Theoretical Explanations of the Optical and EPR Spectra for Tetragonal Yb^{3+} Center in $KMgF_3$ Crystal

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In this paper, the EPR g factors $g_\parallel$ and $g_\perp$ of Yb^{3+} and hyperfine structure constants $A_\parallel$ and $A_\perp$ of $^{171}Yb^{3+}$ and $^{173}Yb^{3+}$ in $KMgF_3$ crystal are calculated from the two-order perturbation formulae. In these formulae, the contribution of the covalence effects, the admixture between $J = 7/2$ and $J = 5/2$ states as well as the second-order perturbation are included. The needed crystal parameters are obtained from optical spectra. The calculated results agree reasonably with the observed values.

Key words: Electron Paramagnetic Resonance; Crystal-field Theory; Yb^{3+}; $KMgF_3$.

1. Introduction

$KMgF_3$ crystals with the perovskite structure have many applications and are convenient models for investigating the optical and magnetic properties of transition-metal or rare-earth impurity ions [1 – 5]. For example, the optical and EPR spectra of Yb^{3+} in $KMgF_3$ crystal were measured [6 – 8]. It is interesting that a trivalent rare-earth (Re^{3+}) can replace two different host cation sites: Mg^{2+} with six coordinated F^- anions and K^+ with twelve coordinated F^- anions. Because substitution of Re^{3+} for a Mg^{2+} or K^+ host gives rise to charge compensation, there may be various Re^{3+} impurity centers with different site symmetries such as cubic, trigonal, tetragonal and orthorhombic in $KMgF_3$:Re^{3+} crystals. For instance, three different Yb^{3+}(cubic, trigonal, tetragonal) centers have been found by EPR measurements. For the tetragonal Yb^{3+} center, a crystal-field analysis of the optical spectra was made. The calculated electronic energy levels are consistent with the observed values [8]. But by considering only the interaction within the ground $^2F_{7/2}$ multiplets, the EPR g factors calculated from the first-order perturbation formulae poorly agree with the experimental findings [7, 8]. In addition, up to now no theoretical calculation of the hyperfine structure constants $A_\parallel$ and $A_\perp$ of $^{171}Yb^{3+}$ and $^{173}Yb^{3+}$ in $KMgF_3$ crystal is reported.

In this paper, we use the second-order perturbation formulae of EPR parameters for an $4f^{13}$ ion in tetragonal symmetry. In these formulae, the contributions to the EPR parameters due to J-mixing between the ground $^2F_{7/2}$ and the excited $^2F_{5/2}$ states via crystal-field interactions, the interactions between the lowest Kramers doublet $\Gamma\gamma$ and the other Kramers doublets Γx via crystal-field and angular momentum as well as the covalence reduction effect due to the covalence of metal-ligand bonds are considered. From these formulae and crystal-field parameters obtained from experimental optical spectra, the EPR g factors $g_\parallel$ and $g_\perp$ of Yb^{3+} and hyperfine structure constants $A_\parallel$ and $A_\perp$ of $^{171}Yb^{3+}$ and $^{173}Yb^{3+}$ in $KMgF_3$ crystal are calculated. The calculated results in agree reasonably with the observed values. The results are discussed.

2. Calculation

A free Yb^{3+} ion has a $4f^{13}$ electronic configuration with a $^2F_{7/2}$ ground state and a $^2F_{5/2}$ excited state. The tetragonal crystal-field lifts the degeneracy of the $^2F_{7/2}$ and $^2F_{5/2}$ states into four and three Kramers doublets, respectively [9, 10]. Considering the crystal-field

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J-mixing effect, the energy levels and wave functions of these doublets can be obtained by diagonalizing the 14×14 energy matrix in tetragonal symmetry. The wave function of the lowest doublet $\Gamma\gamma$ can be expressed as

$$\begin{aligned}\Gamma\gamma(\gamma'))\rangle = &\sum_{M_{J1}} C(^2\mathrm{F}_{7/2};\Gamma\gamma(\gamma')M_{J1})|^2\mathrm{F}_{7/2}M_{J1}\rangle \\ &+ \sum_{M_{J2}} C(^2\mathrm{F}_{5/2};\Gamma\gamma(\gamma')M_{J2})|^2\mathrm{F}_{5/2}M_{J2}\rangle,\end{aligned} \tag{1}$$

where γ and γ' stand for the two components of the Γ irreducible representation, and M_{J1} and M_{J2} are the half-integers in the ranges $-7/2 \sim 7/2$ and $-5/2 \sim 5/2$, respectively.

