Spin-lattice Coupling Coefficient $G_{44}$ of KMgF$_3$:Mn$^{2+}$
Calculated from Two Cases

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The high (fourth) order perturbation formulas based on the dominant spin-orbit coupling mechanism for the zero-field splittings $D_m$ of a $^6$S-state ion in trigonal symmetry and $E_{\text{rho}}$ in rhombic symmetry are derived from the strong field scheme. Two analytic expressions of the spin-lattice coupling coefficient $G_{44}$ obtained from the formulas of $D_m$ and $E_{\text{rho}}$ are established by using a simple and uniform method. Based on the two expressions, the coefficients $G_{44}$ for KMgF$_3$:Mn$^{2+}$ are calculated in two cases. The results show that the lowest (third) order perturbation formulas of $D^{(3)}_m$ and $E^{(3)}_{\text{rho}}$ are too simple and too approximate to give reasonable and consistent values of $G_{44}$, whereas when the fourth-order perturbation terms $D^{(4)}_m$ and $E^{(4)}_{\text{rho}}$ are considered, the calculated values of $G_{44}$ ($= G^{(3)}_4 + G^{(4)}_4$) in both cases are not only close to each other, but also in agreement with the observed value. So, the fourth-order perturbation terms cannot be neglected.

Key words: Spin-lattice Coupling Coefficient; Electron Paramagnetic Resonance (EPR); Crystal-field Theory, Mn$^{2+}$; KMgF$_3$.

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1. Introduction

The interaction of phonons with paramagnetic spin systems is characterized by the spin-lattice coupling coefficients $G_{ij}$, which relate the energy change in the spin system to the strain introduced into the lattice. Studies of these coefficients are of significance because they give valuable information on the spin-lattice relaxation time of magnetic center, the angular variation of EPR linewidths, the internal stress of a crystal and the microscopic mechanism of zero-field splittings [1 - 5]. To simplify the calculation of $G_{ij}$ and give their clear physical meaning, in [6] a unified and convenient method of calculating the coefficients $G_{11}$ and $G_{44}$ for a $^{3}d^{3}$ ion in cubic octahedral symmetry from the formulas of zero-field splittings in low symmetries was established. According to this method, $G_{44}$ can be obtained for two cases, one for the splitting $D_{\text{tri}}$ in a trigonal symmetry and the other from the splitting $E_{\text{rho}}$ in a rhombic symmetry, i.e.

$$G_{44}(D) = -\frac{\sqrt{2}}{6} \left( \frac{\partial D_{\text{tri}}}{\partial \beta} \right)_0, \quad G_{44}(E) = -\frac{1}{2} \left( \frac{\partial E_{\text{rho}}}{\partial \theta} \right)_0,$$

(1)

where the subscript 0 denotes that the differentiation is done for the case of cubic symmetry. The angles $\beta$ and $\theta$ are, respectively, related to the trigonal and rhombic distortions and are defined in [6]. Thus, we can, to a certain degree, check whether the formulas $D_{\text{tri}}$ and $E_{\text{rho}}$ are consistent and reliable by comparing the coefficients $G_{44}$ calculated for the two cases. Since the derivations of the formulas, particularly the high-order perturbation formulas, of zero-field splittings are often very tedious, the above simple method is profitable and practical. In the previous paper [6] we successfully checked the formulas of $D_{\text{tri}}$ and $E_{\text{rho}}$ for the $^6$S-state ion, based on some mechanisms and models by comparing the analytic expressions of $G_{44}$ obtained from the two cases. However the high (fourth) order perturbation formulas $D_{\text{tri}}$ and $E_{\text{rho}}$ from the...
strong field scheme based on the dominant spin-orbit coupling mechanism for the $^6S$-state ion were not reported (note: only the lowest (third) order perturbation formulas were given in [7]) and so a check of these formulas was not made. In this paper, we derive the fourth-order (and also third-order) perturbation formulas $D_{\text{tr}}$ and $E_{\text{rho}}$ from the strong field scheme. To check these formulas, the expressions $G^E$ obtained from the formulas $D_{\text{tr}}$ and $E_{\text{rho}}$ are established, and they are applied to calculate the coefficient $G_{44}$ of KMgF$_3$:Mn$^{2+}$ crystal. The results and the importance of the contributions from the fourth-order terms $D^{(3)}_{\text{tr}}$ and $E^{(4)}_{\text{rho}}$ are discussed.

