Studies on the EPR Parameters for the Rhombic Co^{2+} Center in Magnesium Acetate

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The electron paramagnetic resonance (EPR) g factors g_i ($i = x, y, z$) and the hyperfine structure constants A_i for the rhombic Co^{2+} center in magnesium acetate are theoretically studied from the perturbation formulas of these parameters for a 3d^7 ion under rhombic symmetry. In these formulas, the contributions from the admixture among different states, covalency effect and rhombic crystal-fields are taken into account. The related crystal-field parameters are determined from the superposition model and the local geometrical relationship of the impurity center. The calculated results show reasonable agreement with the observed values. In addition, the nuclear quadrupole interaction constant Q is analyzed, and its negative sign is verified theoretically.

Key words: Electron Paramagnetic Resonance (EPR); Crystal- and Ligand-fields; Co^{2+}; Magnesium Acetate.

1. Introduction

Magnesium acetate is a useful material widely adopted in the investigations of kinetics of magnesia hydration [1], compound formation [2, 3], vapour pressures of saturated aqueous solutions [4], Raman spectroscopy [5, 6] and irradiation measurements [7]. In addition, electron paramagnetic resonance (EPR) studies were carried out on this material doped with transition-metal ions. For example, the EPR g factors g_i ($i = x, y, z$) and the hyperfine constants A_i (as well as the nuclear quadrupole interaction constant Q) for Co^{2+} doped magnesium acetate were measured decades ago [8, 9]. Up to now, however, theoretical explanations have not been made for these experimental results, although the EPR parameters were assigned to the impurity Co^{2+} occupying the rhombic Mg^{2+} site [8, 9]. In this work, the EPR parameters for the rhombic Co^{2+} center in magnesium acetate are studied from perturbation formulas of these parameters for a 3d^7 ion under rhombic symmetry based on the cluster approach. In these formulas, the contributions from the admixture of different states, covalency effect and rhombic crystal-fields are taken into account.

2. Calculations

Magnesium acetate [Mg(CH$_3$COO)$_2$·4H$_2$O] is monoclinic with space group $P2_1/c$ [9, 10]. When Co^{2+} is doped into magnesium acetate, it may substitute the host Mg^{2+} and conserve the original rhombic (C_{2v}) point symmetry [9, 10], since no charge compensation is needed. The formulas of the g factors g_i and the hyperfine structure constants A_i for a 3d^7 ion in rhombic octahedra can be written as follows [11]:

$$g_x = \left\{ 4\left[\left(\frac{\alpha}{\alpha'}\right)^2 + \frac{2k\alpha}{(x+2)}\left(\frac{\alpha'}{\alpha''}\right) + \frac{12}{x(x+2)} \right] + \left(\frac{\alpha}{\alpha'}\right)^2 \nu_{4x} + \frac{8\nu_5}{(x+2)^2} + \frac{12\nu_6}{(x+2)} - \frac{\alpha}{(\alpha'\alpha'')^{1/2}}\frac{4\nu_{7x}}{(x+2)} \right\} / Z,$$

$$g_y = \left\{ 4\left[\left(\frac{\alpha}{\alpha''}\right)^2 + \frac{2k\alpha}{(x+2)}\left(\frac{\alpha''}{\alpha'}\right) + \frac{12}{x(x+2)} \right] + \left(\frac{\alpha}{\alpha''}\right)^2 \nu_{4y} + \frac{8\nu_5}{(x+2)^2} + \frac{12\nu_6}{(x+2)} - \frac{\alpha}{(\alpha'\alpha'')^{1/2}}\frac{4\nu_{7y}}{(x+2)} \right\} / Z,$$

$$g_z = 2 + \left\{4(k\alpha+2)\left[\frac{3}{x^2}-\frac{4}{(x+2)^2}\right]+\left[\frac{9}{x^2}-\frac{4}{(x+2)^2}\right](\nu_{1x}+\nu_{1y})-\frac{\alpha(\nu_{3x}+\nu_{3y})}{(\alpha'\alpha'')^{1/2}}\left(\frac{3}{x}-\frac{4}{(x+2)}\right)\right\}/Z, \quad (1)$$

