

Optical spectra and spin-Hamiltonian parameters of trivalent ytterbium in lead tungstate

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Abstract. By using crystal-field theory, the optical spectra and spin-Hamiltonian parameters (abbr. SH parameters, i.e. the anisotropic g factors g_{\parallel} , g_{\perp} , and hyperfine structure constants A_{\parallel} , A_{\perp}) of $^{171}\text{Yb}^{3+}$ and $^{173}\text{Yb}^{3+}$ isotopes in the tetragonal PbWO_4 are calculated. The theoretical results agree well with the experimental values. The crystal-field parameters and the signs of the hyperfine structure constants for both $^{171}\text{Yb}^{3+}$ and $^{173}\text{Yb}^{3+}$ isotopes are determined. The validities of the theoretical results are discussed.

Keywords. Crystal-field theory; optical spectrum; spin-Hamiltonian parameters; Yb^{3+} ; PbWO_4 .

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1. Introduction

PbWO_4 , as a scintillator, has been intensively investigated due to its important applications in scintillator detectors, high-energy electromagnetic calorimeters, etc. [1,2]. For Yb^{3+} -doped PbWO_4 , the optical absorption spectra have been recorded in a broad region (850–1050 nm) at room temperature [3]. In addition, the SH parameters were studied using electron paramagnetic resonance technique by Sattler and Nemarich [4]. Up to now, there is no unified theoretical interpretation for these experimental data (i.e. optical and EPR data). To understand the detailed physical and chemical properties of the $\text{PbWO}_4:\text{Yb}^{3+}$ crystal, in this paper, the optical spectra and SH parameters (g factors g_{\parallel} , g_{\perp} and hyperfine structure constants A_{\parallel} , A_{\perp}) of Yb^{3+} centre in $\text{PbWO}_4:\text{Yb}^{3+}$ are explained uniformly by diagonalizing the full-energy Hamiltonian matrix method. The theoretical results are in reasonable agreement with the experimental findings. The results are discussed.

2. Theoretical methods

Yb^{3+} ion in PbWO_4 crystal occupies the Pb^{2+} site and thus possesses a S_4 point symmetry. Because this point symmetry is very nearly D_{2d} , some reports [5–7] used D_{2d} symmetry as a good approximation to investigate the optical spectra and SH parameters for the rare-earth ions in the tetragonal scheelite-type structure crystals. For simplicity, D_{2d} symmetry is used here. In this case, Yb^{3+} ion has the $4f^{13}$ electronic configuration with a ${}^2F_{7/2}$ ground state and a ${}^2F_{5/2}$ excited state. In a tetragonal crystal field, the ground state ${}^2F_{5/2}$ will split into three Kramers doublets and the ground state ${}^2F_{7/2}$ into four. Thus there are seven optical spectral band positions in $\text{PbWO}_4:\text{Yb}^{3+}$. These energy levels of the Kramers doublets can be calculated by diagonalizing a 14×14 energy Hamiltonian matrix of $4f^{13}$ ion in a tetragonal symmetry,

$$H = H_{\text{fr}} + H_{\text{CF}}(D_{2d}) + H_{\text{SO}}(\zeta) + H_{\text{Ze}} + H_{\text{hyper}} \quad (1)$$

in which

$$H_{\text{CF}} = B_2^0 C_2^0 + B_4^0 C_4^0 + B_4^4 (C_4^4 + C_4^{-4}) + B_6^0 C_6^0 + B_6^4 (C_6^4 + C_6^{-4}). \quad (2)$$

H_{fr} , H_{CF} and H_{SO} are the free ion, the crystal-field and the spin-orbit coupling terms, respectively. The C_k^q is the Racah spheric tensor operator. The crystal-field parameter B_k^q and spin-orbit coupling coefficient are regarded as empirical parameters. Here we take $\zeta \approx 2900 \text{ cm}^{-1}$ [7] and B_k^q as the adjustable parameters. For ${}^{2S+1}L_J$ manifold, the Zeeman and hyperfine interaction terms H_{Ze} and H_{hyper} can be written as [8,9]

$$H_{\text{Ze}} = g_J \mu_B J \cdot B, \quad (3)$$

$$H_{\text{hyper}} = P(N \cdot J) = P N_J N, \quad (4)$$

where B is the external magnetic field intensity and P is the dipolar hyperfine structure constant. For the free Yb^{3+} ion values, $P(^{171}\text{Yb}^{3+}) \approx 392 \times 10^{-4} \text{ cm}^{-1}$ and $P(^{173}\text{Yb}^{3+}) \approx -108 \times 10^{-4} \text{ cm}^{-1}$ [8]. They are obtained from [8,9]

$$P = g_s g_N \beta \beta_N \langle r^{-3} \rangle \quad (5)$$

in which $\langle r^{-3} \rangle = 12.50$ a.u. and $g_N = \mu/I$. Here nuclear magneton $\mu \approx 0.49188$, nuclear spin $I = 1/2$ for ^{171}Yb and $\mu \approx -0.67755$, $I = 5/2$ for ^{173}Yb , respectively [8,10,11]. N_J is the diagonal matrix element for ${}^{2S+1}L_J$ state and N is the equivalent operator [8,9]. Thus, from eqs. (1) to (5), the full-energy Hamiltonian matrix (14×14) has been established on the basis of the crystal-field theory. In addition, the matrix elements between different J -manifolds are included in eq. (1).

