A Study of Spin-Hamiltonian Parameters and Defect Structure for Co^{2+} Ion in the Tetragonal Zn^{2+} Site of Ba_2ZnF_6 Crystal

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The spin-Hamiltonian (SH) parameters (g factors $g_\parallel$, $g_\perp$ and hyperfine structure constants $A_\parallel$, $A_\perp$) for the Co^{2+} ion in the tetragonal Zn^{2+} site of a Ba_2ZnF_6 crystal are calculated from the second-order perturbation formulas based on the cluster approach for the SH parameters of $3d^7$ ions in tetragonal symmetry with the effective spin $S = 1/2$. In the calculations, a reduction factor due to the dynamical Jahn-Teller effect is used. The calculated results are in reasonable agreement with the experimental values, suggesting that the dynamical Jahn-Teller effect should be considered here. The defect structure of the Co^{2+} center in Ba_2ZnF_6:Co^{2+} is also obtained from the calculations. The results are discussed.

Key words: Electron Paramagnetic Resonance (EPR); Crystal- and Ligand-Field Theory; Defect Structure; Co^{2+}; Ba_2ZnF_6.

1. Introduction

Fluoride Ba_2ZnF_6 has a tetragonal layered structure derived from the perovskites type. There are two cationic sites, the 12-fold coordinated tetrakaidecahedral Ba^{2+} site and 6-fold coordinated octahedral Zn^{2+} site, in a Ba_2ZnF_6 crystal [1]. This crystal is used as host for the studies of interaction between $3d^n$ impurity and host lattice. For example, Ba_2ZnF_6 is one of the few host crystals in which Cu^{2+} can be stabilized – by substitution of Zn^{2+} – with a d_z^2 ground state [2]. So, various spectroscopic studies were made for Ba_2ZnF_6 doped with $3d^n$ ions [2 – 6]. The electron paramagnetic resonance (EPR) experiment of Co^{2+} in Ba_2ZnF_6 suggested that Co^{2+} occupies the tetragonally-distorted octahedral Zn^{2+} site with the effective spin $S = 1/2$ and its spin-Hamiltonian (SH) parameters (g factors $g_\parallel$, $g_\perp$ and hyperfine structure constants $A_\parallel$, $A_\perp$) were measured [6]. No theoretical calculations for these SH parameters have been carried out. In addition, since the SH parameters of a paramagnetic ion in crystals are sensitive to its immediate environment, it can be expected that the defect structure (characterized by the tetragonal distortion $R_\parallel - R_\perp$, where $R_\parallel$ and $R_\perp$ denote the metal-ligand distances parallel with and perpendicular to the tetragonal axis, respectively) of the tetragonal Co^{2+} center in a Ba_2ZnF_6 crystal can be obtained from the calculations of SH parameters. However, such studies were not made. Motivated by these, in this paper, we calculate the SH parameters and study the defect structure for Co^{2+} in the Ba_2ZnF_6 crystal from the second-order perturbation formulas of the SH parameters based on the cluster approach for $3d^7$ ions in tetragonal octahedra. Considering that the crystal-field theory [7 – 9] and lots of experimental results [10 – 13] show that for Co^{2+} ions in the octahedral sites of many crystals with the effective spin $S = 1/2$ the average g value is close to 4.3 and that the average g value $\bar{g}$ $[= (g_\parallel + 2g_\perp)/3]$ for Ba_2ZnF_6:Co^{2+} is about 3.7. The reduction (or partial quenching) in the spin-orbit parameters and orbital reduction factors due to the dynamical Jahn-Teller effect [14 – 18] is considered in the calculations. The results (including the calculated SH parameters and defect structure) are discussed.

2. Calculation

For a $3d^7$ ion in the tetragonal octahedral sites of crystals, the figure showing the splitting of the ground

term ^{4}F by the cubic field, the tetragonal field, and the spin-orbit coupling is given in [19–21]. By using the effective spin $S = 1/2$ [19–21], the second-order perturbation formulas of SH parameters based on the cluster approach are written as [22]