$$\begin{aligned}
A_x &= P\left\{(-\kappa/2)\left[\left(\frac{\alpha^2}{\alpha'\alpha''}\right)+\frac{12}{x(x+2)}\right]+\frac{8k\alpha}{x+2}-\left(\frac{\alpha^2}{\alpha'\alpha''}\right)W_z-\frac{32W_{xy}}{(x+2)^2}-\frac{12W_x}{x(x+2)}+\frac{4\alpha W_{xz}}{(x+2)(\alpha'\alpha'')^{1/2}}\right\}/Z \\
&\quad + P'\left\{\left(\frac{\alpha}{\alpha'}\right)^2\nu_{4x}+\frac{8\nu_5}{(x+2)^2}+\frac{12\nu_6}{x(x+2)}-\frac{4\alpha\nu_{7x}}{(x+2)(\alpha'\alpha'')^{1/2}}\right\}/Z, \\
A_y &= P\left\{(-\kappa/2)\left[\left(\frac{\alpha^2}{\alpha'\alpha''}\right)+\frac{12}{x(x+2)}\right]+\frac{8k\alpha}{x+2}-\left(\frac{\alpha^2}{\alpha'\alpha''}\right)W_z-\frac{32W_{xy}}{(x+2)^2}-\frac{12W_y}{x(x+2)}+\frac{4\alpha W_{yz}}{(x+2)(\alpha'\alpha'')^{1/2}}\right\}/Z \\
&\quad + P'\left\{\left(\frac{\alpha}{\alpha'}\right)^2\nu_{4y}+\frac{8\nu_5}{(x+2)^2}+\frac{12\nu_6}{x(x+2)}-\frac{4\alpha\nu_{7y}}{(x+2)(\alpha'\alpha'')^{1/2}}\right\}/Z, \\
A_z &= P\left\{(-\kappa/2)\left[2+8\left(\frac{3}{x^2}-\frac{4}{(x+2)^2}\right)\right]+4k\alpha\left(\frac{3}{x^2}-\frac{4}{(x+2)^2}\right)+(W_x+W_y)\left(\frac{9}{x^2}-\frac{4}{(x+2)^2}\right)+\frac{\alpha^2W_z}{\alpha'\alpha''}\right\}/Z \\
&\quad - P\frac{2\alpha(W_{xz}+W_{yz})\left(\frac{3}{x}-\frac{4}{x+2}\right)}{Z(\alpha'\alpha'')^{1/2}}+P'\left\{(\nu_{1x}+\nu_{1y})\left(\frac{9}{x^2}-\frac{4}{(x+2)^2}\right)-\frac{\alpha(\nu_{3x}+\nu_{3y})\left(\frac{3}{x}-\frac{4}{x+2}\right)}{(\alpha'\alpha'')^{1/2}}\right\}/Z. \quad (2)
\end{aligned}$$

Here $Z = \left(\frac{\alpha}{\alpha'\alpha''}\right)+\frac{6}{x^2}+\frac{8}{(x+2)^2}$. κ is the core polarization constant. x can be determined from the energy splittings Δ $(= E\{^4\mathrm{B}_1[^4\mathrm{T}_1(\mathrm{F})]\} - E\{^4\mathrm{B}_3[^4\mathrm{T}_1(\mathrm{F})]\})$ and δ $(= E\{^4\mathrm{B}_2[^4\mathrm{T}_1(\mathrm{F})]\} - E\{^4\mathrm{B}_3[^4\mathrm{T}_1(\mathrm{F})]\})$ of the $^4\mathrm{T}_1$ ground state in rhombic crystal-fields by the expression $\Delta = \frac{\zeta\alpha'\alpha''}{3}\left[\frac{3}{\alpha x}+\frac{4\zeta}{\alpha\zeta(x+2)+6\delta}\right]-\frac{\zeta\alpha}{6}(x+3)$. The splittings Δ, δ can be calculated from the d-d transition energy matrices of the 3d^7 ion in rhombic symmetry. The related parameters f_i, q_i, α^i, ν_{ij} and W_{ij} in the above formulas are related to the admixture of the ground and excited states in rhombic symmetry and can be found in [11] (for saving space, they are not written here).

Based on the cluster approach, the spin-orbit coupling coefficients ζ, ζ', the orbital reduction factors k, k' and the dipole hyperfine structure parameters P and P' for the 3d^7 ion in octahedra should include the contributions from the p orbitals of ligands. They can be written as [11,12]

$$\begin{aligned}
&\zeta = N_\mathrm{t}({\zeta_\mathrm{d}}^0+{\lambda_\mathrm{t}}^2{\zeta_\mathrm{p}}^0/2), \\
&\zeta' = (N_\mathrm{t}N_\mathrm{e})^{1/2}({\zeta_\mathrm{d}}^0-\lambda_\mathrm{t}\lambda_\mathrm{e}{\zeta_\mathrm{p}}^0/2), \\
&k = N_\mathrm{t}(1+{\lambda_\mathrm{t}}^2/2),\ k' = (N_\mathrm{t}N_\mathrm{e})^{1/2}(1-\lambda_\mathrm{t}\lambda_\mathrm{e}/2), \\
&P = N_\mathrm{t}P_0,\ P' = (N_\mathrm{t}N_\mathrm{e})^{1/2}P_0,
\end{aligned} \quad (3)$$

