Explanation of the g-factors and Hyperfine Structure Constants of Co^{2+} in Tetragonal K_2ZnF_4

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The formulas of the g-factors $g_\parallel$, $g_\perp$ and the hyperfine structure constants $A_\parallel$, $A_\perp$ for $3d^7$ ions in tetragonal octahedral crystals are established from a cluster approach. Differing from previous formulas, in these formulas the role of configuration interaction (CI)- and covalency (CO)-effects is considered, and the parameters related to both effects are obtained from the optical spectra and the structural parameters of the studied crystal. From these formulas, the EPR parameters g_i and A_i for K_2ZnF_4:Co^{2+} are calculated. The results show good agreement with the observed values. The contributions to the EPR parameters g_i and A_i from the CI and CO effects, and the relationship between the sign of Δg ($=g_\perp - g_\parallel$) and the tetragonal distortion (elongated or compressed) of the ligand octahedron are discussed.

1. Introduction

The crystal structure of K_2ZnF_4 is isomorphous with that of K_2NiF_4 (space group D_{4h}^{17}). This structure is of considerable current interest because it is believed to be the relevant structure for the presently most frequently studied superconducting phase in high T_c oxide superconductors. Many studies for the optical and paramagnetic properties of $3d^n$ ion in K_2ZnF_4 crystal were made [1–3]. Among them, the g factors $g_\parallel$ $g_\perp$ and the hyperfine structure constants $A_\parallel$ $A_\perp$ for Co^{2+} in K_2ZnF_4 were measured from EPR experiments decades ago [3], but until now no theoretical explanations have been made for them. The reason may be the lack of an effective calculation method for the EPR parameters of the $3d^7$ ion in tetragonal octahedral crystals. Abragam and Pryce [4] established the second-order perturbation formulas of g_i and A_i for $3d^7$ ions in axial (tetragonal and trigonal) symmetry. Although these formulas are often quoted and applied in many works [5–8], there are three problems in them: (i) The configuration interaction (CI) due to the admixture of ground state with the excited states is considered in these formulas, but the covalency (CO) effect due to the admixture between the d electrons of the central $3d^7$ ion and the p electrons of ligands is neglected. (ii) There are several adjustable parameters. (iii) For Co^{2+} ($3d^7$) in the elongated ligand octahedron the assumption Δg ($=g_\perp - g_\parallel$) <0, is not correct. So, these formulas cannot yield reasonable results of g_i and A_i for $3d^7$ ions in crystals. On the other hand, by considering CO effect, Tinkham [9] established first-order and Robbroeck et al. [10] developed second-order perturbation formulas of g_i and A_i for $3d^7$ ions in rhombic (also including tetragonal) symmetry. However, in these formulas the CI effect is not considered, and the treatment of the contribution of low symmetry field is oversimplified. Even so, there still are four adjustable parameters in these formulas. So, the EPR parameters g_i and A_i for the $3d^7$ ion in tetragonal symmetry cannot be reasonably and quantitatively explained by using these formulas.

In order to overcome the above difficulties, in this paper we present a cluster approach to the calculation formulas of g_i and A_i for $3d^7$ ions in tetragonal octahedral crystals. In these formulas, the role of CI and CO effects is considered (note: because of the large spin-orbit coupling coefficient of the Co^{2+} ion, the role of the Jahn-Teller effect is not important and should be neglected for Co^{2+} in octahedra [11–13], as made in many previous papers [4–10]). The parameters related to both effects can be obtained from the optical spectra and the structural parameters of the studied crystals. From these formulas the EPR parameters $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ for Co^{2+} in tetragonal K_2ZnF_4 crystal are calculated. The results show good agreement with the observed values. The role of CI and CO effects and the relationship between the sign of Δg and the tetragonal distortion (elongated or compressed) of the ligand octahedron are discussed.

