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_{tri} of a ^{6}S-state ion in trigonal symmetry and E_{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_{tri} and E_{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 $D_{tri}^{(3)}$ and $E_{rho}^{(3)}$ are too simple and too approximate to give reasonable and consistent values of G_{44}, whereas when the fourth-order perturbation terms $D_{tri}^{(4)}$ and $E_{rho}^{(4)}$ are considered, the calculated values of G_{44} $(= G_{44}^{(3)} + G_{44}^{(4)})$ 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);
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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 $3d^n$ 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_{tri} in a trigonal symmetry and the other from the splitting E_{rho} in a rhombic symmetry, i. e.

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

where the subscript 0 denotes that the differentitation is done for the case of cubic symmetry. The angles β and θ 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_{tri} and E_{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_{tri} and E_{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_{tri} and E_{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_{tri} and E_{rho} from the strong field scheme. To check these formulas, the expressions $G_{44}(D)$ and $G_{44}(E)$ obtained from the formulas D_{tri} and E_{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 $D_{tri}^{(4)}$ and $E_{rho}^{(4)}$ 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

$$
\begin{aligned}
H &= H_0 + H', \\
H_0 &= V_{cub}(D_q) + H_{Coul}^a(B, C), \\
H' &= H_{Coul}^b(B, C) + V_{low} + H_{SO}(\zeta),
\end{aligned} \tag{2}
$$

where V_{cub}, V_{low}, H_{Coul}^a and H_{Coul}^b 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 ζ. Thus, the third- and fourth-order perturbation formulas of D_{tri} and E_{rho} can be derived. They are

$$
D = D_{tri}^{(3)} + D_{tri}^{(4)}, \tag{3}
$$

$$
D_{tri}^{(3)} = (1/10)V\zeta^2(1/E_1{}^2 - 1/E_3{}^2) + (3\sqrt{2}/10)V'\zeta^2(1/E_1E_2 - 1/E_2E_3),
$$

$$
\begin{aligned}
D_{tri}^{(4)} = \;& V\Big\{\zeta^2 C(1/E_1 - 1/E_3)/(5E_1E_3) + 3\zeta^2 B(1/E_1{}^2 - 1/E_3{}^2)/(5E_2) \\
& - \zeta^3\big[(1/E_1{}^2 + 1/E_3{}^2)/(30E_2) + 1/(10E_1E_2E_4) - 1/(15E_1E_2E_5) - 1/(15E_2{}^2E_5) \\
& \quad - 1/(15E_2E_3E_5) + 1/(10E_2E_3E_6) + 2(2/E_1 - 1/E_2 + 2/E_3)/(15E_2E_7)\big]\Big\} \\
& + \sqrt{2}V'\Big\{-3\zeta^2\big[(3B/E_2 + C/E_1)/(10E_2E_3) - 3B(1/E_1 + 1/E_3)/(5E_1E_2)\big] \\
& \quad + \zeta^3\big[(2/E_1 - 1/E_2)/(20E_2E_3) + 1/(10E_1{}^2E_5) + 1/(10E_1E_2E_5) + 1/(20E_2{}^2E_4) \\
& \qquad + 1/(20E_2{}^2E_6) - 1/(10E_2E_3E_5) - 1/(10E_3{}^2E_5) - (1/E_1E_3 + 1/E_1{}^2 + 1/E_3{}^2)/(5E_8)\big]\Big\} \\
& + V^2\zeta^2\big[2/(15E_2{}^2E_7) + 1/(10E_1{}^2E_4) + 1/(15E_2{}^2E_5) + 1/(10E_3{}^2E_6)\big] \\
& + V'^2\zeta^2\big[(1/E_1{}^2 + 2/E_1E_3 + 1/E_3{}^2)/(5E_8) + 3/(10E_1{}^2E_5) - 3/(5E_1E_3E_5) + 3/(10E_3{}^2E_5) \\
& \qquad + 1/(20E_2{}^2E_4) + 1/(20E_2{}^2E_6) + 2/(5E_9)(2/E_1E_3 - 1/E_1{}^2 - 1/E_3{}^2)\big] \\
& + \sqrt{2}VV'\zeta^2(1/E_1E_4 - 1/E_1E_5 + 2/E_3E_5 + 1/E_3E_6)/(10E_2),
\end{aligned}
$$

$$
E = E_{rho}^{(3)} + E_{rho}^{(4)}, \tag{4}
$$

$$
E_{rho}^{(3)} = (-7/5)\zeta^2(1/E_1{}^2 - 1/E_3{}^2)D_\eta,
$$

$$
\begin{aligned}
E_{rho}^{(4)} = \;& \zeta^3\big[28D_\eta(1/E_1{}^2 + 1/E_3{}^2)/(10E_2) + 12(D_\xi + D_\eta)(1/E_1E_4 + 1/E_3E_6)/(5E_2) \\
& \quad + 2(3D_\xi + D_\eta)(1/E_1 + 1/E_2 + 1/E_3)/(5E_2E_5)\big] \\
& + \zeta^2\big[14BD_t(1/E_1{}^2 - 1/E_3{}^2)/(5E_2) + 14CD_t(1/E_3 - 1/E_1)/(15E_1E_3) - (49/6)D_tD_\eta(1/E_1{}^3 + 1/E_3{}^3) \\
& \quad + (3/10)(D_\xi + D_\eta)(4D_s + 5D_t)(1/E_1{}^3 + 1/E_3{}^3) + 2(3D_s - 5D_t)(3D_\xi - 4D_\eta)/(5E_2{}^3)\big],
\end{aligned}
$$

where V and V' are the trigonal field parameters and D_s, D_t, D_ξ and D_η are the rhombic parameters. The zero-order energy denominators are

$$
\begin{aligned}
E_1 &= 10B + 6C - 10D_q, \; E_2 = 19B + 7C, \; E_3 = 10B + 6C + 10D_q, \; E_4 = 18B + 6C - 10D_q, \\
E_5 &= 13B + 5C, \; E_6 = 18B + 6C + 10D_q, \; E_7 = 13B + 5C, \; E_8 = 14B + 5C, \; E_9 = 22B + 7C.
\end{aligned} \tag{5}
$$

