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A unified calculation of the optical spectral band positions and electron paramagnetic resonance spectral data for Yb^{3+} in InP semiconductor

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ABSTRACT

The complete energy matrix for a $4f^{13}$ ion in cubic crystals and under an external magnetic field is established by means of the irreducible tensor operator and/or equivalent operator methods. By diagonalizing the energy matrix, four optical spectrum band positions and three spin-Hamiltonian parameters [g factor and hyperfine structure constants $A(^{171}Yb^{3+})$ and $A(^{173}Yb^{3+})$] for Yb^{3+} in InP semiconductor are calculated together. The calculated results are in good agreement with the experimental values. The signs of hyperfine structure constants $A(^{171}Yb^{3+})$ and $A(^{173}Yb^{3+})$ are determined from the calculations. The results are discussed.

1. Introduction

Semiconductors doped with rare earth ions have attracted considerable attention because of the possible applications to new optical devices [1–4]. Among the possible combinations of rare earth ions and semiconductor hosts, the Yb^{3+}-doped InP is one of the most widely studied materials owing to its strong Yb^{3+}-related luminescence at about 1 μm [5,6]. The optical spectra [6] and electron paramagnetic resonance (EPR) spectra [7,8] for Yb^{3+} at cubic In^{3+} site of InP were measured. Five crystal-field energy levels (or four optical spectrum band positions) and three spin-Hamiltonian parameters [g factor and hyperfine structure constants $A(^{171}Yb^{3+})$ and $A(^{173}Yb^{3+})$] were given from the measurements [6–8]. These spectroscopic data have not been explained in a unified way. In this paper, we calculate these spectroscopic data by using a complete diagonalization (of energy matrix) method for $4f^{13}$ ion in cubic crystal field and under an external magnetic field. Differing from the traditional diagonalization method used in the study of optical spectra, in the present diagonalization method, the Hamiltonian concerning the energy matrix also includes the Zeeman and hyperfine interaction terms and so the optical spectrum band positions and spin-Hamiltonian parameters can be calculated together. The results are discussed.

2. Calculation

The electronic configuration of Yb^{3+} is $4f^{13}$. It has a ground state $^2F_{7/2}$ and an excited state $^2F_{5/2}$. When Yb^{3+} ion occupies the cubic In^{3+} site in InP semiconductor crystal, the cubic crystal field splits the $^2F_{7/2}$ into three components $\Gamma_7 + \Gamma_8 + \Gamma_6$ and the $^2F_{5/2}$ into two components $\Gamma_7 + \Gamma_8$ [6,9]. In the conventional diagonalization method used in the study of crystal-field energy levels, the Hamiltonian contains only the free-ion term H_f (including the spin–orbit interaction term $H = \zeta L \cdot S$, where ζ is the spin–orbit coupling parameter) and the crystal-field interaction term H_{CF}. Since the measurement of g factor in EPR spectra requires an external magnetic field H_M and the hyperfine structure constants are related to the hyperfine interaction, the complete Hamiltonian used in the studies of optical spectrum band positions and spin-Hamiltonian parameters for a $4f^{13}$ (or $4f^n$) ion in crystals should take the form

$$H = H_f + H_{CF} + H_{Ze} + H_{hf}, \qquad (1)$$

in which the crystal-field interaction term H_{CF} for a $4f^n$ ion in cubic crystal can be given in Wybourne notation as [10]

$$H_{CF} = B_4^0 \left[C_4^0 + \sqrt{\tfrac{5}{14}} (C_4^{-4} + C_4^4) \right] + B_6^0 \left[C_6^0 + \sqrt{\tfrac{7}{2}} (C_6^{-4} + C_6^4) \right], \qquad (2)$$

where C_k^q are the Racah spheric tensor operators. B_k^q are the crystal-field parameters which are often determined experimentally.

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Table 1
The crystal-field energy levels (or optical spectrum band positions, in cm^{-1}) of InP:Yb^{3+}.

	$\Gamma_{7/2}$			$\Gamma_{5/2}$	
	Γ_7	Γ_8	Γ_6	Γ_7	Γ_8
Calc.	0	35	98	10010	10074
Expt. [6]	0	35	98	10023	10070

Table 2
The electron paramagnetic resonance spectral data (spin-Hamiltonian parameters, g factor and hyperfine structure constants A) of InP:Yb^{3+}.

	g	$A(^{171}\text{Yb}^{3+})$ $(10^{-4}\ \text{cm}^{-1})$	$A(^{173}\text{Yb}^{3+})$ $(10^{-4}\ \text{cm}^{-1})$
Calc.	3.291(1)	890	−245
Expt. [7,8]	3.291	886[a]	247[a]

[a] The values are actually the absolute values.