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2. Calculation Method

For $3d^7$ (or $3d^{n}$) ions in crystals, considering the mixture of d electrons of the $3d^7$ ion and p electrons of ligands via the CO effect, one should apply a cluster approach and take the LCAO molecular orbital [14, 15],

$$|\gamma\rangle = N_\gamma^{1/2}\,(|d_\gamma\rangle - \lambda_\gamma |p_\gamma\rangle), \tag{1}$$

as one-electron basis function, where $\gamma = t_{2g}$ or e_g denotes the irreducible representation of the O_h group, $|d_\gamma\rangle$ is the d orbital of $3d^7$ ions and $|p_\gamma\rangle$ is the p orbital of ligands. N_γ is the normalization factor and λ_γ is the orbital mixing coefficient. From the one-electron basis function, the spin-orbit coupling operator $H_{SO}\,[= H_{SO}(d) + H_{SO}(p)]$, the orbital momentum L [16] and the hyperfine interaction operator H_{hf} [17], we have the spin-orbit coupling coefficients ζ, ζ', the orbital reduction factors k, k' and the dipolar hyperfine parameters P, P' for $3d^7$ octahedral clusters as follows [14, 15]

$$\begin{aligned}
&\zeta = N_t\,(\zeta_d^0 + \lambda_t^2\,\zeta_p^0/2), && \zeta' = (N_t\,N_e)^{1/2}\,(\zeta_d^0 - \lambda_t\,\lambda_e\,\zeta_p^0/2),\\
&k = N_t\,(1 + \lambda_t^2/2), && k' = (N_t\,N_e)^{1/2}\,(1 - \lambda_t\,\lambda_e/2),\\
&P = N_t\,P_0, && P' = (N_t\,N_e)^{1/2}\,P_0,
\end{aligned} \tag{2}$$

where ζ_d^0 and ζ_p^0 are, respectively, the spin-orbit coupling coefficient of d electrons of the free $3d^7$ ion and that of p electrons of the free ligand ion. $P_0\,[= g_e\,g_N\,\beta_e\,\beta_N\,\langle r^{-3}\rangle]$ is the dipolar hyperfine parameter of the free $3d^7$ ion [17].

The ground state ^4F of the $3d^7$ ion is split by the octahedral field, and an orbital triplet $^4T_1$ lies lowest, which further splits into ^4E and $^4A_2$ states under the effect of tetragonal field. The Hamiltonian for the system can be expressed as

$$\begin{aligned}
H &= H_0 + H',\\
H_0 &= H_{Coul} + V_c^a\,(D_q, D_s, D_t),\\
H' &= H_z\,(k, k', \alpha, \alpha') + H_{SO}\,(\zeta, \zeta')\\
&\quad + V_c^b\,(D_q, D_s, D_t) + H_{hf}\,(P, P'),
\end{aligned} \tag{3}$$

where H_{Coul} is the Coulomb repulsion interaction. $V_c^a\,(D_q, D_s, D_t)$ and $V_c^b\,(D_q, D_s, D_t)$ are, respectively, the diagonal and off-diagonal parts of the crystal-field. D_q is the cubic crystal-field parameter, and D_s and D_t, are the tetragonal ones. H_z is the Zeeman term with the effective Lande factors α and α' in the axial and perpendicular directions. By use of the perturbation method, the second-order perturbation formulas of g_i and A_i of the lowest Kramers doublet ± 1/2 for the $3d^7$ ion in tetragonal symmetry can be expressed as

$$\begin{aligned}
g_\parallel &= 2 + \frac{4\,(k\,\alpha + 2)\left[\dfrac{3}{x^2} - \dfrac{4}{(x+2)^2}\right] + 2\left[\dfrac{9}{x^2} - \dfrac{4}{(x+2)^2}\right]\nu_1 - 2\left(\dfrac{\alpha}{\alpha'}\right)\left[\dfrac{3}{x} - \dfrac{4}{x+2}\right]\nu_3}{\left[\left(\dfrac{\alpha}{\alpha'}\right)^2 + \dfrac{6}{x^2} + \dfrac{8}{(x+2)^2}\right]},\\
g_\perp &= \frac{4\left[\left(\dfrac{\alpha}{\alpha'}\right)^2 + \dfrac{2\,k\,\alpha}{x+2} + \dfrac{12}{x\,(x+2)}\right] + \left(\dfrac{\alpha}{\alpha'}\right)^2 \nu_4 + \dfrac{8}{(x+2)^2}\,\nu_5 + \dfrac{12}{x\,(x+2)}\,\nu_6 - \left(\dfrac{\alpha}{\alpha'}\right)\dfrac{4}{(x+2)}\,\nu_7}{\left[\left(\dfrac{\alpha}{\alpha'}\right)^2 + \dfrac{6}{x^2} + \dfrac{8}{(x+2)^2}\right]},
\end{aligned} \tag{4}$$