From (1), we obtain the expressions of $G_{44}(D)$ and $G_{44}(E)$ from two cases as follows:

$$G_{44}(D) = G_{44}^{(3)}(D) + G_{44}^{(4)}(D), \tag{6}$$

$$G_{44}^{(3)}(D) = (\sqrt{2}/6)\zeta^2\left[(1/10)\left(\frac{\partial V}{\partial \beta}\right)_0(1/E_1{}^2 - 1/E_3{}^2) + (3\sqrt{2}/10)\left(\frac{\partial V'}{\partial \beta}\right)_0(1/E_1E_2 - 1/E_2E_3)\right]$$

$$G_{44}^{(4)}(D) = (\sqrt{2}/6)\left\{\zeta^2\left(\frac{\partial V}{\partial \beta}\right)_0\left[C(1/E_1 - 1/E_3)/(5E_1E_3) + 3B(1/E_1{}^2 - 1/E_3{}^2)/(5E_2)\right]\right.$$

$$\zeta^3\left(\frac{\partial V}{\partial \beta}\right)_0\left[(1/E_1{}^2 + 1/E_3{}^2)/(30E_2) + 1/(10E_1E_2E_4) - 1/(15E_1E_2E_5) - 1/(15E_2{}^2E_5)\right.$$

$$\left. - 1/(15E_2E_3E_5) + 1/(10E_2E_3E_6) + 2(2/E_1 - 1/E_2 + 2/E_3)/(15E_2E_7)\right]$$

$$- 3\sqrt{2}\left(\frac{\partial V'}{\partial \beta}\right)_0\zeta^2\left[(C/E_1 - B/E_2)/(10E_2E_3) + 3B(1/E_1 + 1/E_3)/(5E_1E_2)\right]$$

$$+ \sqrt{2}\left(\frac{\partial V'}{\partial \beta}\right)_0\zeta^3\left[1/(10E_1{}^2E_5) + 1/(10E_1E_2E_5) + (2/E_1 - 1/E_2)/(20E_2E_3) + 1/(20E_2{}^2E_4)\right.$$

$$+ 1/(20E_2{}^2E_6) - 1/(10E_2E_3E_5) - 1/(10E_3{}^2E_5)$$

$$\left.\left. - (1/E_1E_3 + 1/E_1{}^2 + 1/E_3{}^2)/(5E_8)\right]\right\},$$

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

$$G_{44}^{(4)}(E) = -\zeta^3\left\{14\left(\frac{\partial D_\eta}{\partial \theta}\right)_0(1/E_1{}^2 + 1/E_3{}^2)/(10E_2) + 6\left[\left(\frac{\partial D_\xi}{\partial \theta}\right)_0 + \left(\frac{\partial D_\eta}{\partial \theta}\right)_0\right](1/E_1E_4 + 1/E_3E_6)/(5E_2)\right.$$

$$\left. + \left[3\left(\frac{\partial D_\xi}{\partial \theta}\right)_0 - 4\left(\frac{\partial D_\eta}{\partial \theta}\right)_0\right](1/E_1 + 1/E_2 + 1/E_3)/(5E_2E_5)\right\}.$$

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

$$\left(\frac{\partial V}{\partial \beta}\right)_0 = [80\sqrt{2}\bar{A}_4(R_0) - 36\bar{A}_2(R_0)]/7, \quad \left(\frac{\partial V'}{\partial \beta}\right)_0 = [40\bar{A}_4(R_0) + 24\bar{A}_2(R_0)]/7, \tag{8}$$

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

$$\tag{9}$$

where the intrinsic parameters $\bar{A}_4(R_0) \approx (3/4)D_q$ [7, 9] and $\bar{A}_2(R_0) \approx n\bar{A}_4(R_0)$ 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.

Noteworthily, 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_{tri} and E_{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

$$D_q \approx 720\ \text{cm}^{-1}, \quad B \approx 860\ \text{cm}^{-1}, \quad C \approx 3100\text{cm}^{-1}. \tag{10}$$

The spin-orbit coupling coefficient ζ in the crystal can be obtained by the expression $\zeta \approx N^2\zeta_d{}^0$ [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.

$G_{44}^{(3)}(D) = -0.05$	$G_{44}^{(4)}(D) = -0.05$	$G_{44}(D) = -0.10$
$G_{44}^{(3)}(E) = -0.13$	$G_{44}^{(4)}(E) = -0.03$	$G_{44}(E) = -0.10$
	Experiment [13]:	$G_{44} = -0.09(2)$

covalency reduction effect, and $\zeta_d^{\,0}$ is the spin-orbit coupling coefficient of the free $3d^n$ ion. For a free Mn^{2+} ion, $B_0 \approx 960$ cm^{-1}, $C_0 \approx 3325$ cm^{-1} and $\zeta_d^{\,0} \approx 347$ 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_{tri} and E_{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.

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