Investigation of the Spin Hamiltonian Parameters of Yb^{3+} in $CaWO_4$ Crystal

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In this paper, the spin Hamiltonian parameters 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 $CaWO_4$ crystal are calculated from the two-order perturbation formulae. In these formulae, the contributions 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 the superposition model and the local structure of the studied system. The calculated results are in reasonable agreement with the observed values. The results are discussed.

Key words: Electron Paramagnetic Resonance; Crystal-field Theory; Superposition Model;Yb^{3+}; $CaWO_4$.

1. Introduction

$CaWO_4$ crystals doped with rare-earth ions are used as laser hosts because of their good fluorescence and large relaxation. Many studies have been done to understand the properties of rare-earth ions in $CaWO_4$ [1 – 5]. For example, the EPR spectra of Yb^{3+} in $CaWO_4$ crystals were measured many years ago [6]. Based on the first-order perturbation formulae and considering only interactions within the ground $^2F_{7/2}$ multiplet, V. Kumar and K. Chandra calculated approximately the spin-Hamiltonian parameters [6].

$CaWO_4$ crystals have a typical scheelite structure which belongs to the $I4_1/a$ space group [7]. According to the similar ionic radii of Yb^{3+} and Ca^{2+} ($r \approx 0.858$ Å for Yb^{3+}, $r \approx 0.99$ Å for Ca^{2+} and $r \approx 0.62$ Å for W^{6+} [8]), the doped Yb^{3+} ion substitutes a Ca^{2+} ion. The point symmetry at the sites of Ca^{2+} in the host crystal is tetragonal (S_4) but approximates the D_{2d} symmetry [9], so it is considered to be D_{2d} by many authors [6, 10, 11]. In this work we choose the actual S_4 site symmetry for the study of the EPR spectra of Yb^{3+}.

We use the second-order perturbation formulae of EPR parameters for $4f^{13}$ ions in tetragonal symmetry. In these formulae, the contributions to the spin-Hamiltonian parameters due to the 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 the crystal-field and angular momentum as well as the covalence reduction effect due to the covalence of metal-ligand bonds, are all considered. From these formulae and the crystal-field parameters obtained from the superposition model and the local structure of the studied system, the spin-Hamiltonian parameters, g factors $g_\parallel$ and $g_\perp$ of Yb^{3+} and hyperfine structure constants $A_\parallel$ and $A_\perp$ of $^{171}Yb^{3+}$ and $^{173}Yb^{3+}$ isotopes in $CaWO_4$ crystal are calculated. The results are discussed.

2. Calculations

The free Yb^{3+} ion has the $4f^{13}$ electronic configuration with a $^2F_{7/2}$ ground state and a $^2F_{5/2}$ excited state. When Yb^{3+} is located on the Ca^{2+} site of the

$\mathrm{CaWO_4}$ crystal, the tetragonal crystal-field lifts the degeneracies of the $^2\mathrm{F}_{7/2}$ and $^2\mathrm{F}_{5/2}$ states into four and three Kramers doublets, respectively [12]. Considering the crystal-field 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 written as

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

where γ and γ' stand for the two components of Γ in the irreducible representation. 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 a crystal under an external magnetic field can be written as [12]

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

where $\hat{H}_{\mathrm{so}}$ is the spin-orbit coupling interaction, $\hat{H}_{\mathrm{CF}}$ the crystal-field interaction, and $\hat{H}_{\mathrm{Z}}$ the Zeeman interaction, which can be expressed in terms of the Landé factor g_J and the angular momentum operator $\hat{J}$ as $\hat{H}_{\mathrm{Z}} = g_J\mu_{\mathrm{B}}\hat{H}\cdot\hat{J}$ [13]. The hyperfine interaction can be written as $\hat{H}_{\mathrm{hf}} = PN_J\hat{N}$, where P is the dipolar hyperfine structure constant and N_J the diagonal matrix element for the $^{2S+1}\mathrm{L}_J$ state. $\hat{H}_{\mathrm{so}}$ can be expressed as

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

where ζ is the spin-orbit coupling coefficient, and $\hat{L}$ and $\hat{S}$ are the orbital and spin momentum operators, respectively. The crystal-field interaction $\hat{H}_{\mathrm{CF}}$ can be expressed in terms of the tensor operators C_k^q [12]:

$$\begin{aligned}\hat{H}_{\mathrm{CF}} = &B_2^0C_2^0 + B_4^0C_4^0 + B_4^4(C_4^4 + C_4^{-4}) \\ &+ B_6^0C_6^0 + B_6^4(C_6^4 + c_6^{-4}),\end{aligned} \quad (4)$$

where B_k^q are crystal field parameters.