$$\begin{aligned}
A_\parallel = P &\left\{(-\kappa/2)\left[2 + \frac{8\left[\dfrac{3}{x^2} - \dfrac{4}{(x+2)^2}\right]}{\left[\left(\dfrac{\alpha}{\alpha'}\right)^2 + \dfrac{6}{x^2} + \dfrac{8}{(x+2)^2}\right]}\right] + \frac{4\,k\,\alpha\left[\dfrac{3}{x^2} - \dfrac{4}{(x+2)^2}\right]}{\left[\left(\dfrac{\alpha}{\alpha'}\right)^2 + \dfrac{6}{x^2} + \dfrac{8}{(x+2)^2}\right]}\right\}\\
&+ P'\left\{\frac{2\left[\dfrac{9}{x^2} - \dfrac{4}{(x+2)^2}\right]W_X + \left(\dfrac{\alpha}{\alpha'}\right)^2 W_Z - 4\left(\dfrac{\alpha}{\alpha'}\right)\left[\dfrac{3}{x} - \dfrac{4}{x+2}\right]W_{XZ}}{\left[\left(\dfrac{\alpha}{\alpha'}\right)^2 + \dfrac{6}{x^2} + \dfrac{8}{(x+2)^2}\right]}\right\},
\end{aligned}$$

$$A_\perp = P\left\{\frac{-2\,\kappa\left[\left(\frac{\alpha}{\alpha'}\right)^2+\frac{12}{x\,(x+2)}\right]+\frac{8\,k\,\alpha}{x+2}}{\left[\left(\frac{\alpha}{\alpha'}\right)^2+\frac{6}{x^2}+\frac{8}{(x+2)^2}\right]}\right\} + P'\left\{\frac{-\frac{12}{x\,(x+2)}\,W_X-\left(\frac{\alpha}{\alpha'}\right)^2 W_Z-\frac{32}{(x+2)^2}\,W_{XY}+\left(\frac{\alpha}{\alpha'}\right)\frac{4}{(x+2)}\,W_{XZ}}{\left[\left(\frac{\alpha}{\alpha'}\right)^2+\frac{6}{x^2}+\frac{8}{(x+2)^2}\right]}\right\}, \tag{5}$$

where κ is the core polarization constant. x is determined from the energy separation $\varDelta\,(=E\{{}^4A_2[{}^4T_1(F)]\}-E\{{}^4E[{}^4T_1(F)]\})$ by using the expression [4]

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

The v_i are defined as

$$\begin{aligned}
v_1&=\frac{k'\zeta'}{3}\left[\frac{15\,f_1^2}{2\,E_{1X}}+\frac{2\,q_1^2}{E_{2X}}\right],\\
v_3&=\frac{k'\zeta'}{3}\left[\frac{15\,f_1\,f_2}{2\,E_{1X}}-\frac{2\,q_1\,q_2}{E_{2X}}\right],\\
v_4&=\frac{k'\zeta'}{3}\left[\frac{15\,f_2^2}{E_{1X}}-\frac{4\,q_2^2}{E_{2X}}\right],\\
v_5&=\frac{4\,k'\,\zeta'\,q_2^2}{3\,E_{ZZ}},\\
v_6&=\frac{k'\zeta'}{3}\left[\frac{15\,f_3^2}{2\,E_{1Z}}+\frac{2\,q_3^2}{E_{2Z}}+\frac{8\,\rho^2}{E_3}\right],\\
v_7&=v_3/2
\end{aligned} \tag{7}$$

where E_{1X}, E_{1Z}, E_{2X}, E_{2Z} and E_3 are, respectively, energy differences between the ground state ${}^4E[{}^4T_1(F)]$ and the excited states ${}^4E[{}^4T_1(P)]$, ${}^4A_2[{}^4T_1(P)]$, ${}^4E[{}^4T_2(F)]$, ${}^4B_2[{}^4T_2(F)]$ and ${}^4B_1[{}^4A_2(F)]$. They, and also the separation $\varDelta$ can be obtained from the d-d transition energy matrices.

