co}^{2+} \) and host cation and the variation \( \Delta r \) in the whole trigonal distortion related to the host cation site are also supplied in Table 2. First, the anisotropy \( \Delta g \) has the same sign as \( \delta \beta \), i.e., \( \Delta g \) is positive (or negative) for \( \text{Co}^{2+} \) in trigonally compressed (or elongated) octahedra. Second, the variation \( \Delta r \) generally shows increasing rule \((|\delta \beta i| > |\delta \beta H|)\) for most systems except \( \text{Ca(OH)}_2 \). 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 distortion 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 \([\text{CoCl}_6]^{2-}\) clusters in the chlorides and the \([\text{CoO}_4]^{10-}\) clusters in \( \text{Ca(OH)}_2 \) and \( \text{ZnSiF}_6 \cdot \text{H}_2\text{O} \). 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 $|r_h - r_i|$. In detail, the Co$^{2+}$ centers prefer to maintain the host trigonal distortion properties ($\delta \beta \cdot \delta \beta_H > 0$) for small size mismatch ($|r_h - r_i| < 0.225 \text{ Å}$) and exchange the host trigonal distortion properties ($\delta \beta \cdot \delta \beta_H < 0$) for large size mismatch ($|r_h - r_i| \geq 0.225 \text{ Å}$), corresponding to small and large lattice modifications, respectively. As regards the moderate $|r_h - r_i|$ ($\approx 0.225 \text{ Å}$) for Co$^{2+}$ in CdCl$_2$ and CdBr$_2$, 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 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. 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 Co$^{2+}$ center in MgCl$_2$ are theoretically studied by considering the contributions from the $J$-admixtures, 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 Mg$^{2+}$ 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 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.

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