

Theoretical studies of the spin-Hamiltonian parameters for the orthorhombic Pr^{4+} centers in Sr_2CeO_4 crystals

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Abstract. Theoretical studies of spin-Hamiltonian (SH) parameters associated with Pr^{4+} in Sr_2CeO_4 single crystals have been made by using the complete diagonalizing energy matrix method (CDM) for the $4f^1$ electronic configuration. The calculated results are in excellent agreement with the experimental data. The negative signs of the anisotropic g_i -factors and hyperfine structure constants A_i (where $i = \parallel$ or \perp) for the orthorhombic Pr^{4+} ion in Sr_2CeO_4 are suggested from the calculations. By comparing the results obtained by the CDM with the experimental data, one finds it is valid to interpret the SH parameters for $4f^1$ ions in crystals. The results are discussed.

Keywords. Crystal-field theory; spin-Hamiltonian parameters; Pr^{4+} ; Sr_2CeO_4 .

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1. Introduction

There is much interest in Sr_2CeO_4 which has one-dimensional chain perovskite-type structure. It not only has good potential application in lamps and in emission display field, but also is a good tunable solid-state laser operating at room temperature [1–4]. It is reported that Sr_2CeO_4 is an orthorhombic cell with $a \approx 6.1190$ Å, $b \approx 10.3495$ Å and $c \approx 3.5970$ Å and is isostructural to Sr_2PbO_4 [5,6]. Pr^{4+} ion in the Sr_2CeO_4 crystal replaces the tetravalent Ce^{4+} cation site. The SH parameters (g_i -factors g_{\parallel} , g_{\perp} and hyperfine splitting A_{\parallel} , A_{\perp}) of Pr^{4+} ions in Sr_2CeO_4 crystals were measured by electron paramagnetic resonance (EPR) technique [3]. Until now, no satisfactory theoretical explanations for these SH parameters have been made. As is known, there are two theoretical methods which can be used to explain the EPR spectra (SH parameters g_{\parallel} , g_{\perp} , A_{\parallel} and A_{\perp}) of these central metal ions in crystals, one of which is the CDM and the other is the perturbation theory method (PTM) [7,8]. As suggested in previous studies [7–10], the PTM

takes into account only the contribution of the partial excited states to SH parameters. So sometimes it is difficult to effectively explain the EPR spectra, such as Sr_2CeO_4 . The results of the first-order approximation of PTM disagree with the experimental values (especially g_{\parallel} and A_{\parallel} , whose errors are more than 10%). When the second-order approximation of PTM is being considered, the crystal field terms will introduce into the ground doublet admixtures from the next excited state. However, as pointed out by Birgeneau *et al* [7], corrections of the PTM may lead to rather large corrections to the SH parameters and covalent contributions to the static crystal field far larger than the actual crystal field. Thus, some literatures proposed the more accurate calculation method CDM which considers the contribution of all states to SH parameters of $3d^n$ ions [8–10]. Also, reasonable results were gained from theoretical calculations. But as much as we know, there is no CDM to apply in rare-earth (especially $4f^1$ electronic configuration) ions in crystals. In this paper, we successfully calculate the SH parameters for $\text{Pr}^{4+}4f^1$ complexes in Sr_2CeO_4 crystals by using CDM. A good agreement between theory and experiment suggests that it is effective to explain the SH parameters for the orthorhombic $4f^1$ ion in crystals, and the validity of the results are discussed.

2. Calculation

The Hamiltonian of a $4f^1$ ion in orthorhombic site symmetry can be expressed as [7]

$$H = H_{\text{CF}}(B_k^q) + H_{\text{SO}}(\xi_f) \quad (1)$$

in which H_{CF} and H_{SO} are, respectively, the crystal-field (characterized by the crystal-field parameter B_k^q) and the spin-orbital coupling (characterized by the spin-orbit coupling parameter ξ_f^0 for Pr^{4+} at its free ion value of 865 cm^{-1} [11]). The crystal-field term of the $4f^1$ ion in orthorhombic symmetry can be expressed as

$$\begin{aligned} H_{\text{CF (orth.)}} = & B_2^0 C_2^0 + B_4^0 C_4^0 + B_6^0 C_6^0 + B_2^2 (C_2^2 + C_2^{-2}) \\ & + B_4^2 (C_4^2 + C_4^{-2}) + B_4^4 (C_4^4 + C_4^{-4}) + B_6^2 (C_6^2 + C_6^{-2}) \\ & + B_6^4 (C_6^4 + C_6^{-4}) + B_6^6 (C_6^6 + C_6^{-6}), \end{aligned} \quad (2)$$

where C_k^q is the tensor operator. The crystal-field parameter B_k^q can be calculated from the superposition model [12]. From the model, one can get

$$B_k^q = \sum_{j=1}^n \bar{A}_k(R_0) \left(\frac{R_0}{R_j} \right)^{t_k} Y_k^q(\theta_j, \phi_j), \quad (3)$$

where the angular functions $Y_k^q(\theta_j, \phi_j)$ can be obtained from the local lattice structural parameters of the studied system. The power-law exponents t_k ($k = 2, 4, 6$), for similar tetravalent rare-earth ions Re^{4+} in oxide compounds, $t_2 \approx 7$, $t_4 \approx 11$ and $t_6 \approx 8$ can be taken [13]. $\bar{A}_k(R_0)$ are the intrinsic parameters with the reference distance R_0 . The R_0 in crystals may be different from the corresponding cation-anion distance R_h in the host crystal because the ionic radius r_i of impurity is often

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Table 1. SH parameters (g_i -factors and hyperfine structure constants A_i) (in units of 10^{-4} cm^{-1}) of the orthorhombic Pr^{4+} center in Sr_2CeO_4 crystal.