The perturbation Hamiltonian for a rare earth ion in the crystal under an external magnetic field can be written as [9]

$$\hat{H}' = \hat{H}_{\mathrm{so}} + \hat{H}_{\mathrm{CF}} + \hat{H}_{\mathrm{Z}} + \hat{H}_{\mathrm{hf}}, \tag{2}$$

where $\hat{H}_{\mathrm{so}}$ is the spin-orbit coupling interaction, $\hat{H}_{\mathrm{CF}}$ the crystal-field interaction, $\hat{H}_{\mathrm{Z}}$ the Zeeman interaction, and $\hat{H}_{\mathrm{hf}}$ the hyperfine interaction term, respectively. $\hat{H}_{\mathrm{so}}$ can be expressed as [10]

$$\hat{H}_{\mathrm{SO}} = \zeta(\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}), \tag{3}$$

where ζ is the spin-orbit coupling coefficient, and $\hat{\boldsymbol{L}}$ and $\hat{\boldsymbol{S}}$ are the orbital and spin momentum operators, respectively. The crystal-field interaction $\hat{H}_{\mathrm{CF}}$ can be expressed in terms of the tensor operators C_k^q [9, 10]:

$$\begin{aligned}\hat{H}_{\mathrm{CF}} = &B_2^0 C_2^0 + B_4^0 C_4^0 + B_4^4(C_4^4 + C_4^{-4}) \\ &+ B_6^0 C_6^0 + B_6^4(C_6^4 + C_6^{-4}),\end{aligned} \tag{4}$$

where B_k^q are crystal field parameters. $\hat{H}_{\mathrm{Z}}$ can be expressed in terms of the Landé factor g_J and the angular momentum operator $\hat{J}$ as [9]

$$\hat{H}_{\mathrm{Z}} = g_J \mu_B \hat{\boldsymbol{H}} \cdot \hat{\boldsymbol{J}}. \tag{5}$$

The hyperfine interaction can be denoted as $\hat{H}_{\mathrm{hf}} = PN_J\hat{N}$, where P is the dipolar hyperfine structure constant and N_J is the diagonal matrix element for the $^{2S+1}\mathrm{L}_J$ state. For free Yb^{3+} ion isotopes, $P(^{171}\mathrm{Yb}) \approx 388.4 \cdot 10^{-4}$ cm^{-1} and $P(^{173}\mathrm{Yb}) \approx -106.5 \cdot 10^{-4}$ cm^{-1} [9, 10].

The contributions to the EPR parameters come mainly from the first-order perturbation terms, which are considered [8–10]. However, the other $(7-1 = 6)$ irreducible representations Γx may mix with the ground $\Gamma\gamma$ doublet via crystal field and angular momentum interactions, and so they contributia to EPR parameters. Based on the perturbation method, the perturbation formulae of the spin-Hamiltonian parameters for the 4f^{13} ion in tetragonal symmetry can be obtained [11]:

Table 1. The crystal-field energy levels (in cm^{-1}) of Yb^{3+} in KMgF$_3$ crystal.

	1	2	3	4	5	6	7
Cal.	0	104	701	1106	10200	10498	11060
Expt. [8]	0	105	700	1006	10200	10500	11175

Table 2. The spin-Hamiltonian parameters of Yb^{3+} in KMgF$_3$ crystal (the hyperfine structure constants A_i are in units of 10^{-4} cm^{-1}).

	Cal.[a]	Cal.[b]	Cal. (tot)	Expt. [8]	Expt. [7]
$g_\parallel$	0.960	0.139	1.099	1.070(1)	1.078
$g_\perp$	4.377	0	4.377	4.430(3)	4.377
$A_\parallel(^{171}\mathrm{Yb})$	246	37	283	281.0(5)	–
$A_\perp(^{171}\mathrm{Yb})$	1131	0	1131	1166(5)	–
$A_\parallel(^{173}\mathrm{Yb})$	67	10	77	74(1)	–
$A_\perp(^{173}\mathrm{Yb})$	311	0	311	344(3)	–

[a] calculated by using the first-order perturbation formula. [b] calculated by using the second-order perturbation formula.