2. Calculation Formulas

Similar to the strong field scheme as done by Macfarlane [8] for the F-state ion, for the S-state ion the cubic field eigenstates are taken as the zero-order eigenstates and the Hamiltonian in low symmetry can be written as

$$H = H_0 + H',$$
$$H_0 = V_{\text{cub}}(D_q) + H^b_{\text{Coul}}(B, C),$$
$$H' = H^b_{\text{Coul}}(B, C) + V_{\text{low}} + H_{SO}(\zeta),$$

where $V_{\text{cub}}$, $V_{\text{low}}$, $H^a_{\text{Coul}}$ and $H^b_{\text{Coul}}$ are, respectively, the cubic and low (trigonal or rhombic) symmetry parts of the crystal field, the diagonal and off-diagonal parts of Coulomb interaction (with Racah parameters $B$ and $C$). $H_{SO}$ is the spin-orbit interaction with the spin-orbit coupling coefficient $\zeta$. Thus, the third- and fourth-order perturbation formulas of $D_{\text{tr}}$ and $E_{\text{rho}}$ can be derived. They are

$$D = D^{(3)}_{\text{tr}} + D^{(4)}_{\text{tr}},$$

$$D^{(3)}_{\text{tr}} = (1/10) V \zeta^2 (1/E_1^2 - 1/E_3^2) + (3/2)(/10) V' \zeta^2 (1/E_1 E_2 - 1/E_2 E_3),$$
$$D^{(4)}_{\text{tr}} = V \{ \zeta^2 C / (1/E_1 - 1/E_3)(5E_1 E_2) + 3\zeta^2 B / (1/E_1^2 - 1/E_3^2)(5E_2) - \zeta^2 [(1/E_1^2 + 1/E_3^2)(30E_2) + 1/(10E_1 E_2 E_4) - 1/(15E_1 E_2 E_5) - 1/(15E_2^2 E_5)] - 1/(15E_2 E_3 E_5) + 1/(10E_2 E_3 E_6) + 2(2/E_1 - 1/E_2 + 2/E_3)(15E_2 E_7)] \} + \sqrt{2} V' \{ -3\zeta^2 (3B/E_2 + C/E_1)(10E_2 E_3) - 3B(1/E_1 + 1/E_3)(5E_1 E_2) \} + \zeta^3 [(2/E_1 - 1/E_2)(20E_2 E_3) + 1/(10E_1 E_2 E_4) + 1/(10E_1 E_2 E_5) + 1/(20E_2^2 E_4) + 1/(20E_2^2 E_5) - 1/(10E_2 E_3 E_5) - 1/(10E_3^2 E_5) - 1/(1/E_1 E_3 + 1/E_2^2 + 1/E_3^2)(5E_8) \} + V^2 \zeta^2 [2/(15E_2^2 E_7) + 1/(10E_1 E_2 E_4) + 1/(15E_2^2 E_5) + 1/(10E_3^2 E_6)] + V'^2 \zeta^2 [(1/E_1^2 + 2/E_1 E_3 + 1/E_3^2)(5E_8) + 3/(10E_1^2 E_5) - 3/(5E_1 E_2 E_5) + 3/(10E_2^2 E_6) + 1/(20E_2 E_3 E_4) + 1/(20E_2 E_3 E_6) + 2/(5E_9)(2/E_1 E_3 - 1/E_2^2 - 1/E_3^2)] + \sqrt{2} V' \zeta^2 (1/E_1 E_4 - 1/E_1 E_5 + 2/E_3 E_5 + 1/E_3 E_6)(1/E_2),$$

$$E = E^{(3)}_{\text{rho}} + E^{(4)}_{\text{rho}},$$

$$E^{(3)}_{\text{rho}} = (-7/5) \zeta^2 (1/E_1^2 - 1/E_3^2) D_{\eta},$$
$$E^{(4)}_{\text{rho}} = \zeta^3 [28D_0(1/E_1^2 + 1/E_3^2)(10E_2) + 12(D_\xi + D_\eta)(1/E_1 E_4 + 1/E_3 E_6)(5E_2) + 2(3D_\xi + D_\eta)(1/E_1 + 1/E_2 + 1/E_3)(5E_2 E_3)] + \zeta^2 [14BD_1(1/E_1^2 - 1/E_3^2)(5E_2) + 14CP_{1/3}(1/E_1 - 1/E_3)(15E_1 E_3) - (49/6)D_1 D_\eta(1/E_1^3 + 1/E_3^3) + (3/10)(D_\xi + D_\eta)(4D_s + 5D_\eta)(1/E_1^3 + 1/E_3^3) + 2(3D_s - 5D_\eta)(3D_\xi - 4D_\eta)(5E_2^3)],$$