The contributions to the EPR parameters come mainly from the first-order perturbation terms, and so in the previous papers only the first-order terms are considered [12, 13]. However, the other $(7-1=6)$ irreducible representations Γx may mix with the ground $\Gamma\gamma$ doublet via the crystal field and angular momentum interactions, and so they contribute to the EPR parameters. Based on the perturbation method, the perturbation formulae of the spin-Hamiltonian parameters for an $4\mathrm{f}^{13}$ ion in tetragonal symmetry can be obtained [14]:

$$\begin{aligned}&g_\parallel = g_\parallel{}^{(1)} + g_\parallel{}^{(2)}, \\ &g_\parallel{}^{(1)} = 2g_J\langle\Gamma\gamma|\hat{J}_Z|\Gamma\gamma\rangle, \\ &g_\parallel{}^{(2)} = 2\sum_X{}' \frac{\langle\Gamma\gamma|\hat{H}_{\mathrm{CF}}|\Gamma_X\gamma_X\rangle\langle\Gamma_X\gamma_X|\hat{J}_Z|\Gamma\gamma\rangle}{E(\Gamma_X)-E(\Gamma)}, \\ &g_\perp = g_\perp{}^{(1)} + g_\perp{}^{(2)}, \\ &g_\perp{}^{(1)} = 2g_J\langle\Gamma\gamma|\hat{J}_X|\Gamma\gamma'\rangle, \quad g_\perp{}^{(2)} = 0,\end{aligned} \quad (5)$$

$$\begin{aligned}&A_\parallel = A_\parallel{}^{(1)} + A_\parallel{}^{(2)}, \\ &A_\parallel{}^{(1)} = 2PN_J\langle\Gamma\gamma|\hat{N}_Z|\Gamma\gamma'\rangle, \\ &A_\parallel{}^{(2)} = 2P\sum_X{}' \frac{\langle\Gamma\gamma|\hat{H}_{\mathrm{CF}}|\Gamma_X\gamma_X\rangle\langle\Gamma_X\gamma_X|\hat{N}_Z|\Gamma\gamma\rangle}{E(\Gamma_X)-E\Gamma,} \\ &A_\perp = A_\perp{}^{(1)} + A_\perp{}^{(2)}, \\ &A_\perp{}^{(1)} = 2PN_J\langle\Gamma\gamma|\hat{N}_X|\Gamma\gamma'\rangle, \quad A_\perp{}^{(2)} = 0,\end{aligned} \quad (6)$$

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].

From the superposition model [15], the crystal-field parameters can be expressed as

$$B_k^q = \sum_{j=1}^{n} \bar{A}_k(R_0)(R_0/R_j)^{t_k}K_k^q(\theta_j,\phi_j), \quad (7)$$

where the coordination factor $K_k^q(\theta_j,\phi_j)$ can be obtained from the local structural data of the studied system. t_k and $\bar{A}_k(R_0)$ are the power law exponents and the intrinsic parameters with the reference distance R_0, respectively. For a $(\mathrm{YbO_8})^{13-}$ cluster, the exponents $t_2 = 7$, $t_4 = 12$ and $t_6 = 11$ are taken as those obtained for Yb^{3+} in zircon-type orthophosphates [14]. $\bar{A}_k(R_0)$ are taken as adjustable parameters, which can be obtained by fitting the calculated EPR parameters $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ to the observed values. In the calculations, the free-ion values of the spin-orbit coupling coefficient $\zeta_{4\mathrm{f}}{}^0$ ($\approx 2950\ \mathrm{cm}^{-1}$ [12]) and the dipolar hyperfine structure constant P_0 ($\approx 388.4(7)\cdot 10^{-4}\ \mathrm{cm}^{-1}$ and $106.5(2)\cdot 10^{-4}\ \mathrm{cm}^{-1}$ for $^{171}\mathrm{Yb}^{3+}$ and $^{173}\mathrm{Yb}^{3+}$, respectively [12]) should be multiplied by the orbital reduction factor k because of the covalence effect of Yb^{3+} in crystals. Here we take $k \approx 0.986$.