$$
\begin{aligned}
g_{\parallel} &= 2+\frac{4(k\alpha+2)\left[\frac{3}{x^2}-\frac{4}{(x+2)^2}\right]+2\left[\frac{9}{x^2}-\frac{4}{(x+2)^2}\right]v_1-2\left(\frac{\alpha}{\alpha'}\right)\left[\frac{3}{x}-\frac{4}{(x+2)}\right]v_3}{\left[\left(\frac{\alpha}{\alpha'}\right)^2+\frac{6}{x^2}+\frac{8}{(x+2)^2}\right]},\\
g_{\perp} &= \frac{4\left[\left(\frac{\alpha}{\alpha'}\right)^2+\frac{2k\alpha}{x+2}+\frac{12}{x(x+2)}\right]+\left(\frac{\alpha}{\alpha'}\right)^2 v_4+\frac{8}{(x+2)^2}v_5+\frac{12}{x(x+2)}v_6-\left(\frac{\alpha}{\alpha'}\right)\frac{4}{(x+2)}v_7}{\left[\left(\frac{\alpha}{\alpha'}\right)^2+\frac{6}{x^2}+\frac{8}{(x+2)^2}\right]},\\
A_{\parallel} &= P\left\{(-\kappa/2)\left[2+\frac{8\left[\frac{3}{x^2}-\frac{4}{(x+2)^2}\right]}{\left[\left(\frac{\alpha}{\alpha'}\right)^2+\frac{6}{x^2}+\frac{8}{(x+2)^2}\right]}\right]+\frac{4k\alpha\left[\frac{3}{x^2}-\frac{4}{(x+2)^2}\right]}{\left[\left(\frac{\alpha}{\alpha'}\right)^2+\frac{6}{x^2}+\frac{8}{(x+2)^2}\right]}\right\}\\
&\quad +P'\left\{\frac{2\left[\frac{9}{x^2}-\frac{4}{(x+2)^2}\right]W_X+\left(\frac{\alpha}{\alpha'}\right)^2 W_Z-4\left(\frac{\alpha}{\alpha'}\right)\left[\frac{3}{x^2}-\frac{4}{(x+2)^2}\right]W_{XZ}}{\left[\left(\frac{\alpha}{\alpha'}\right)^2+\frac{6}{x^2}+\frac{8}{(x+2)^2}\right]}\right\},\\
A_{\perp} &= P\left\{\frac{(-2\kappa)\left[\left(\frac{\alpha}{\alpha'}\right)^2+\frac{12}{x(x+2)}\right]+\frac{8k\alpha}{x+2}}{\left[\left(\frac{\alpha}{\alpha'}\right)^2+\frac{6}{x^2}+\frac{8}{(x+2)^2}\right]}\right\}+P'\left\{\frac{\left[-\frac{12}{x(x+2)}\right]W_X-\left(\frac{\alpha}{\alpha'}\right)^2 W_Z-\frac{32}{(x+2)^2}W_{XY}+\left(\frac{\alpha}{\alpha'}\right)\frac{4}{(x+2)}W_{XZ}}{\left[\left(\frac{\alpha}{\alpha'}\right)^2+\frac{6}{x^2}+\frac{8}{(x+2)^2}\right]}\right\},
\end{aligned}
\tag{1}
$$

with

$$
\begin{aligned}
v_1 &= \frac{k'\zeta'}{3}\left[\frac{15f_1^2}{2E_{1x}}+\frac{2q_1^2}{E_{2x}}\right],\\
v_3 &= \frac{k'\zeta'}{3}\left[\frac{15f_1f_2}{2E_{1x}}-\frac{2q_1q_2}{E_{2x}}\right],\\
v_4 &= \frac{k'\zeta'}{3}\left[\frac{15f_2^2}{E_{1x}}+\frac{4q_2^2}{E_{2x}}\right],\quad v_5=\frac{4k'\zeta'q_3^2}{3E_{2z}},\\
v_6 &= \frac{k'\zeta'}{3}\left[\frac{15f_3^2}{2E_{1z}}+\frac{2q_3^2}{E_{2z}}+\frac{8\rho^2}{E_3}\right],\quad v_7=\frac{v_3}{2},
\end{aligned}
\tag{2}
$$

in which k and k' are the orbital reduction factors. ζ and ζ' are the spin-orbit parameters. P and P' represent the dipolar hyperfine parameters, and κ denote the core polarization constant. E_{1x}, E_{1z}, E_{2x}, E_{2z}, and E_3 denote the energy differences between the ground state ^{4}E[^{4}T$_1$(F)] and the excited states ^{4}E[^{4}T$_1$(P)], ^{4}A$_2$[^{4}T$_1$(P)], ^{4}E[^{4}T$_2$(F)], ^{4}B$_2$[^{4}T$_2$(F)], and ^{4}B$_1$[^{4}A$_2$(F)], respectively. x can be calculated from the energy splitting Δ[= E(^{4}A$_2$) − E(^{4}E)] of the ground state ^{4}T$_1$ by the tetragonal crystal field, i. e.,

$$
\Delta = \frac{\zeta\alpha'^2}{3\alpha}\left[\frac{3}{x}+\frac{4}{x+2}\right]+\frac{\zeta\alpha}{6}(x+3). \tag{3}
$$

The splitting Δ and the energy differences E_{1x}, E_{1z}, E_{2x}, E_{2z}, and E_3 can be calculated from the d-d transition matrices of 3d^7 ions in tetragonal symmetry. The expressions and calculated methods of parameters α, α', f_i, q_i, and w_{ij} in the above formulas are given in [22]. The tetragonal field parameters D_s and D_t are included in these expressions and d-d transition energy matrices.

