A Theoretical Study on the Spin-Hamiltonian Parameters for Samarium(III) Ion in Potassium Yttrium Tungstate Crystal

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The nine spin-Hamiltonian (SH) parameters (g-factors g_i and hyperfine structure constants ${}^{147}A_i$ and ${}^{149}A_i$ for ${}^{147}\mathrm{Sm}^{3+}$ and ${}^{149}\mathrm{Sm}^{3+}$ isotopes, where $i = x, y, z$) for the Samarium(III) ion in monoclinic potassium yttrium tungstate [KY(WO$_4$)$_2$] crystal are calculated within the rhombic symmetry approximation from a diagonalization of energy matrix method. Differing from the conventional diagonalization method used in the calculation of crystal-field levels, in the present method, we attach the Zeeman (or magnetic) and hyperfine interaction terms to the conventional Hamiltonian and construct the 66×66 energy matrix for $4f^5$ ions in rhombic crystal field and under an external magnetic field by considering all the ground-term multiplets $4H_\mathrm{J}$. The calculated results are in reasonable agreement with the experimental values.

Key words: Electron Paramagnetic Resonance (EPR); Crystal Field Theory; Diagonalization Method; KY(WO$_4$)$_2$; Sm^{3+}.

1. Introduction

Rare-earth ions doped into double tungstate crystals have attracted much attention for the possible application of these crystals as active materials for solid state lasers [1, 2]. So, many spectroscopy studies for rare-earth ions in these crystals, such as the electron paramagnetic resonance (EPR) spectra of Gd^{3+} [3], Dy^{3+}[4], Er^{3+} [5], Nd^{3+} [6], Yb^{3+} [7], and Sm^{3+} [8] in KY(WO$_4$)$_2$ crystals, were reported. From the EPR experiment, the spin-Hamiltonian parameters (g-factors g_i and hyperfine structure constants ${}^{147}A_i$ and ${}^{149}A_i$ for ${}^{147}\mathrm{Sm}^{3+}$ and ${}^{149}\mathrm{Sm}^{3+}$ isotopes, where $i = x, y, z$) of Sm^{3+} ions in KY(WO$_4$)$_2$ crystals are given [8]. The structure of KY(WO$_4$)$_2$ is described in detail in [9, 10] and presented by the interconnected space group: I_2/c and C_2/c. The Y^{3+} ions are located on double rotary axis and surrounded by eight oxygen ions. The point symmetry of the Y^{3+} position is monoclinic C_2. The Sm^{3+} ion in the KY(WO$_4$)$_2$ crystal occupies the Y^{3+} position. Until now, no theoretical calculation for the spin-Hamiltonian parameters of Sm^{3+} at the Y^{3+} site of the KY(WO$_4$)$_2$ crystal has been performed. The purpose of this paper is to calculate theoretically these spin-Hamiltonian parameters from a diagonalization (of energy matrix) method. Considering that the monoclinic part is not large, for simplicity, we apply the rhombic symmetry approximation for the Sm^{3+} center in KY(WO$_4$)$_2$ crystal. Since there is a need of an external magnetic field in the measurement of spin-Hamiltonian parameters using an EPR experiment, we attach the Zeeman (or magnetic) and hyperfine interaction terms (concerning the hyperfine structure constants) to the traditional Hamiltonian used in the calculations of crystal-field energy levels and establish the energy matrix related to the $4f^5$ ions in a rhombic crystal field and under an external magnetic field. The results are discussed.

2. Calculation

The complete Hamiltonian for a rare-earth $(4f^n)$ ion in a rhombic crystal field and under an external magnetic field H_M can be expressed in the form [11, 12]

$$H = H_\mathrm{f} + H_\mathrm{CF} + H_\mathrm{Ze} + H_\mathrm{hf}, \tag{1}$$

where H_f (including the spin-orbit interaction) and H_CF represent, respectively, the free ion and crystal field interaction terms. The term H_CF for $4f^n$ ions in rhombic symmetry in the Wybourne notation [14] takes the

Table 1. Mean free-ion parameters (in cm^{-1}) for Sm^{3+} ion [14].