Obviously, if the CO effect is ignored, i.e., $\lambda_\gamma=0$ and so $N_\gamma=1$, $k=k'=1$, $\zeta=\zeta'=\zeta_d^0$, (4) and (5) become the formulas in [4].

The parameters f_i, q_i, and W_{ij} in the above formulas are related to the admixture among the ground state ϕ_i and the excited states π_i, ψ_i via the CI effect by means of Coulomb repulsion and crystal field interaction. There are 5 energy levels involved in the CI effect, i.e., ${}^4E[{}^4T_1(F)]$, ${}^4E[{}^4T_1(P)]$, ${}^4A_2[{}^4T_1(P)]$, ${}^4E[{}^4T_2(F)]$, and ${}^4A_2[{}^4T_1(F)]$, belonging to the matrices containing ${}^4E[{}^4T_1(F)]$ or ${}^4A_2[{}^4T_1(F)]$ representation in the energy matrices for the $3d^7$ ion in tetragonal symmetry. So, similar to those in [4], the complete wave functions ϕ_i' of the ground state can be written as

$$\phi_x'=\varepsilon\,\phi_1-\tau\,\pi_1+\rho\,\psi_1\,,\quad \phi_z'=\varepsilon'\,\phi_1-\tau'\,\pi_1 \tag{8}$$

with the normalization relationship

$$\varepsilon^2+\tau^2+\rho^2=1,\quad \varepsilon'^2+\tau'^2=1, \tag{9}$$

Similarly, considering the CI between the excited states and ground states, we can write the wave functions of the excited states as

$$\begin{aligned}
\pi_x'&=\varepsilon''[\pi_1+(\tau/\varepsilon)\,\phi_1+(\tau''/\varepsilon'')\,\psi_1],\\
\psi_x'&=\varepsilon'''[\psi_1-(\rho/\varepsilon)\,\phi_1-(\tau''/\varepsilon'')\,\pi_1]
\end{aligned} \tag{10}$$

with the normalization relationship

$$\begin{aligned}
&\varepsilon''[1+(\tau/\varepsilon)^2+(\tau''/\varepsilon'')^2]^{1/2}=1,\\
&\varepsilon'''[1+(\rho/\varepsilon)^2+(\tau''/\varepsilon'')^2]^{1/2}=1.
\end{aligned} \tag{11}$$

From a modified perturbation procedure and the d-d transition energy matrices of the $3d^7$ ion in tetragonal symmetry, we have

$$\begin{aligned}
\frac{\tau}{\varepsilon}&\approx\frac{-20\,D_q+6\,(D_s-25/12\,D_t)}{-30D_q+75\,B+9\,(D_s-25/12\,D_t)},\\
\frac{\rho}{\varepsilon}&\approx\frac{-2\sqrt{15}\,(D_s+5/4\,D_t)}{-80D_q-75\,D_t+4\,D_s},\\
\frac{\tau'}{\varepsilon'}&\approx\frac{-20\,D_q-12\,D_s}{-30D_q+75\,B-18\,D_s},\\
\frac{\tau''}{\varepsilon''}&\approx\frac{-2\sqrt{15}\,(4\,D_s+5\,D_t)}{-40D_q+300\,B+(75\,D_t+28\,D_s)}.
\end{aligned} \tag{12}$$

So, if the optical spectra parameters B, C, D_q, D_s, D_t are obtained from the optical spectra of the studied crystal (also, the tetragonal field parameters D_s and D_t are often calculated from the structural parameters), the above 8 CI coefficients, i.e., ε, τ, ρ, ε', τ', ε'', τ'', and ε''' can be calculated from the 8 expressions in (9), (11) and (12). Thus, by using the perturbation method, the parameters f_i, q_i, and W_{ij} in the formulas of g_i and A_i can be expressed in terms of these CI coefficients, i.e.,

$$\alpha = \frac{3}{2}\varepsilon^2 - \sqrt{15}\,\varepsilon\rho + \frac{1}{2}\rho^2 - \tau^2,$$