where $V$ and $V'$ are the trigonal field parameters and $D_s$, $D_\xi$, $D_\eta$ and $D_\gamma$ are the rhombic parameters. The zero-order energy denominators are

$$E_1 = 10B + 6C - 10D_q, \quad E_2 = 19B + 7C, \quad E_3 = 10B + 6C + 10D_q, \quad E_4 = 18B + 6C - 10D_q,$$
$$E_5 = 13B + 5C, \quad E_6 = 18B + 6C + 10D_q, \quad E_7 = 13B + 5C, \quad E_8 = 14B + 5C, \quad E_9 = 22B + 7C.$$
From (1), we obtain the expressions of $G_{44}(D)$ and $G_{44}(E)$ from two cases as follows:

$$G_{44}(D) = G_{44}^{(3)}(D) + G_{44}^{(4)}(D),$$

$$G_{44}^{(3)}(D) = (\sqrt{2/6})\zeta^2 [(1/10)\left(\frac{\partial V}{\partial \beta}\right)_0 (1/E_1^2 - 1/E_3^2) + (3\sqrt{2/10})\left(\frac{\partial V'}{\partial \beta}\right)_0 (1/E_1 E_2 - 1/E_2 E_3)]$$

$$G_{44}^{(4)}(D) = (\sqrt{2/6})\zeta \left\{ \zeta^2 \left(\frac{\partial V}{\partial \beta}\right)_0 [C(1/E_1 - 1/E_3)/(5E_1 E_3) + 3B(1/E_1^2 - 1/E_3^2)/(5E_2)] \right.$$ 

$$- 1/(15E_2 E_3 E_6) + 1/(10E_2 E_3 E_6) + 2(2E_1 - 1/E_2 + 2/E_3)/(15E_2 E_7)]$$

$$+ \sqrt{2} \left(\frac{\partial V'}{\partial \beta}\right)_0 \zeta^3 [1/(10E_1^2 E_3) + 1/(10E_1 E_2 E_3) + 2(2E_1 - 1/E_2)/(20E_2 E_3) + 1/(20E_2^2 E_4)$$

$$+ 1/(20E_2^2 E_6) - 1/(10E_2 E_3 E_5) - 1/(10E_3^2 E_5)$$

$$- (1/E_1 E_3 + 1/E_1^2 + 1/E_3^2)/(5E_8)] \right\},$$

$$G_{44}(E) = G_{44}^{(3)}(E) + G_{44}^{(4)}(E), \quad G_{44}^{(3)}(E) = (7/10)\zeta^2 (1/E_1^2 - 1/E_3^2) \left(\frac{\partial D_\phi}{\partial \theta}\right)_0,$$

$$G_{44}^{(4)}(E) = -\zeta \left\{ 14 \left(\frac{\partial D_\phi}{\partial \theta}\right)_0 (1/E_1^2 + 1/E_3^2)/(10E_2) + 6 \left[ \left(\frac{\partial D_\xi}{\partial \theta}\right)_0 + \left(\frac{\partial D_\eta}{\partial \theta}\right)_0 \right] (1/E_1 E_4 + 1/E_3 E_6)/(15E_2) \right.$$

$$+ 3 \left(\frac{\partial D_\xi}{\partial \theta}\right)_0 + 4 \left(\frac{\partial D_\eta}{\partial \theta}\right)_0 \right\} (1/E_1^2 + 1/E_2 + 1/E_3)/(5E_2 E_5) \right\}.$$

