Theoretical Investigations of the EPR g Factors for Er^{3+} in Pr_2CuO_4 Superconductor

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The electron paramagnetic resonance g factors $g_\parallel$ and $g_\perp$ for Er^{3+} in the superconductor Pr_2CuO_4 are investigated by using the perturbation formulas of g factors for a $4f^{11}$ ion in tetragonal symmetry. In these formulas, the contributions to the g factors due to the second-order perturbation terms and the admixture of different states are considered. The crystal field parameters used in the calculations are obtained from the superposition model and the local structural parameters of the impurity Er^{3+} located on the host Pr^{3+} site. The superposition model parameters adopted in this paper are comparable with those for similar tetragonal Er^{3+} centers in some zircon compounds in previous work. The above investigations may be helpful to understand the electronic and magnetic properties and hence the superconductivity of the Er^{3+} doped Pr_2CuO_4.

Key words: EPR; High-T_c Superconductor; Pr_2CuO_4; Crystal Field Theory; Er^{3+}.

1. Introduction

Pr_2CuO_4 belongs to the family of high-T_c electron superconductors $R_{2-x}Ce_xCuO_{4-y}$ (R = Pr, Nd, or Sm), having the T'-type crystal structure of Nd_2CuO_6 instead of the T-type structure of K_2NiF_4 [1, 2]. The magnetic properties of Pr_2CuO_4 (and also this class of compounds) are believed to be of interest considering superconductivities [3 – 6]. Obviously, these properties are closely related to the electronic properties of the CuO_2 plane in the Pr_2CuO_4 superconductor. Since Er^{3+} ion has an effective spin $S' = 1/2$, a large g value ($g \gg 2$) and a long spin-lattice relaxation time compared with other rare earth ions having a non-zero orbital angular momentum, it is suitable to act as electron paramagnetic resonance (EPR) probe in studying the electronic and magnetic properties of CuO_2 planes [7 – 11]. In order to study the relationship between the magnetism and superconductivity, Rettori *et al.* [12] made EPR measurements on the g factors for Pr_2CuO_4:Er^{3+} and obtained $g_\parallel \approx 17.9$ and $g_\perp \leq 0.2$. Up to now, however, the above useful results have not been theoretically investigated. Since information about the electronic properties of Er^{3+} ion in Pr_2CuO_4 is helpful to the understandings of the properties of superconductivity of the host material (or other superconductors in the $R_{2-x}Ce_xCuO_{4-y}$ series), theoretical studies on the g factors of the above Er^{3+} center in Pr_2CuO_4 are significant. In this paper, we investigate theoretically the anisotropic g factors for Er^{3+} in Pr_2CuO_4 by using the perturbation formulas of the g factors for a $4f^{11}$ ion in tetragonal symmetry. In these formulas, the contributions to g factors from the second-order perturbation terms and the admixture of different states are taken into account. The validity of the results is discussed.

2. Calculation

Pr_2CuO_4 belongs to the T'-phase of the R_2CuO_4 (where R denotes a rare earth ion), with I4/mmm symmetry [1, 2, 12]. When the impurity ion Er^{3+} enters the lattice of Pr_2CuO_4, the Er^{3+} would locate on the host Pr^{3+} site with approximately tetragonal (C_{4V}) point symmetry [1, 2]. For an $Er^{3+}(4f^{11})$ ion in tetragonal symmetry, its $^4I_{15/2}$ ground state may be split into eight Kramers doublets. The lowest doublet can be Γ_6

or Γ_7, corresponding to the average value $\bar{g}[=(g_\parallel + 2g_\perp)/3]$ of about 6 or 6.8, respectively [13, 14]. According to the observed $\bar{g}(\approx 5.98 \sim 6.11)$ for Er^{3+} in Pr_2CuO_4 [12], the lowest doublet should be Γ_6. Thus, the perturbation formulas of the g factors for a $4f^{11}$ ion in tetragonal symmetry may be written as [15]:

$$g_\parallel = {g_\parallel}^{(1)} + {g_\parallel}^{(2)}, \tag{1}$$

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

$$g_\perp = {g_\perp}^{(1)} + {g_\perp}^{(2)}, \tag{2}$$

$$\begin{aligned} {g_\perp}^{(1)} &= g_J\langle\Gamma\gamma|\hat{J}_+|\Gamma\gamma'\rangle, \\ {g_\perp}^{(2)} &= 0, \end{aligned}$$