$$\alpha' = \frac{3}{2}\varepsilon\varepsilon' - \frac{\sqrt{15}}{2}\varepsilon'\rho - \tau\tau',$$

$$f_1 = -\varepsilon\varepsilon'''\left[1+\frac{2}{\sqrt{15}}\left(\frac{\rho}{\varepsilon}-\frac{\tau\tau''}{\varepsilon\varepsilon''}\right)-\frac{\rho^2}{\varepsilon^2}\right],$$

$$f_2 = -\varepsilon'\varepsilon'''\left[1-\frac{3}{\sqrt{15}}\frac{\rho}{\varepsilon}+\frac{2}{\sqrt{15}}\frac{\tau'\tau''}{\varepsilon'\varepsilon''}\right],$$

$$f_3 = \varepsilon\left[1+\frac{\rho}{\sqrt{15}\,\varepsilon}\right],$$

$$q_1 = -\varepsilon\varepsilon''\left[\frac{5\tau}{2\varepsilon}+\frac{\sqrt{15}}{2}\left(\frac{\tau''}{\varepsilon''}-\frac{\tau\rho}{\varepsilon^2}\right)-\frac{\rho\tau''}{2\varepsilon\varepsilon''}\right],$$

$$q_2 = -\varepsilon'\varepsilon''\left[\frac{\tau'}{\varepsilon'}+\frac{3\tau}{2\varepsilon}-\frac{\sqrt{15}}{2}\frac{\tau''}{\varepsilon''}\right],$$

$$q_3 = \varepsilon\varepsilon'\left[\frac{\tau}{\varepsilon}+\frac{3\tau'}{2\varepsilon'}+\frac{\sqrt{15}}{2}\frac{\tau'\rho}{\varepsilon'\varepsilon}\right],$$

$$W_X = \frac{2}{105}\left[2\varepsilon^2+12\varepsilon\tau-7\tau^2-2\sqrt{15}\,\rho(\varepsilon-2\tau)\right],$$

$$W_Z = -\frac{4}{105}\left[2\varepsilon'^2+12\varepsilon'\tau'-7\tau'^2\right].$$

$$W_{XZ} = \frac{1}{70}\left[\varepsilon\varepsilon'+8\varepsilon\tau'+8\varepsilon'\tau+\sqrt{5/3}\,\rho(\varepsilon'+8\tau')\right],$$

$$W_{XY} = \frac{1}{70}\left[\varepsilon^2+16\varepsilon\tau+14\tau^2 -2\sqrt{5/3}\,\rho(\varepsilon+8\tau)-5\rho^2\right]. \qquad (13)$$

3. Calculations on K_2ZnF_4: Co^{2+}

Now we apply the above formulas to the calculations of the EPR parameters g_i and A_i for Co^{2+} in tetragonal K_2ZnF_4 crystal. From the superposition model [18], the tetragonal field parameters can be written as

$$D_s = (4/7)\,\bar{A}_2(R_0)\,[(R_0/R_\perp)^{t_2}-(R_0/R_\parallel)^{t_2}],$$

$$D_t = (16/21)\,\bar{A}_4(R_0)\,[(R_0/R_\perp)^{t_4}-(R_0/R_\parallel)^{t_4}], \qquad (14)$$

where t_2 and t_4 are the power-law exponents. We take $t_2 \approx 3$ and $t_4 \approx 5$ because to the ionic nature of the bonds [18, 19]. $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are the intrinsic parameters with the reference distance R_0 [$\approx \bar{R} = (2R_\perp + R_\parallel)/3$]. $R_\perp$ and $R_\parallel$ are the bond lengths perpendicular to and parallel with the tetragonal axis. For K_2ZnF_4, X-ray studies [20, 21] show that $R_\parallel^h \approx 1.994$ Å and $R_\perp^h \approx 2.03$ Å. In general, the bond length R for an impurity-ligand pair is different from the corresponding bond length R^h in the host crystal because the ionic radius r_i of impurity is unlike the radius r_h of the replaced host ion. We can estimate reasonably the impurity-ligand distance R from the empirical formula [22, 23]

$$R \approx R^h + (r_i - r_h)/2. \qquad (15)$$

For K_2ZnF_4:Co^{2+}, $r_i \approx 0.72$ Å, $r_h \approx 0.74$ Å [24], so, we obtain $R_\parallel \approx 1.984$ Å and $R_\perp \approx 2.02$ Å (so, the ligand octahedron is compressed as that in pure K_2ZnF_4).