where ${\zeta_\mathrm{d}}^0$ and ${\zeta_\mathrm{p}}^0$ are the spin-orbit coupling coefficients of a free 3d^7 ion and a free ligand ion, respectively. P_0 is the dipolar hyperfine structure parameter of the free 3d^7 ion. N_γ and λ_γ are, respectively, the normalization factors and the orbital mixing coefficients. They can be determined by the semiempirical LCAO method with the normalization condition [11,12]

$$N_\gamma(1-2\lambda_\gamma S_\mathrm{dp}(\gamma)+\lambda_\gamma^2)=1, \quad (4)$$

and the approximate relation [11,12]

$$f_\gamma = {N_\gamma}^2[1+{\lambda_\gamma}^2{S_\mathrm{dp}}^2(\gamma)-2\lambda_\gamma S_\mathrm{dp}(\gamma)], \quad (5)$$

where $S_\mathrm{dp}(\gamma)$ is the group overlap integral. f_γ [$\approx (B/B_0+C/C_0)/2$] is the ratio of the Racah parameter for the 3d^7 ion in a crystal to that in free state.

For the Mg^{2+} site in magnesium acetate, the Mg distance (R_1) along the two-fold (z or C_2) axis is about 2.13 Å, the other Mg-OH$_2$ distances (R_{21} and R_{22}) in the nearly perpendicular direction of C_2 axis are 2.08 and 2.09 Å, respectively [9,10]. The bonding angles θ between R_{21} (or R_{22}) and the C_2 axis are about 88°, and the rhombic distortion angle ϕ in the plane perpendicular to the C_2 axis is 85° [9,10]. According to the superposition model [13] and the geometrical relation of the studied Co^{2+} center, the rhombic field parameters can be expressed as follows:

$$\begin{aligned}
D_\mathrm{s} &= (-2/7)\bar{A}_2(R_0)\{(1-3\cos^2\theta) \\
&\quad \cdot [(R_0/R_{21})^{t_2}+(R_0/R_{22})^{t_2}]/2-(R_0/R_1)^{t_2}\}, \\
D_\xi &= (-2/7)\bar{A}_2(R_0)\sin^2\theta\cos\phi \\
&\quad \cdot [(R_0/R_{21})^{t_2}+(R_0/R_{22})^{t_2}],
\end{aligned}$$

$$
\begin{aligned}
D_t &= (4/21)(R_0)\{(7\sin^4\theta\cos\phi + 35\cos^4\theta \\
&\quad - 30\cos^2\theta + 3)[(R_0/R_{21})^{t_4} + (R_0/R_{22})^{t_4}]/2 \\
&\quad + 4(R_0/R_1)^{t_4}\} \\
D_\eta &= (-2/21)(R_0)\sin^2\theta(1-7\cos^2\theta) \\
&\quad \cdot \cos\phi[(R_0/R_{21})^{t_4} + (R_0/R_{22})^{t_4}]. \qquad (6)
\end{aligned}
$$

Here t_2 and t_4 are the power-law exponents, and $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are the intrinsic parameters, with the reference distance (or impurity-ligand distance R_0) [13, 14]. For 3d^n ions in octahedral clusters, $\bar{A}_4(R_0) \approx (3/4)Dq$, and the ratio $\bar{A}_2(R_0)/\bar{A}_4(R_0) \approx 9 \sim 12$ is valid for many systems [13–15]. Thus, we take $\bar{A}_2(R_0) \approx 11\bar{A}_4(R_0)$ here. The power-law exponents are adopted as $t_2 \approx 3$ and $t_4 \approx 5$ due to the ionic nature of the bonds [13, 14]. Since the ionic radius r_i (≈ 0.72 Å [16]) of the impurity Co^{2+} differs from the radius r_h (≈ 0.66 Å [16]) of the host Mg^{2+}, one can approximately estimate the impurity-ligand distances R'_j (j = 1, 21 and 22) from the distances R_j in the host and the empirical formula [17, 18]

$$
R'_j \approx R_j + (r_i - r_\mathrm{h})/2. \qquad (7)
$$

Thus, the average impurity-ligand distance $\bar{R}$ (≈ 2.13 Å) is taken as the reference distance. From the Slater-type SCF functions [19, 20] and $\bar{R}$, the integrals $S_\mathrm{dp}(\mathrm{t_{2g}}) \approx 0.0091$ and $S_\mathrm{dp}(\mathrm{e_g}) \approx 0.0312$ are calculated.