F^2	F^4	F^6	α	β	γ	T^2	T^3	T^4	T^6	T^7	T^8	ζ	M^0	M^2	M^4	P^2	P^4	P^6
79012	56979	40078	20.50	−616	1565	282	23	83	−294	403	340	1170	2.38	1.33	0.9	336	252	168

form

$$\begin{aligned}H_{\mathrm{CF}} = {} & B_{20}C_{20}+B_{40}C_{40}+B_{60}C_{60}\\ & +B_{22}(C_{22}+C_{2-2})+B_{42}(C_{42}+C_{4-2})\\ & +B_{44}(C_{44}+C_{4-4})+B_{62}(C_{62}+C_{6-2})\\ & +B_{64}(C_{64}+C_{6-4})+B_{66}(C_{66}+C_{6-6}),\end{aligned} \tag{2}$$

where B_{kq} ($k=2,4,6,|q|\le k$) are the crystal field parameters and $C_{q(k)}$ are the normalized spherical harmonics. The Zeeman and hyperfine interaction terms H_{Ze} and H_{hf} are written as

$$H_{\mathrm{Ze}} = g_{\mathrm{J}}\mu_{\mathrm{B}}J\cdot H_{\mathrm{M}}, \quad H_{\mathrm{hf}} = P(N\cdot I) = PN_{\mathrm{J}}\widehat{N} \tag{3}$$

in which g_{J}, P, $\widehat{N}$, and N_{J} are, respectively, the Landé factor, the dipolar hyperfine structure constant, the equivalent operator of magnetic hyperfine structure and the diagonal matrix element for ^{2S+1}L state; the remaining notations are standard [11,12]. In (3), the parameters g_{J} and N_{J} should be replaced by $g_{\mathrm{J}'}$ and $N_{\mathrm{J}'}$ in the matrix elements between different J-manifold [11,12].

Sm^{3+} ion has a $4f^5$ electronic configuration with the free ion ground-term multiplets $^6H_{\mathrm{J}}$, where $J = 5/2$ is the ground multiplet, and $J = 7/2$, 9/2, 11/2, 13/2, and 15/2 are the first to fifth excited multiplets. When an Sm^{3+} ion occupies a rhombic site, the rhombic crystal field can split the ground-term multiplets $^6H_{\mathrm{J}}$ into $(J+1/2)$ Kramers doublets and the lowest or ground Kramers doublet from $^6H_{5/2}$ may be Γ_6 or Γ_7 [11,12]. Generally speaking, the influence of the high lying multiplets on the spin-Hamiltonian parameters of the ground Kramers doublet is small because of the great energy separation between them [13]. For simplicity, in the construction of energy matrix concerning the above complete Hamiltonian, we take only the ground-term multiplets $^6H_{\mathrm{J}}$ into account. Thus, in terms of the equivalent operator and/or the irreducible tensor operator method, a 66×66 energy matrix including all the ground-term states for $4f^5$ ions in rhombic symmetry and under an external magnetic field is obtained. Diagonalizating the energy matrix, one can obtain the Zeeman splitting $\Delta E_{\mathrm{Ze}}(i)$ (where $i = x,y,z$) for the external magnetic field H_{M} along i axis and the hyperfine splitting $\Delta E_{\mathrm{hf}}[= E_{\mathrm{hf}}(i,m_{\mathrm{I}}=1/2)-E_{\mathrm{hf}}(i,m_{\mathrm{I}}=-1/2)]$ for the operator $\widehat{N}$ along the i axis and $H_{\mathrm{M}} = 0$. Thus, the spin-Hamiltonian parameters g_i and A_i can be calculated using the formulas:

Table 2. Structural data of Sm^{3+} at Y^{3+} site of KY(WO$_4$)$_2$ crystal [9].

j	1	2	3	4
R_j(Å)	2.265	2.282	2.323	2.690
θ_j(deg.)	138.2	47.7	71.9	115.9
φ_j(deg.)	0	44.4	132.3	73.6

$$g_i = \frac{\Delta E_{\mathrm{Ze}}(i)}{\mu_{\mathrm{B}}H_{\mathrm{M}}(i)}, \quad A_i = \Delta E_{\mathrm{hf}}(i). \tag{4}$$