$$\begin{aligned}&g_\parallel = g_\parallel{}^{(1)} + g_\parallel{}^{(2)}, \\ &\quad g_\parallel{}^{(1)} = 2g_J\langle\Gamma\gamma|\hat{J}_z|\Gamma\gamma\rangle, \\ &\quad g_\parallel{}^{(2)} = 2\sum_X{}' \frac{\langle\Gamma\gamma|\hat{H}_{\mathrm{CF}}|\Gamma_X\gamma_X\rangle\langle\Gamma_X\gamma_X|\hat{J}_Z|\Gamma\gamma\rangle}{E(\Gamma_X)-E(\Gamma)}, \\ &g_\perp = g_\perp{}^{(1)} + g_\perp^{(2)}, \\ &\quad g_\perp{}^{(1)} = 2g_J\langle\Gamma\gamma|\hat{J}_x|\Gamma\gamma'\rangle, \\ &\quad g_\perp{}^{(2)} = 0,\end{aligned} \tag{6}$$

$$\begin{aligned}&A_\parallel = A_\parallel{}^{(1)} + A_\parallel{}^{(2)}, \\ &\quad Ag_\parallel{}^{(1)} = 2PN_J\langle\Gamma\gamma|\hat{N}_z|\Gamma\gamma'\rangle, \\ &\quad A_\parallel{}^{(2)} = 2P\sum_X{}' \frac{\langle\Gamma\gamma|\hat{H}_{\mathrm{CF}}|\Gamma_X\gamma_X\rangle\langle\Gamma_X\gamma_X|\hat{N}_Z|\Gamma\gamma\rangle}{E(\Gamma_X)-E(\Gamma)}, \\ &A_\perp = A_\perp{}^{(1)} + A_\perp^{(2)}, \\ &\quad A_\perp{}^{(1)} = 2PN_J\langle\Gamma\gamma|\hat{N}_x|\Gamma\gamma'\rangle, \\ &\quad A_\perp{}^{(2)} = 0,\end{aligned} \tag{7}$$

where the parameters g_J, g_J', N_J and N_J' (g_J' and N_J' occur in the expansions of the above formulae) for various states can be obtained from [12] and [13].

Applying all these parameters to the energy matrix, and fitting the theoretical optical spectra to those observed [8], we can obtain the best fitting results of the crystal-field parameters and spin-orbit coupling coefficient for $\mathrm{KMgF_3}$:Yb^{3+} crystal, i. e.,

$$\begin{aligned} &B_2^0 \approx 1691\ \mathrm{cm}^{-1},\ B_4^0 \approx 319\ \mathrm{cm}^{-1},\\ &B_4^4 \approx 1206\ \mathrm{cm}^{-1},\ B_6^0 \approx -18\ \mathrm{cm}^{-1},\\ &B_6^4 \approx 215\ \mathrm{cm}^{-1},\ \zeta \approx 2902\ \mathrm{cm}^{-1}. \end{aligned} \tag{8}$$

The comparisons between the calculated and experimental energy levels is shown in Table 1.

Considering the covalence reduction effect, the orbital angular momentum $\hat{L}$ in (6) and (7) should be multiplied by an orbit reduction factor k. We take $k \approx 0.965$ here. Thus, from the above parameters and formulae, the g factors $g_\parallel$, $g_\perp$ of Yb^{3+} and hyperfine structure constants $A_\parallel$, $A_\perp$ of $^{171}\mathrm{Yb}$ and $^{173}\mathrm{Yb}$ in $\mathrm{KMgF_3}$ crystal are calculated. The calculated results of EPR parameters are compared with those of the observed values in Table 2.

3. Discussion

Table 1 shows that the calculated energy levels agree well with the observed ones. So the parameters adopted in this paper are reasonable.

Table 2 shows that, by using the second-order perturbation formulae considering the above admixtures or interactions, the EPR g factors $g_\parallel$, $g_\perp$ for Yb^{3+} and hyperfine structure parameters $A_\parallel$, $A_\perp$ for $^{171}\mathrm{Yb}^{3+}$ and $^{173}\mathrm{Yb}^{3+}$ in $\mathrm{KMgF_3}$ crystals are satisfactorily explained. The calculated values of $g_\parallel$ and $A_\parallel$ from the second-order perturbation terms amount to about 14% of the corresponding values from the first-order perturbation terms. So, for the exact calculation of EPR parameters of $4\mathrm{f}^{13}$ ions in crystals, the second-order perturbation contributions should be taken into account.

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