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 $J = \frac{7}{2}$ and $J = \frac{5}{2}$ 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 perowskite 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 4$^f_{13}$ 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 $\Gamma_x$ 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 agree reasonably with the observed values. The results are discussed.

2. Calculation

A free Yb$^{3+}$ ion has a 4$^f_{13}$ 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
J-mixing effect, the energy levels and wave functions of these doublets can be obtained by diagonalizing the $14 \times 14$ energy matrix in tetragonal symmetry. The wave function of the lowest doublet $\Gamma \gamma$ can be expressed as

$$\Gamma\gamma(\gamma') = \sum_{M_J} C(\hat{F}_{7/2}\Gamma\gamma(\gamma')M_J)\langle \hat{F}_{7/2}M_J\rangle \quad (1)$$

$$+ \sum_{M_J} C(\hat{F}_{5/2}\Gamma\gamma(\gamma')M_J)\langle \hat{F}_{5/2}M_J\rangle,$$

where $\gamma$ and $\gamma'$ stand for the two components of the $\Gamma$ irreducible representation, and $M_J$ and $M_J'$ 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]

$$\hat{H} = \hat{H}_{so} + \hat{H}_{CF} + \hat{H}_{Z} + \hat{H}_{hf}, \quad (2)$$

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

$$\hat{H}_{so} = \zeta(\hat{L} \cdot \hat{S}), \quad (3)$$

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

$$\hat{H}_{CF} = B_{4}^{0}C_{4}^{0} + B_{4}^{0}C_{4}^{0} + B_{4}^{0}(C_{4}^{2} + C_{4}^{-2})$$

$$+ B_{6}^{0}C_{6}^{0} + B_{6}^{0}(C_{6}^{2} + C_{6}^{-2}), \quad (4)$$

where $B_{j}^{0}$ are crystal field parameters. $\hat{H}_{Z}$ can be expressed in terms of the Landé factor $g_{J}$ and the angular momentum operator $J$ [9]

$$\hat{H}_{Z} = g_{J} \mu_{B} \hat{H} \cdot \hat{J}. \quad (5)$$

The hyperfine interaction can be denoted as $\hat{H}_{hf} = PN_{J}\hat{N}$, where $P$ is the dipolar hyperfine structure constant and $N_{J}$ is the diagonal matrix element for the $5S^{1}L_{J}$ state. For free Yb$^{3+}$ ion isotopes, $P(\text{171Yb}) \approx 388.4 \cdot 10^{-4}$ cm$^{-1}$ and $P(\text{173Yb}) \approx -106.5 \cdot 10^{-4}$ 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 $\Gamma \gamma$ may mix with the ground $\Gamma \gamma$ doublet via crystal field and angular momentum interactions, and so they contributa 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]:

$$g_{||} = g_{||}^{(1)} + g_{||}^{(2)},$$

$$g_{||}^{(1)} = 2g_{J}(\Gamma\gamma\hat{J}_{z}\Gamma\gamma),$$

$$g_{||}^{(2)} = 2\sum_{X} \langle \Gamma\gamma,\hat{H}_{CF}\mid \hat{I}_{X}\rangle \langle \hat{I}_{X}\mid \hat{J}_{z}\rangle E(\Gamma) - E(\Gamma_{||}), \quad (6)$$

$$g_{\perp} = g_{\perp}^{(1)} + g_{\perp}^{(2)},$$

$$g_{\perp}^{(1)} = 2g_{J}(\Gamma\gamma\hat{I}_{X}\mid \Gamma\gamma),$$

$$g_{\perp}^{(2)} = 0,$$

$$A_{||} = A_{||}^{(1)} + A_{||}^{(2)},$$

$$A_{||}^{(1)} = 2PN_{J}(\Gamma\gamma\hat{N}_{z}\mid \Gamma\gamma),$$

$$A_{||}^{(2)} = 2P\sum_{X} \langle \Gamma\gamma,\hat{H}_{CF}\mid \hat{I}_{X}\rangle \langle \hat{I}_{X}\mid \hat{N}_{z}\rangle E(\Gamma_{||}) - E(\Gamma_{||}), \quad (7)$$

$$A_{\perp} = A_{\perp}^{(1)} + A_{\perp}^{(2)},$$

$$A_{\perp}^{(1)} = 2PN_{J}(\Gamma\gamma\hat{N}_{z}\mid \Gamma\gamma),$$

$$A_{\perp}^{(2)} = 0,$$

where the parameters $g_{J}, g_{J}', N_{J}$ and $N_{J}'$ ($g_{J}'$ and $N_{J}'$ occ-
cur 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 KMgF₃:Yb³⁺ crystal, i.e.,

\[
\begin{align*}
B_2^0 &\approx 1691 \text{ cm}^{-1}, \\
B_4^0 &\approx 319 \text{ cm}^{-1}, \\
B_4^2 &\approx 1206 \text{ cm}^{-1}, \\
B_6^0 &\approx -18 \text{ cm}^{-1}, \\
\zeta &\approx 2902 \text{ cm}^{-1}.
\end{align*}
\]

(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 Yb³⁺ and hyperfine structure constants \( A_{\parallel} \), \( A_{\perp} \) of \(^{171}\)Yb and \(^{173}\)Yb in KMgF₃ 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 Yb³⁺ and hyperfine structure parameters \( A_{\parallel} \), \( A_{\perp} \) for \(^{171}\)Yb³⁺ and \(^{173}\)Yb³⁺ in KMgF₃ 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 4f\(^{13}\) ions in crystals, the second-order perturbation contributions should be taken into account.