The spectral parameters Dq, B and C of the studied system can be obtained from those of a similar octahedral Co^{2+} cluster in MgO [21], i. e.,

$$
Dq \approx -950\ \mathrm{cm^{-1}}, B \approx 810\ \mathrm{cm^{-1}}, C \approx 4150\ \mathrm{cm^{-1}}. \qquad (8)
$$

The values $B_0 \approx 1115$ cm^{-1} and $C_0 \approx 4366$ cm^{-1} for the free Co^{2+} ion [22] yield $f_\gamma \approx 0.838$, and then $N_\mathrm{t} \approx 0.918$, $N_\mathrm{e} \approx 0.925$, $\lambda_\mathrm{t} \approx 0.308$ and $\lambda_\mathrm{e} \approx 0.318$ from (4) and (5). Substituting the free ion parameters $\zeta_\mathrm{d}{}^0 \approx 533$ cm^{-1} [22], $P_0 \approx 254 \times 10^{-4}$ cm^{-1} [23] for Co^{2+} and $\zeta_\mathrm{p}{}^0 \approx 151$ cm^{-1} for O^{2-} (or that in H$_2$O) [24] into (3), we have

$$
\begin{aligned}
&\zeta \approx 496\ \mathrm{cm^{-1}},\ \zeta' \approx 484\ \mathrm{cm^{-1}}, \\
&k \approx 0.962,\ k' \approx 0.876, \qquad (9) \\
&P \approx 233 \times 10^{-4}\ \mathrm{cm^{-1}},\ P' \approx 234 \times 10^{-4}\ \mathrm{cm^{-1}}.
\end{aligned}
$$

For Co^{2+} in tutton salts, the core polarization constant $\kappa \approx 0.325$ [25] is obtained and also adopted here. Substituting the above parameters into (1) and (2), the g and A factors are calculated and shown in Table 1.

Table 1. The g factors g_i, hyperfine structure constants A_i and the nuclear quadrupole interaction constant Q (in units of 10^{-4} cm^{-1}) for the rhombic Co^{2+} center in magnesium acetate.

	g_x	g_y	g_z	A_x	A_y	A_z	Q^a
Calc.	2.604	3.942	6.033	30	98	199	−0.5
Expt. [8]	2.518(8)	4.046(12)	6.018(18)	31(3)	92(5)	192(4)	
[9]	2.532(5)	3.895(5)	6.030(3)	28(4)	88(6)	190(2)	−1.0(5)

[a] The negative sign of Q is determined from the calculations of Q and the positive signs of the A factors in this work.

The formula of the nuclear quadrupole interaction constant Q can be similarly derived from the perturbation method in [25]. Thus, we have

$$
\begin{aligned}
Q \approx 9eq\langle r^{-3}\rangle\{&[3/x^2 + 4/(x+2)^2](W_x + W_y)/2 \\
&+ (\alpha^2/\alpha'\alpha'')W_z\}/[4I(2I-1)]. \qquad (10)
\end{aligned}
$$

Here I (= 7/2) is the nuclear spin, and q (≈ 0.40 b) the nuclear quadrupole moment for ^{59}Co [26]. $\langle r^{-3}\rangle$ (≈ 6.035 a.u. [26]) is the expectation value of the inverse cube of the 3d radial wavefunction. The other parameters have the same meanings as those in (1) and (2). Substituting these parameters in (10), the nuclear quadrupole interaction constant is calculated and also collected in Table 1.

3. Discussion

From Table 1 one can find that the calculated g factors, hyperfine structure constants and the nuclear quadrupole interaction constant Q are in reasonable agreement with the experimental data. Therefore the theoretical formulas and the related parameters (e.g., superposition model parameters) can be regarded as suitable. Thus, the EPR results [8, 9] are quantitatively interpreted in this work.

The large anisotropies $\Delta g[= g_z - (g_x + g_y)/2]$ and $\Delta A[= A_z - (A_x + A_y)/2]$ of the g and A factors may be attributed to the axial (z-direction) distortion, characterized by the difference between R_1 and R_{21} (or R_{22}) and the discrepancy of the angle θ related to the ideal value 90°. On the other hand, the relatively smaller anisotropies δg $(= g_x - g_y)$ and δA $(= A_x - A_y)$ originate mainly from the perpendicular (x-direction) distortion, characterized by the difference between R_{21} and R_{22} and the deviation of the angle ϕ from that (= 90°) in regular octahedra. Considering the small difference in the experimental EPR parameters [8, 9], the theoretical results in the present work can be regarded as reasonable.

The sign of the nuclear quadrupole interaction constant Q was not determined by the EPR experiments. It was assumed to be opposite to the sign of the A factors [9]. According to the calculations in this work, we suggest that Q is negative. On the other hand, the theoretical studies show that the A factors are actually positive (see Table 1). Thus, the negative sign of Q can be verified here. Obviously, the theoretical formulas in the present work can also be applied to analyses of EPR experiments for Co^{2+} impurity (or other $3d^7$ ions, e. g., Fe^+, Ni^{3+}) in rhombic environments.

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