The parameters ζ, ζ', k, k', P, and P' in the cluster approach are written as [22, 23]

$$
\begin{aligned}
\zeta &= N_t\left(\zeta_d^0+\lambda_t^2\zeta_p^0/2\right),\\
\zeta' &= (N_tN_e)^{1/2}\left(\zeta_d^0-\lambda_t\lambda_e\zeta_p^0/2\right),\\
k &= N_t\left[1-2\lambda_tS_{dp}\left(t_{2g}\right)+\lambda_t^2/2\right],\\
k' &= (N_tN_e)^{1/2}\left[1-\lambda_tS_{dp}\left(t_{2g}\right)-\lambda_eS_{dp}\left(e_g\right)-\lambda_t\lambda_e/2\right],\\
P &= N_tP_0,\quad P'=(N_tN_e)^{1/2}P_0,
\end{aligned}
\tag{4}
$$

where ζ_d^0, ζ_p^0 are the spin-orbit parameters of free 3d^n ion and free ligand ion, respectively. P_0 is the dipolar hyperfine structure constant of free 3d^n ion. In the studied Ba_2ZnF_6:Co^{2+}, we have $\zeta_d^0 \approx 533$ cm^{-1} [24], $\zeta_p^0 \approx 220$ cm^{-1} [25], and $P_0 \approx 254\times10^{-4}$ cm^{-1} [26]. N_γ and λ_γ (where γ = t or e, the irreducible representation of O$_h$ group) are the normalization factor

and the orbital mixing coefficient in the one-electron basis functions based on the cluster approach. From the basis functions, we have the normalization correlation [22]

$$N_\gamma(1-2\lambda_\gamma S_{\rm dp}(\gamma)+\lambda_\gamma^2)=1 \tag{5}$$

and the approximate relation (obtained from a semi-empirical molecular orbital method) [22]

$$f_\gamma = N_\gamma^2\left[1+\lambda_\gamma^2 S_{\rm dp}^2(\gamma)-2\lambda_\gamma S_{\rm dp}(\gamma)\right], \tag{6}$$

in which $S_{\rm dp}(\gamma)$ is the group overlap integral which can be calculated from the Slater-type self-consistent field (SCF) functions [27, 28] and the average metal-ligand distance $\bar{R}$. For Ba_2ZnF_6, $\bar{R}\approx 2.02$ Å [1] and we have $S_{\rm dp}(t)\approx 0.00835$ and $S_{\rm dp}(e)\approx 0.03057$. f_γ $[=(B/B_0+C/C_0)/2]$ is the ratio of the Racah parameters for a $3d^n$ ion in a crystal to those of a free ion. For free Co^{2+} ion, we have $B_0\approx 1115\ {\rm cm}^{-1}$ and $C_0\approx 4366\ {\rm cm}^{-1}$ [24]. The parameters B and C can be determined from the optical spectra of the system under study. No optical spectral data of the Ba_2ZnF_6:Co^{2+} crystal were reported, we therefore estimate the values of B and C form the optical spectra of CoF_6^{4-} clusters in similar crystals. From the optical spectra of Rb_2MgF_4:Co^{2+} [29], we estimate for Ba_2ZnF_6:Co^{2+}

$$B\approx 990\,{\rm cm}^{-1},\ C\approx 3980\,{\rm cm}^{-1},\ Dq\approx -780\,{\rm cm}^{-1}. \tag{7}$$

Thus, the parameters N_γ and λ_γ can be calculated from (5)–(6) and then from (4), $\zeta\approx p\times 512.4\ {\rm cm}^{-1}$, $\zeta\approx p\times 501.8\ {\rm cm}^{-1}$, $k\approx p\times 0.973$, $k'\approx p\times 0.916$, $P\approx 241.4\times 10^{-4}\ {\rm cm}^{-1}$, and $P\approx 242.1\times 10^{-4}\ {\rm cm}^{-1}$, where the factor p represents, as mentioned in the introduction, the reduction due to the dynamical Jahn-Teller effect (so, $p\le 1$) and is taken as an adjustable parameter. It should be pointed out that the reduction factors in the spin-orbit parameter and in the orbital reduction factor may be different [15]. In order to decrease the number of adjustable parameters, we assume both the spin-orbit parameters and the orbital reduction factor having the same reduction factor p. This point is in accordance with the first-order perturbation treatment of Ham [16].