For a $3d^n$ ion in octahedra, we have $\bar{A}_4(R_0) \approx (3/4)\,D_q$ [18, 19]. For K_2ZnF_4:Co^{2+}, no optical spectrum data are reported. We can estimate them reasonably from the optical spectra of a similar crystal. From the optical spectra of K_2CoF_4 [25], and in consideration of the average Co^{2+}-F^- distance (≈ 2.008 Å) in K_2ZnF_4:Co^{2+} being slightly smaller than that (≈ 2.033 Å [26]) of K_2CoF_4, we estimate for K_2ZnF_4:Co^{2+}

$$D_q \approx -880\ \text{cm}^{-1},\quad B \approx 810\ \text{cm}^{-1},\quad C \approx 3270\ \text{cm}^{-1}. \qquad (16)$$

The ratio $\bar{A}_2(R_0)/\bar{A}_4(R_0)$ is in the range of 9 ~ 12 for $3d^n$ ions in many crystals [19, 27, 28], we take $\bar{A}_2(R_0) \approx 11\,\bar{A}_4(R_0)$ here. Thus, from (14) we obtain

$$D_s \approx 226\ \text{cm}^{-1},\quad D_t \approx 46\ \text{cm}^{-1}. \qquad (17)$$

The results are close to those obtained for the similar K_2CoF_4 crystal [25]. By using the optical spectrum parameters B, C, D_q, D_s, and D_t, the parameters in (9), (11)–(13) can be calculated (There are too many, so we do not list them here).

The LCAO coefficients in (2) can be determined from a semiempirical LCAO method [14, 15], which yields the approximate relationship

$$f_\gamma = N_\gamma^2\,[1+\lambda_\gamma^2 S_{dp}^2(\gamma) - 2\lambda_\gamma S_{dp}(\gamma)] \qquad (18)$$

and the normalization correlation

$$N_\gamma\,(1-2\lambda_\gamma S_{dp}(\gamma)+\lambda_\gamma^2) = 1, \qquad (19)$$

where $S_{dp}(\gamma)$ is the group overlap integral. f_γ [$\approx (B/B_0 + C/C_0/2$] is the ratio of the Racah parameters for an ion in a crystal to those of a free ion. For free Co^{2+} ion, $B_0 \approx 1115$ cm^{-1} and $C_0 \approx 4366$ cm^{-1} [29]. So, from the

Table 1. The EPR parameters g_i and A_i for $K_2ZnF_4:Co^{2+}$.

	Cal[a)]	Cal[b)]	Cal[c)]	Expt. [3]
$g_\parallel$	5.76	6.42	6.36	6.30
$g_\perp$	3.63	3.36	3.19	3.13
$A_\parallel$	223	318	285	290
$A_\perp$	49	47	25	

[a)] Calculated neglecting the CI effect, i.e., $\varepsilon=\varepsilon'=\varepsilon''=\varepsilon'''=1$, $\tau=\tau'=\tau''=\rho=0$, $\alpha=\alpha'=3/2$.
[b)] Calculated neglecting the CO effect, i.e., $k=k'=1$, $\zeta=\zeta'=\zeta_d^0$.
[c)] Calculated considering both effects.

B and *C* values in (16) we obtain $f_\gamma\approx0.7377$. Since the tetragonal distortion of the $(CoF_6)^{4-}$ cluster in K_2ZnF_4: Co^{2+} is small, we obtain S_{dp} $(t_{2g})\approx0.00878$ and S_{dp} $(e_g)\approx$ 0.03184 by using the Slater-type SCF functions [30, 31] and the above average Co^{2+}-F^- distance $\bar{R}$ ($\approx$2.008 Å). Thus, from (18) and (19) we obtain $N_t\approx0.8620$, $N_e\approx0.8705$, $\gamma_t\approx0.4090$ and $\gamma_e\approx0.4188$. For a $(CoF_6)^{4-}$ cluster, $\zeta_d^0\approx533$ cm^{-1} [29], $\zeta_p^0\approx220$ cm^{-1} [32] and $P_0\approx254\times10^{-4}$ cm^{-1} [17], so we obtain

$$k\approx0.9341,\quad k'\approx0.7920,\quad \zeta\approx475\ \mathrm{cm}^{-1},\quad \zeta'\approx445\ \mathrm{cm}^{-1},$$
$$P\approx189\times10^{-4}\ \mathrm{cm}^{-1},\quad P'\approx191\times10^{-4}\ \mathrm{cm}^{-1}. \qquad (20)$$