From the superposition model of crystal field parameters [9] we have

$$\left(\frac{\partial V}{\partial \beta}\right)_0 = [(80\sqrt{2}\tilde{A}_4(R_0) - 36\tilde{A}_2(R_0))/7, \quad \left(\frac{\partial V'}{\partial \beta}\right)_0 = [(40\tilde{A}_4(R_0) + 24\tilde{A}_2(R_0))/7,$$

$$\left(\frac{\partial D_\phi}{\partial \theta}\right)_0 = -8\tilde{A}_2(R_0)/7, \quad \left(\frac{\partial D_\xi}{\partial \theta}\right)_0 = -40\tilde{A}_4(R_0)/21,$$

where the intrinsic parameters $\tilde{A}_4(R_0) \approx (3/4)D_q$ [7, 9] and $\tilde{A}_2(R_0) \approx n\tilde{A}_4(R_0)$ with $n$ in the range of 9 - 12 obtained from many studies for 3d$^n$ ions in crystals [10 - 12]. We take $n \approx 9$ here.

Noteworthy, since only part of the electrostatic potential (i.e., off-diagonal elements) is combined with the spin-orbit interaction and low symmetry components of the crystal field as the perturbation, the analytic expressions of $G_{44}(D)$ and $G_{44}(E)$ from the two cases may not be the same, but the numerical results should be close to each other when the formulas of $D_{\text{tr}}$ and $E_{\text{rho}}$ are consistent and reliable.

### 3. Results and Discussions

Now we apply the above formulas to calculate the coefficient $G_{44}$, which was measured by an acoustic paramagnetic resonance experiment [13], for two cases of the KMgF$_3$:Mn$^{2+}$ crystal. From the optical spectra of KMgF$_3$:Mn$^{2+}$ [14], we have

$$D_q \approx 720 \text{ cm}^{-1}, \quad B \approx 860 \text{ cm}^{-1}, \quad C \approx 3100 \text{ cm}^{-1}.$$ 

The spin-orbit coupling coefficient $\zeta$ in the crystal can be obtained by the expression $\zeta \approx N^2 \xi_0$ [15, 16], where $N^2 \approx \frac{1}{2}(\sqrt{B/B_0} + \sqrt{C/C_0})$ is related to the
Table 1. Spin-lattice coefficient $G_{44} = G_{44}^{(3)} + G_{44}^{(4)}$ (in cm$^{-1}$) of KMgF$_3$:Mn$^{2+}$, calculated in two ways.

<table>
<thead>
<tr>
<th></th>
<th>$G_{44}^{(3)}(D)$</th>
<th>$G_{44}^{(4)}(D)$</th>
<th>$G_{44}(D)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_{44}^{(3)}(D)$</td>
<td>-0.05</td>
<td>0.05</td>
<td>-0.10</td>
</tr>
<tr>
<td>$G_{44}^{(4)}(E)$</td>
<td>-0.13</td>
<td>0.03</td>
<td>-0.10</td>
</tr>
<tr>
<td>Experiment [13]:</td>
<td></td>
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<td>-0.09(2)</td>
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covalency reduction effect, and $\zeta_0^0$ is the spin-orbit coupling coefficient of the free 3$d^n$ ion. For a free Mn$^{2+}$ ion, $B_0 \approx 960$ cm$^{-1}$, $C_0 \approx 3325$ cm$^{-1}$ and $\zeta_0^0 \approx 347$ cm$^{-1}$ [17], thus, we have $\zeta \approx 332$ cm$^{-1}$. Substituting these parameters into the above expressions, we have calculated the coefficient $G_{44}$ for the two cases. The results (including the contributions from the third-order and fourth-order perturbation terms) are compared with the observed value in Table 1.

From Table 1, two points shall be discussed:

(i) The values of $G_{44}(D)$ and $G_{44}(E)$, calculated in the two ways, are not only close to each other but also compatible with the observed value of KMgF$_3$:Mn$^{2+}$. This suggests that the above high-order perturbation formulas for $D_{\text{tri}}$ and $E_{\text{rho}}$ are consistent and reasonable, and that the simple check method by using (1) is useful and feasible.

(ii) If only the contribution from the lowest (third) order perturbation terms is considered, the calculated $D_{\text{tri}}^{(3)}$ and $E_{\text{rho}}^{(3)}$ are not only quite unlike, but also in disagreement with the observed value. So, the third-order perturbation formulas $D_{\text{tri}}^{(3)}$ and $E_{\text{rho}}^{(3)}$ are too simple and too approximate to be applicable.