Table 1. The spin-Hamiltonian parameters of Yb^{3+} in $CaWO_4$ crystal (the hyperfine structure constants A_i are in units of 10^{-4} cm^{-1}).

	Cal.$^{(1)\ a}$	Cal.$^{(2)\ b}$	Cal.$^{(tot)}$	Expt. [6]
$g_\parallel$	0.9368	0.1224	1.0592	1.05
$g_\perp$	3.9209	0	3.9209	3.93
$A_\parallel(^{171}Yb)$	237.7	31.4	269.1	270(1)
$A_\perp(^{171}Yb)$	1002.0	0	1002.0	1034(4)
$A_\parallel(^{173}Yb)$	65.2	8.6	73.8	72(1)
$A_\perp(^{173}Yb)$	274.8	0	274.8	285(3)

[a] Calculation by considering the first-order perturbation terms.[b] Calculation by considering the second-order perturbation terms.

In the $CaWO_4$ crystal, the host Ca^{2+} ion is coordinated to eight nearest O^{2-} ions, with four of them at a distance $^{H}_{1}$ and angle θ_1, and the other four at a different distance R_2^H and angle θ_2, (here θ_j is the angle between R_1^H and the fourfold axis of the crystal) [4]. According to [10] we have

$$\begin{aligned} R_1^H &\approx 2.438\ \text{Å},\ \theta_1 \approx 139.88^\circ,\ \phi_1 \approx -30.30^\circ, \\ R_2^H &\approx 2.479\ \text{Å},\ \theta_2 \approx\ \ 66.73^\circ,\ \phi_2 \approx -27.87^\circ. \end{aligned} \tag{8}$$

Generally, the impurity-ligand distance R_j in doped crystals is different from the cation-anion distance R_j^H in the host crystal because of the different radii of Yb^{3+} and the replaced host ion. Considering the local lattice relaxation due to the size mismatch, R_j can be reasonably estimated from the approximate formula [5]

$$R_j = R_j^H + (r_i - r_h/2, \tag{9}$$

where r_i and r_h are the ionic radii of the impurity and host, respectively. According to [8], $r_i \approx 0.858$ Å, and $r_h \approx 0.99$ Å. Thus, we can estimate the Yb^{3+}–O^{2-} distances R_1 and R_2 for Yb^{3+} in the $CaWO_4$ crystal.

Applying all these parameters to the energy matrix and (6)–(7), and fitting the theoretical spin-Hamiltonian parameters to that of the observed values [6], we obtain the best fitting superposition parameters $\bar{A}_k(R_0)$ for the $CaWO_4$:Yb^{3+} crystal, *i. e.*,

$$\begin{aligned} \bar{A}_2(R_0) &\approx 125\ \text{cm}^{-1}, \\ \bar{A}_4(R_0) &\approx 24\ \text{cm}^{-1}, \\ \bar{A}_6(R_0) &\approx 19\ \text{cm}^{-1}. \end{aligned} \tag{10}$$

Thus, from the above parameters and formulae, the g factors $g_\parallel$, $g_\perp$ of Yb^{3+} and the hyperfine structure constants $A_\parallel$, $A_\perp$ of ^{171}Yb and ^{173}Yb in $CaWO_4$ crystal are calculated. The calculated SH parameters are compared with those of the observed values in Table 1.

Discussions

From Table 1 one can find that the theoretical spin-Hamiltonian parameters for Yb^{3+} in $CaWO_4$ crystal are reasonably consistent with the experimental findings. So the perturbation formulae of the spin-Hamiltonian parameters g factors $g_\parallel$ and $g_\perp$ and the hyperfine structure constants $A_\parallel$ and $A_\perp$ for the $4f^{13}$ ion in tetragonal symmetry can be regarded as reasonable. Obviously this calculation method is also effective for other similar systems.

From the above studies we find that the calculated SH parameters by considering only the first-order perturbation terms within the ground $^2F_{7/2}$ manifolds are smaller than the observed values. We also find that the contribution of the covalence effect and the J-mixing between ground $^2F_{7/2}$ and first excited $^2F_{5/2}$ states amounts to about 3%, whereas that of the second-order perturbation terms amounts to about 12%. So, in order to explain the spin-Hamiltonian parameters for Yb^{3+} ions in crystals to a better extent, sometimes the contributions from the above admixtures and interactions should be taken into account.

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