	$g_{ }$	g_{\perp}	$^{141}A_{ }$	$^{141}A_{\perp}$
Calculation	-1.168	-0.972	-703.5	-666.9
Experiment [3] ^a	1.169	0.966	703	669

^aThe values are actually the absolute values.

unlike the radius r_h of the replaced host ion. We can estimate the distance R_0 from the empirical formula $R_0 \approx R_h + 1/2(r_i - r_h) \approx 2.23 \text{ \AA}$ [14,15]. The structural data R_j and θ_j of Pr^{4+} center in Sr_2CeO_4 can be estimated from ref. [5]. From the weak-field basis functions and eq. (1), the complete energy Hamiltonian matrix (14×14) can be gained for $4f^1$ ion in orthorhombic site symmetry. The SH parameters g_i and A_i (where $i = ||$ or \perp) are related to the Zeeman interaction $H_Z = g_J \mu_B \hat{H} J$ (where the symbols have their usual meanings [6,16]) and the hyperfine interaction $H_{hf} = PN_J \hat{N}$ (where P denotes the dipolar hyperfine structure constant and \hat{N} is the diagonal matrix element for $^{2S+1}L_J$ state [6,16]). Thus, from the crystal-field theory, we have

$$g_{||} = 2g_J \langle \Gamma_{\gamma} | \hat{J}_z | \Gamma_{\gamma} \rangle, \quad (4)$$

$$g_{\perp} = 2g_J \langle \Gamma_{\gamma} | \hat{J}_x | \Gamma_{\gamma'} \rangle, \quad (5)$$

$$A_{||} = 2PN_J \langle \Gamma_{\gamma} | \hat{N}_z | \Gamma_{\gamma} \rangle, \quad (6)$$

$$A_{\perp} = 2PN_J \langle \Gamma_{\gamma} | \hat{N}_x | \Gamma_{\gamma'} \rangle, \quad (7)$$

where Γ_{γ} and $\Gamma_{\gamma'}$ (γ and γ' denote the two components of Γ irreducible representation) are the wave functions of the lowest doublet obtained by diagonalizing the above 14×14 energy matrix, i.e. $|\Gamma_{\gamma}(\gamma')\rangle = \sum_{i=1}^{14} C_i(\Gamma_{\gamma}(\gamma') | J, M_J \rangle$, where C_i are the coefficients of the corresponding states, $J = 5/2$ or $7/2$, M_J are the half-integers in the ranges $-5/2 \rightarrow +5/2$ and $-7/2 \rightarrow +7/2$, respectively. Thus, we consider all excited $^2F_{7/2}$ states admixture in the ground $^2F_{5/2}$ states in the calculations. g_J and N_J can be obtained from refs [6,16]. For free Pr^{4+} ions, the dipolar hyperfine structure constants $P_0(^{141}\text{Pr}) \approx 307 \times 10^{-4} \text{ cm}^{-1}$ can be estimated from the expression $P_0(^{141}\text{Pr}) \approx g_e g_N \beta_e \beta_N \langle r^{-3} \rangle_{\text{av}}$ [6]. Considering the covalence of $\text{Pr}^{4+} - \text{O}^{2-}$ bonds, the orbital reduction factor k should be used (here $k \approx 0.933$). So, $\xi_f \approx k^2 \xi_f^0$ and $P \approx k^2 P_0$. By fitting the calculated SH parameters g_i and A_i to the experimental values, we have

$$\bar{A}_2(R_0) \approx 626 \text{ cm}^{-1}, \quad \bar{A}_4(R_0) \approx 285 \text{ cm}^{-1}, \quad \bar{A}_6(R_0) \approx 2.3 \text{ cm}^{-1}. \quad (8)$$

The calculated SH parameters are compared with the experimental values in table 1.

3. Discussion and conclusion

- (1) From the above calculations, one can find that $\bar{A}_2(R_0)$ is maximum and $\bar{A}_6(R_0)$ is minimum among them for the orthorhombic Pr^{4+} ion in Sr_2CeO_4 crystal. The results agree well with those obtained from many rare-earth ions in crystals [17,18] and can be regarded as reasonable. Based on these suitable intrinsic parameters, the SH parameters $g_{||}, g_{\perp}, A_{||}$ and A_{\perp} for $\text{Sr}_2\text{CeO}_4:\text{Pr}^{4+}$ are reasonably explained.
- (2) From table 1, one finds that by CDM, the SH parameters $g_{||}, g_{\perp}, A_{||}$ and A_{\perp} are in excellent agreement with those from experimental findings. It should be pointed that CDM is also effective for the orthorhombic $4f^1$ ion in other similar crystals.
- (3) It is difficult to determine experimentally the signs of the anisotropic g_i -factors and hyperfine structure constants A_i for f^n and d^n ions in crystals [6,19,20]. So, the experimental results of g_i and A_i given in many systems (including those of Pr^{4+} in Sr_2CeO_4 under the present study) are actually the absolute values [3,19,20]. From our calculations, we find that their signs are negative, which are in agreement with those obtained from many f^n and d^n ions in various crystals [7,9,21,22]. Therefore, they are reasonable. At the same time, the negative signs confirm the experimental prediction, and the doubt is removed.

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