In the above matrix, the free-ion parameters are taken as the average values obtained for Sm^{3+} ions in many crystals [14]. These values are collected in Table 1. The dipolar hyperfine structure constant P is calculated using the formula [15]

$$P = g_{\mathrm{e}}g_{\mathrm{N}}\beta\beta_{\mathrm{N}}\langle r^{-3}\rangle, \tag{5}$$

in which $g_{\mathrm{N}} = \mu_{\mathrm{I}}/I$. From the expectation value $\langle r^{-3}\rangle \approx 7.4943$ a.u. [16], $I = 7/2$, and $\mu = -0.813$ and -0.66 for the isotopes ^{147}Sm^{3+} and ^{149}Sm^{3+} [17], we obtain

$$\begin{aligned}&P(^{147}\mathrm{Sm}^{3+}) \approx -55.5\times 10^{-4}\ \mathrm{cm}^{-1},\\ &P(^{149}\mathrm{Sm}^{3+}) \approx -45.0\times 10^{-4}\ \mathrm{cm}^{-1}.\end{aligned} \tag{6}$$

The crystal field parameters B_{kq} used in the energy matrix are often calculated by using the superposition model [18,19]. This model suggests that the crystal field parameters B_{kq} are due to the sum of axially symmetry contribution of the n ligands of a MX$_n$ cluster in crystals, so the crystal field parameters B_{kq} are expressed as [18,19]

$$B_{\mathrm{kq}} = \sum_j \bar{A}_k(R_0)\left(\frac{R_0}{R_j}\right)^{t_k} K_k^q(\theta_j,\varphi_j), \tag{7}$$

where $K_k^q(\theta_j,\varphi_j)$ are the coordination factors depending upon the structural data of the MX$_n$ cluster. For the Sm^{3+} ion at the Y^{3+} site of the KY(WO$_4$)$_2$ crystal within rhombic symmetry approximation, from the superposition model, we can divide the eight ligands surrounding the Y^{3+} (or Sm^{3+}) ion into four groups.

The structural data, i. e., the metal-ligand distances R_j $(j = 1,2,3,4)$, the polar angles θ_j, and the azimuthal angles φ_j, are calculated from the X-ray diffraction data [9] and listed in Table 2. Thus, from (7), the crystal field parameters can be written as

$$\begin{aligned}
B_{20} &= 2\sum_j \bar{A}_2(R_0)\left(\frac{R_0}{R_j}\right)^{t_2}\left(3\cos^2\theta_j - 1\right),\\
B_{22} &= \sqrt{6}\sum_j \bar{A}_2(R_0)\left(\frac{R_0}{R_j}\right)^{t_2}\sin^2\theta_j\cos 2\varphi,\\
B_{40} &= 2\sum_j \bar{A}_4(R_0)\left(\frac{R_0}{R_j}\right)^{t_4}(35\cos^4\theta_j - 30\cos^2\theta_j + 3),\\
B_{42} &= 2\sqrt{10}\sum_j \bar{A}_4(R_0)\left(\frac{R_0}{R_j}\right)^{t_4}\\
&\quad\cdot\sin^2\theta_j\left(7\cos^2\theta_j - 1\right)\cos 2\varphi,\\
B_{44} &= \sqrt{70}\sum_j \bar{A}_4(R_0)\left(\frac{R_0}{R_j}\right)^{t_4}\sin^4\theta_j\cos 4\varphi,\\
B_{60} &= 2\sum_j \bar{A}_6(R_0)\left(\frac{R_0}{R_j}\right)^{t_6}\big(231\cos^6\theta_j - 315\cos^4\theta_j\\
&\quad + 105\cos^2\theta_j - 5\big),\\
B_{62} &= \sqrt{105}\sum_j \bar{A}_6(R_0)\left(\frac{R_0}{R_j}\right)^{t_6}\sin^2\theta_j\\
&\quad\cdot\left(33\cos^4\theta_j - 18\cos^2\theta_j + 1\right)\cos 2\varphi,\\
B_{64} &= \frac{3\sqrt{14}}{2}\sum_j \bar{A}_6(R_0)\left(\frac{R_0}{R_j}\right)^{t_6}\sin^4\theta_j\\
&\quad\cdot\left(11\cos^2\theta_j - 1\right)\cos 4\varphi,\\
B_{66} &= \sqrt{231}\sum_j \bar{A}_6(R_0)\left(\frac{R_0}{R_j}\right)^{t_6}\sin^6\theta_j\cos 6\varphi, \qquad (8)
\end{aligned}$$