Since the point-charge model with the expectation values $\langle r^n\rangle$ of free d^n ions can not reproduce the experimental crystal-field parameters, e. g., the cubic field parameter Dq [30, 31], we calculate the tetragonal field parameters $D_{\rm s}$ and $D_{\rm t}$ from the empirical superposition model [32]. According to the model, we have

$$\begin{aligned} D_{\rm s} &= \frac{4}{7}\bar{A}_2(R_0)\left[\left(\frac{R_0}{R_\perp}\right)^{t_2}-\left(\frac{R_0}{R_\parallel}\right)^{t_2}\right],\\ D_{\rm t} &= \frac{16}{21}\bar{A}_4(R_0)\left[\left(\frac{R_0}{R_\perp}\right)^{t_4}-\left(\frac{R_0}{R_\parallel}\right)^{t_4}\right], \end{aligned} \tag{8}$$

in which the power-law exponents $t_2\approx 3$ and $t_4\approx 5$ [22, 23, 32, 33]. $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are the intrinsic parameters with the reference distance R_0 (here we take $R_0\approx\bar{R}\approx 2.02$ Å, the average metal-ligand distance in the host crystal). For $3d^n$ ions in octahedra, we have $\bar{A}_4(R_0)\approx(3/4)Dq$ [32–34], and many studies have suggested that the ratio $\bar{A}_2(R_0)/\bar{A}_4(R_0)$ is in the range of $8\sim 12$ [33–37]. We take $\bar{A}_2(R_0)\approx 11\bar{A}_4(R_0)$ here. In the CoF_6^{4-} octahedron of Ba_2ZnF_6:Co^{2+}, for simplicity, we assume $R_\perp\approx 2.05$ Å [1], the value in the host crystal. The assumption can be regarded as reasonable because in the isomorphous pure crystal Ba_2CoF_6, $R_\perp$ is equal to 2.05 Å [1]. $R_\parallel$ is taken as an adjustable parameter here. Thus, there are three unknown parameters p, $R_\parallel$, κ in the above formulas. By matching the calculated SH parameters $g_\parallel$, $g_\perp$, $A_\parallel$, and $A_\perp$ to the experimental values, we obtain

$$p\approx 0.73,\quad R_\parallel\approx 1.966\ {\rm Å},\quad \kappa\approx 0.263. \tag{9}$$

The calculated SH parameters are compared with the experimental values in Table 1. For comparison, the SH parameters are calculated without considering the reduction due to the dynamical Jahn-Teller effect (i. e., $p=1$). The results are also collected in Table 1.

Table 1. Spin-Hamiltonian parameters $g_\parallel$, $g_\perp$, $A_\parallel$, and $A_\perp$ for Co^{2+} ions in the Ba_2ZnF_6 crystal.

	$g_\parallel$	$g_\perp$	$A_\parallel$ (10^{-4} cm^{-1})	$A_\perp$ (10^{-4} cm^{-1})
Calculation[a]	8.17	2.24	593	14
Calculation[b]	7.66	1.81	415	−17
Experiment [6]	7.6	1.76	420[c]	20[c]

[a] Calculated without considering the reduction due to the dynamical Jahn-Teller effect. [b] Calculated by considering the reduction due to the dynamical Jahn-Teller effect. [c] The values are actually the absolute values.

3. Discussion

Many studies show that for Co^{2+} in octahedral clusters in crystals, the core depolarization constant $\kappa\approx 0.3\pm 0.1$ [22, 38, 39]. The above value of κ in Ba_2ZnF_6:Co^{2+} is within the range and can be regarded as suitable.

The EPR experiments of d^n and f^n ions in crystals can not resolve solely the signs of hyperfine structure constants [8, 26, 40]. So the values of A_i obtained by EPR experiments are actually the absolute values. The above calculations suggest that $A_\parallel$ is positive and $A_\perp$ is negative for the Ba_2ZnF_6:Co^{2+} crystal (see Table 1).