The Zeeman (or magnetic) interaction term H_{Ze} and hyperfine interaction term H_{hf} in Eq. (1) can be written as [9,11]

$$H_{\text{Ze}} = g_J \mu_B J \cdot H_M, \quad H_{\text{hf}} = P(N \cdot I) = PN_J \hat{N}, \tag{3}$$

where P, N and $\hat{N}$ denote, respectively, the dipolar hyperfine structure constant, the diagonal matrix element for $^{2s+1}L_J$ state and the equivalent operator of magnetic hyperfine structure, and the other symbols have their usual meanings [9,11]. In the matrix elements between different J-manifolds, the g_J and N_J in Eq. (3) should be replaced by g'_J and N'_J, respectively [9,11]. In terms of the irreducible tensor operator and/or equivalent operator methods, the 14×14 complete energy matrix for $4f^{13}$ ion in cubic crystal and under an external magnetic field is established. The crystal-field energy levels can be obtained from the eigenvalues of the matrix and the spin-Hamiltonian parameters are calculated by using the formulas

$$g = \frac{\Delta E_{\text{Ze}}}{\mu_B H_M}, \quad A = \Delta E_{\text{hf}} = E_{\text{hf}}\left(m_I = \frac{1}{2}\right) - E_{\text{hf}}\left(m_I = -\frac{1}{2}\right), \tag{4}$$

where ΔE_{Ze} and ΔE_{hf} are the Zeeman splitting and hyperfine splitting. Both splittings and the above eigenvalues can be obtained by diagonalizing the complete energy matrix.

For free Yb^{3+} ion, the dipolar hyperfine structure constants are P_0 $(^{171}\text{Yb}^{3+}) \approx 392 \times 10^{-4}\ \text{cm}^{-1}$ and P_0 $(^{173}\text{Yb}^{3+}) \approx -108 \times 10^{-4}\ \text{cm}^{-1}$ [12]. They are the theoretical values obtained from the formula $P = g_s g_N \beta \beta_N \langle r^{-3} \rangle$ [13] with the related values given in Ref. [9]. The value of P for $4f^n$ ions in crystals may be slightly smaller than the theoretical free-ion value and is different from crystal to crystal because of the covalence reduction effect. Here we introduce a covalence reduction factor k (≤ 1) to characterize the covalence effect, i.e., $P = kP_0$. Thus, in the energy matrix, there are four adjustable parameters B_4^0, B_6^0, k and ζ. They are determined by matching the calculated crystal-field energy levels and spin-Hamiltonian parameters to the observed values. From the calculations using the diagonalization method, we obtain for Yb^{3+} in InP crystal

$$B_4^0 \approx -221\ \text{cm}^{-1}, \quad B_6^0 \approx -67\ \text{cm}^{-1},$$
$$\zeta \approx 2860\ \text{cm}^{-1}, \quad k \approx 0.945. \tag{5}$$

The comparisons between the calculated and experimental crystal-field energy levels and spin-Hamiltonian parameters are given in Tables 1 and 2.

3. Discussion and conclusion

The sign of hyperfine structure constant A for a transition-metal or rare earth ion in crystals is hardly determined only by EPR experiments [9,13,14]. So although the hyperfine structure constant A obtained by EPR experiments for these ions in many crystals (also including the studied crystal InP:Yb^{3+}) are written as the position values, they are actually the absolute values. In fact, the sign of hyperfine structure constant A is related to the sign of dipolar hyperfine structure constant P. The different signs between $P(^{171}\text{Yb}^{3+})$ and $P(^{173}\text{Yb}^{3+})$ should lead the sign of $A(^{171}\text{Yb}^{3+})$ to be different from that of $A(^{173}\text{Yb}^{3+})$. According to our calculations, we find for InP:Yb^{3+}, the sign of $A(^{171}\text{Yb}^{3+})$ is positive, whereas that of $A(^{171}\text{Yb}^{3+})$ is negative (see Table 2). These signs are in agreement with those found for the constants A of the $^{171}\text{Yb}^{3+}$and $^{173}\text{Yb}^{3+}$ isotopes in many other cubic crystals [9] and can be regarded as reasonable.

The spin–orbit parameter ζ for rare earth ions in crystals is nearly a constant and changes slightly from crystal to crystal owing to the different covalence of rare earth clusters in crystals [15–18]. If the covalence of cluster is stronger, the spin–orbit parameter will be smaller. For Yb^{3+} ion in crystals, a lot of studies of optical and EPR spectra showed that $\zeta \approx 2900 \pm 50\ \text{cm}^{-1}$ [9,11,16–20]. For InP:Yb^{3+}, the small spin–orbit parameter ζ ($\approx 2860\ \text{cm}^{-1}$, which is very close to the value, $2864\ \text{cm}^{-1}$, obtained by analyzing only the optical spectrum in Ref. [6]) and the covalence reduction factor $k < 1$ used in the constant P are due to the strong covalence of the host InP crystal. So, they are suitable. Thus, by using four adjustable parameters, the five crystal-field energy levels and three electron paramagnetic resonance spectral data (spin-Hamiltonian parameters) are reasonably explained in a unified way by the diagonalization (of energy matrix) method (see Tables 1 and 2).

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