The core polarization constant $\kappa\approx0.325\pm0.01$ [4] we take $\kappa\approx0.316$ here. Using all these parameters in the above formulas, we calculate the EPR parameters $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ for $K_2ZnF_4:Co^{2+}$. The calculated results and the observed values are shown in Table 1. For comparison, the calculated values by considering only CI effect or CO effect are also shown in Table 1.

4. Discussion

Table 1 shows that the calculated EPR parameters $g_\parallel$, $g_\perp$, $A_\parallel$ from the perturbation formulas based on the cluster approach for the tetragonal $K_2ZnF_4:Co^{2+}$ crystal agree well with the observed values (note: the experimental value of $A_\perp$ was not reported), suggesting that these formulas are reasonable and can be applied to similar systems.

Both the CI and CO effects contribute to the EPR parameters. If the CI effect is neglected, the calculated g_i and A_i agree poorly with the observed values (see Table 1). If the CO effect is neglected, all the calculated values of g_i and A_i are greater than the observed values. It can be expected that in the case of crystals having stronger covalency (for example, Br^- or I^- as the ligands), the role of the CO effect is greater and neglect of the CO effect should result in greater calculated errors. So, reasonable explanations of EPR parameters for $3d^7$ ion in tetragonal octahedral crystals should take both effects into account.

From the above studies we conclude that for Co^{2+} in compressed ligand octahedra, Δg $(=g_\perp-g_\parallel)<0$, and for Co^{2+} in elongated ligand octahedra, $\Delta g>0$. The conclusion is opposite to that given in [4–6], where for Co^{2+} in elongated octahedra, $\Delta g<0$. The following points support our conclusion: (i) Susceptibility analysis [3] showed that for K_2CoF_4. Δg ($\approx$3.3–6.5)<0. From the X-ray diffraction studies [26], one can find that the $(CoF_6)^{4-}$ octahedra in K_2CoF_4 are compressed. (ii) In the previous paper [33], we obtain for $3d^n$ ions in tetragonal octahedra

$$\Delta g=(\theta-\theta_0)\left(\frac{\partial\Delta g}{\partial\theta}\right)_0\approx2\,(\theta-\theta_0)\,(F_{11}-F_{12}), \qquad (21)$$

where F_{11} and F_{12} are the spin-lattice coupling coefficients, θ is the angle defined by $\tan\theta=R_\perp/R_\parallel$, and $\theta_0(=\pi/4)$ is the same angle in cubic symmetry. Obviously, if $\theta-\theta_0<0$, then $R_\perp>R_\parallel$, the ligand octahedron is compressed, and if $\theta-\theta_0<0$, it is elongated. For $3d^7$ ions in octahedral crystals, we have $F_{11}-F_{12}<0$ (for example, $F_{11}-F_{12}\approx-101$ for $MgO:Co^{2+}$ [34] and $F_{11}-F_{12}\approx-56$ for $MgO:Fe^+$ [35]). So, one can find that for Co^{2+} in a compressed octahedron $(\theta-\theta_0>0)$, $\Delta g<0$ rather than $\Delta g>0$. (iii) In [4–6], the tetragonal parameters D_s, D_t, and hence the separation Δ are the adjustable parameters. They are not calculated from the crystal-field theory related to the structural parameters of ligand octahedron. From the crystal-field theory (note: for a $3d^7$ ion, $D_q<0$) it can be found that for Co^{2+} in elongated octahedra, the ground state is $^4A_2$ rather than ^4E given in [4–6]. This misassignment of the ground state results in the incorrect sign of Δg. So, the relationship between the sign of Δg and the tetragonal distortion of a ligand octahedron obtained in the present paper is reasonable and correct.

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