From Table 1, one can find that if the reduction due to the dynamical Jahn-Teller effect is not considered, the calculated SH parameters are in disagreement with the observed values even though the calculated $\bar{g}(\approx 4.21)$ is close to 4.3 obtained from the conventional crystal-field theory and the experimental values in many other crystals [7 – 13]. However, if the above reduction is considered, the calculated SH parameters are consistent with the observed values. So, when the observed $\bar{g}$ is much smaller than 4.3, the reduction due to the dynamical Jahn-Teller effect should be taken into account in the calculations of SH parameters.

The calculated tetragonal distortion $R_\perp - R_\parallel \approx 0.084$ Å for CoF_6^{4-} octahedron in Ba_2ZnF_6:Co^{2+} suggest that this octahedron is tetragonally-compressed. Tetragonal distortion (compression or elongation) is characterized by the sign $\alpha - \alpha_0$ or $R_\perp - R_\parallel$, where α is the angle defined as $\tan\alpha = R_\perp/R_\parallel$ and $\alpha_0 = \pi/4$, the angle in cubic symmetry. When $\alpha - \alpha_0 > 0$ and then $R_\perp - R_\parallel > 0$, the ligand octahedron is compressed, whereas if $\alpha - \alpha_0 < 0$ and then $R_\perp - R_\parallel < 0$, the octahedron is elongated. In fact, as pointed out in [41, 42], the sign of tetragonal distortion for a d^n MX_6 octahedron can be determined by analyzing the sign of the SH parameters Δg $(= g_\perp - g_\parallel)$ or D (zero-field splitting) from the formulas [41, 42]

$$\begin{aligned} \Delta g &\approx 2(\alpha - \alpha_0)(F_{11} - F_{12}), \\ D &\approx -3(\alpha - \alpha_0) G_{11}, \end{aligned} \tag{10}$$

where F_{11}, F_{12}, and G_{11} are the spin-lattice coupling coefficients. For $3d^7$ ions in octahedral clusters, we have $F_{11} - F_{12} < 0$ (e. g., for Fe^+ and Co^{2+} in MgO, $F_{11} - F_{12} \approx -56$ and -101, respectively [7, 43]). Thus, when $\Delta g > 0$, $\alpha - \alpha_0 < 0$ the $3d^7$ octahedron is tetragonally-elongated, whereas if $\Delta g < 0$, $\alpha - \alpha_0 > 0$ the $3d^7$ octahedron becomes tetragonally-compressed. For Ba_2ZnF_6:Co^{2+} under study, from the observed $\Delta g < 0$, one can conclude that the CoF_6^{4-} octahedron is, as calculated above, tetragonally-compressed. This point is consistent with that (≈ 0.09 Å [1]) in the corresponding octahedron of the host crystal Ba_2ZnF_6, but it is opposite to that (≈ -0.08 Å [1], where the CoF_6^{4-} octahedron is tetragonally-elongated) in the isomorphous pure crystal Ba_2CoF_6, where the Co^{2+} ion is the host ion rather than the impurity. The sign of tetragonal distortion of octahedral environment of the paramagnetic impurities Ni^{2+} and Mn^{2+} in K_2MgF_4 and K_2ZnF_4 crystals were studied by analyzing their zero-field splitting [42]. It is found that for Ni^{2+} in K_2MgF_4 or Mn^{2+} in K_2ZnF_4, the sign of octahedral environment of paramagnetic impurity is different from that of the host ion it replaces, but in agreement with the one in the isomorphous pure crystal K_2NiF_4 or K_2MnF_4 (note: for K_2ZnF_4: Ni^{2+} and K_2MgF_4: Mn^{2+}, the signs of octahedra in impurity cluster and in pure crystal are the same [42]). A similar case can also be found for Cu^{2+} in K_2MgF_4 crystal. The density functional theory (DFT) calculations [30, 44] reveal that the octahedral environment of Cu^{2+} in K_2MgF_4 is tetragonally-compressed. This point is also unlike the corresponding octahedron in the host crystal K_2MgF_4, but in agreement with that in the isomorphous pure crystal K_2CuF_4 [45]. These results are different from that in Ba_2ZnF_6:Co^{2+} obtained in this paper. One of the causes may be, in our opinion, due to the fact that the tetragonal distortion $|R_\perp - R_\parallel|$ (≈ 0.014 Å [45] or 0.0198 Å [46]) of K_2MgF_4 and that (≈ 0.003 Å [45] or 0.013Å [46]) of K_2ZnF_4 is small, it is easy to change the sign of tetragonal distortion of octahedron due to the introduction of an impurity. However, for Ba_2ZnF_6, the tetragonal distortion $|R_\perp - R_\parallel|$ (≈ 0.09 Å [1]) is greater and so the change of sign of tetragonal distortion caused by impurity is difficult. This point remains to be further studied.

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