Diagonalizing the energy Hamiltonian matrix, the crystal-field energy levels can be obtained from the eigenvalues of this matrix and the SH parameters are computed from the following formulas [7,10]:

$$g_{\parallel} = \frac{\Delta E_{\parallel}}{\mu_B B_{\parallel}}, \quad g_{\perp} = \frac{\Delta E_{\perp}}{\mu_B B_{\perp}}, \quad A_{\parallel} = \Delta E'_{\parallel}, \quad A_{\perp} = \Delta E'_{\perp}, \quad (6)$$

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where Zeeman splitting energy level $\Delta E(i)$ ($i = \parallel$ or \perp) can be obtained by the full-energy Hamiltonian matrix under the external magnetic field B along Z (or X) axis. The hyperfine splitting energy level $\Delta E'_i$ represents the equivalent operator N of magnetic hyperfine structure along Z (or X) axis. Therefore, the unified calculations of all the optical spectra and SH parameters for Yb^{3+} -doped PbWO_4 can be achieved using the present theoretical model. By fitting the calculated crystal-field energy levels, g factors g_{\parallel} , g_{\perp} and hyperfine structure constants A_{\parallel} , A_{\perp} to the experimental values, the crystal-field parameters B_k^q for Yb^{3+} in PbWO_4 crystal have been determined and listed in table 1. The calculated optical spectra and SH parameters are compared with the experimental data in tables 2 and 3.

Table 1. The crystal-field parameters B_k^q (in cm^{-1}) for $\text{PbWO}_4:\text{Yb}^{3+}$.

B_2^0	B_4^0	B_4^4	B_6^0	B_6^4
408	-800	930	-510	550

Table 2. The optical spectra (or crystal-field energy levels, in cm^{-1}) of $\text{PbWO}_4:\text{Yb}^{3+}$.

	${}^2F_{7/2}$				${}^2F_{5/2}$		
Calc.	0	335	428	556	10279	10468	10712
Expt. [3]	0	-	-	-	10225	-	10718

Table 3. The spin-Hamiltonian parameters (g factors g_i and hyperfine structure constants A_i , A_i is in unit of 10^{-4} cm^{-1}) for Yb^{3+} ion in PbWO_4 .

	g_{\parallel}	g_{\perp}	${}^{171}A_{\parallel}$	${}^{171}A_{\perp}$	${}^{173}A_{\parallel}$	${}^{173}A_{\perp}$
Calc.	0.6513	3.8914	156.6	1024.0	-43.2	-283.0
Expt. [4]	0.6513(1)	3.886(1)	160(1)	1024(1)	44.4 ^a	283.1 ^a

^aThe values are actually the absolute values.

3. Discussions

(1) From table 2, the optical spectral band positions (${}^2F_{7/2}$ - ${}^2F_{5/2}$) are coincident with the observed values. Although some optical spectral bands are missing in the experiment, the two absorption spectra of $\text{PbWO}_4:\text{Yb}^{3+}$ are similar to those findings within $4f$ electronic shell in many other Yb^{3+} -doped isostructural crystals [7,12,13].

(2) In many experiments, the signs of the hyperfine structure constants A_i are often given as positive, so that the determination of the signs of A_i is a significant investigation

[14–18]. From table 3, the hyperfine structure constants A_{\parallel} , A_{\perp} for $^{171}\text{A}_i$ are positive but those for $^{173}\text{A}_i$ are negative which agree very well with many studies for Yb^{3+} in crystals [7,10,11]. The different sign between $^{171}\text{A}_i$ and $^{173}\text{A}_i$ is due to the different dipolar hyperfine structure constant P which is related to the two Yb^{3+} isotopes. Thus, they can be regarded as reasonable in physics.

(3) For rare-earth ion-doped crystals, the ratio between the isotope nuclei for hyperfine structure constants A_i is very close to that for the nuclear magneton μ_i [19]. In this case the $^{171}\text{A}_{\parallel}/^{173}\text{A}_{\parallel} \approx -3.625$ and $^{171}\text{A}_{\perp}/^{173}\text{A}_{\perp} \approx -3.618$ agree well with $^{171}\mu/^{173}\mu \approx -3.630$ [8], which proved that the theoretical parameters are valid.

4. Conclusion

The above calculation shows that the present method is effective in the unified calculations of the optical spectra and SH parameters for $4f^{13}$ ions in crystals with D_{2d} symmetry.

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