where the power-law exponents t_k for $4f^n$ ions in crystals are taken as $t_2 = 5$, $t_4 = 6$, and $t_6 = 10$ [20,21]. $\bar{A}_k(R_0)$ are the intrinsic parameters with the reference distance $R_0[= \bar{R} = (R_1 + R_2 + R_3 + R_4)/4]$. These parameters $\bar{A}_k(R_0)$ are normally obtained empirically though fits to experimental data of optical and/or EPR spectra. By fitting the calculated spin-Hamiltonian parameters using the diagonalization method to the experimental values, we obtain for Sm^{3+} in the KY(WO$_4$)$_2$ crystal

$$\begin{aligned}
&\bar{A}_2(R_0) \approx 1038\ \mathrm{cm}^{-1}, \quad \bar{A}_4(R_0) \approx 203\ \mathrm{cm}^{-1},\\
&\bar{A}_6(R_0) \approx 35\ \mathrm{cm}^{-1}.
\end{aligned} \qquad (9)$$

Table 3. Spin-Hamiltonian parameters (g factors g_i and hyperfine structure constants $^{147}A_i$, $^{149}A_i$, where $i = x,y,z$ and A_i are in units of 10^{-4} cm^{-1}) for KY(WO$_4$)$_2$: Sm^{3+} crystal.

	Calc.	Expt. [8]
g_x	0.1962	0.1963(9)
g_y	0.1657	0.1659(15)
g_z	0.700	0.6997(2)
$^{147}A_x$	−27	$\le 30^a$
$^{147}A_y$	−22	$\le 30^a$
$^{147}A_z$	−389.9	384.5(8)^a
$^{149}A_x$	−21	$\le 25^a$
$^{149}A_y$	−17	$\le 25^a$
$^{149}A_z$	−313.6	317.8(8)^a

[a] The values are actually the absolute values.

The calculated spin-Hamiltonian parameters are compared with the experimental values in Table 3.

3. Discussion

The signs of the hyperfine structure constants $^{147}A_i$ and $^{149}A_i$ for KY(WO$_4$)$_2$:Sm^{3+} in [8] are written as positive. In fact, it is difficult to determine the signs of the constants A_i for transition-metal (d^n) and rare-earth (f^n) ions in crystals only by an EPR experiment [11,15,22,23]. So the observed values of the hyperfine structure constants A_i for d^n and f^n ions in crystals are actually the absolute values although they are often written as positive. It is agreed that the signs of the hyperfine structure constants A_i are related to the signs of the dipolar hyperfine structure constant P and hence to the nuclear magnetic moment μ_I [11,15,24]. From the above calculations, we suggest that the signs of $^{147}A_i$ and $^{149}A_i$ are negative, may be due to the negative values of ^{147}P and ^{149}P. In fact, the negative signs of the hyperfine structure constants A_i for the Sm^{3+} ions in many crystals were pointed out in [11].

Although the intrinsic parameters $\bar{A}_k(R_0)$ in the superposition model are adjustable, from a great number of studies of optical and EPR spectra for $4f^n$ ions in crystals, a trend that $\bar{A}_2(R_0) > \bar{A}_4(R_0) > \bar{A}_6(R_0)$ is found [18–21, 25–28]. The above values of $\bar{A}_k(R_0)$ obtained from the calculations of the spin-Hamiltonian parameters for KY(WO$_4$)$_2$:Sm^{3+} are in keeping with the trend and so they are suitable. Thus, by using these reasonable parameters, the nine spin-Hamiltonian parameters g_i, $^{147}A_i$, and $^{149}A_i$ are explained satisfactorily from the diagonalization (of energy matrix) method (see Table 3).

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