where the Landé factors g_J for various states can be obtained from [13, 14], and the nondiagonal elements g'_J may occur in the expansions of (1) and (2) for the interactions between different ^{2S+1}L configurations. In the above formulas, apart from the contributions to the g factors from the first-order perturbation terms, we also include the contributions from the second-order perturbation terms, which arise from the admixture of the lowest Γ_6 doublet with the other 14 irreducible representations Γ_x (*i.e.*, six Γ_6 and eight Γ_7) due to the tetragonal splitting of the ground $^4I_{15/2}$ and the first excited $^4I_{13/2}$ levels via crystal-field $\hat{H}_{CF}$ and orbital angular momentum $\hat{J}$ interactions [15, 16]. In (2), the second-order perturbation term ${g_\perp}^{(2)}$ vanishes because none of the fourteen Γ_x has a non-zero matrix element with the lowest Γ_6 doublet for both $\hat{H}_{CF}$ and the x or y component of $\hat{J}$ operators. $\Gamma\gamma$ (or γ', where γ and γ' denote the two components of the Γ irreducible representation) is the basis function of the lowest doublet Γ_6. In this basis function, the admixtures of different states are included, *i. e.*, the admixture between the ground $^4I_{15/2}$ and the excited $^4I_{13/2}$ states via crystal-field interaction, the admixture among $^2K_{15/2}$, $^2L_{15/2}$ and $^4I_{15/2}$, and that among $^2K_{13/2}$, $^2I_{13/2}$ and $^4I_{13/2}$ via spin-orbit coupling interaction. Thus, the formula for $\Gamma\gamma$ (or γ') can be expressed as [15, 16]

$$\begin{aligned} |\Gamma\gamma(\text{or }\gamma')\rangle = &\sum_{M_{J1}} C(^4I_{15/2};\Gamma\gamma(\text{or }\gamma')M_{J1})N_{15/2} \\ &\cdot(|^4I_{15/2}M_{J1}\rangle + \lambda_K|^2K_{15/2}M_{J1}\rangle + \lambda_L|^2L_{15/2}M_{J1}\rangle) \\ + &\sum_{M_{J2}} C(^4I_{13/2};\Gamma\gamma(\text{or }\gamma')M_{J2})N_{13/2} \\ &\cdot(|^4I_{13/2}M_{J2}\rangle + \lambda'_K|^2K_{13/2}M_{J2}\rangle + \lambda_I|^2L_{13/2}M_{J2}\rangle), \end{aligned} \tag{3}$$

where M_{J1} and M_{J2} are in the ranges of $-15/2 \sim 15/2$ and $-13/2 \sim 13/2$, respectively. The coefficients $C(^4I_{15/2};\Gamma\gamma(\text{or }\gamma')M_{J1})$ and $C(^4I_{13/2};\Gamma\gamma(\text{or }\gamma')M_{J2})$ can be obtained by diagonalizing the 30×30 energy matrix including $^4I_{15/2}$ and $^4I_{13/2}$ states. N_i and λ_i are, respectively, the normalization factors and the mixing coefficients, which can be determined by using spin-orbit coupling matrix elements and the perturbation method.

For an $Er^{3+}(4f^{11})$ ion in tetragonal (C_{4V}) symmetry, the crystal-field interaction $\hat{H}_{CF}$ in the above formulas may be expressed in terms of the Stevens operator equivalents, *i.e.*, [14, 15]

$$\hat{H}_{CF} = B_2^0O_2^0 + B_4^0O_4^0 + B_6^0O_6^0 + B_4^4O_4^4 + B_6^4O_6^4, \tag{4}$$

where B_k^q(where $k = 2, 4, 6; |q| \le k$) are the crystal-field parameters. According to the superposition model [17], they can be written as

$$B_k^q = \sum_{j=1}^{n} \bar{A}_k(R_0)(R_0/R_j)^{t_k}K_k^q(\theta_j,\phi_j), \tag{5}$$

where $k_k^q(\theta_j,\phi_j)$ are the coordination factors [17, 18] obtained from the local structural data of the studied Er^{3+} center. $\bar{A}(R_0)$ and t_k are, respectively, the intrinsic parameters (with the reference distance R_0) and the power law exponents. In Pr_2CuO_4, the host Pr^{3+} is surrounded by eight nearest O^{2-} ions, with four of them at the distance ${R_1}^H(\approx 2.678$ Å) and the angle $\theta_1(\approx 47.60^\circ)$, and the other four at the quite different distance ${R_2}^H(\approx 2.333$ Å) and the angle $\theta_2(\approx 57.94^\circ$, here θ_j is the angle between ${R_j}^H$ and the four-fold axis of the crystal) [1, 2]. Since the ionic radius $r_i(\approx 0.881$ Å [19]) of the impurity Er^{3+} is smaller than the radius $r_h(\approx 1.013$ Å [19]) of the host Pr^{3+}, the impurity-ligand distances R_j in the doped crystal may be unlike the host values ${R_j}^H$. According to the approximate formulas [20, 21]

$$R_j \approx {R_j}^H + (r_i - r_h)/2 \tag{6}$$

one can reasonably estimate the distances R_j for Pr_2CuO_4:Er^{3+}. Thus, the average impurity-ligand distance $\bar{R}$ (≈ 2.440 Å) is taken as the reference distance

(*i.e.*, $R_0 \approx \bar{R}$). In our previous work [15], the power law exponents $t_2 \approx 7$, $t_4 \approx 12$, $t_6 \approx 11$ and the intrinsic parameters $\bar{A}_2 \approx 280$ cm^{-1} were obtained for similar tetragonal $(ErO_8)^{13-}$ clusters in zircon-type compounds and can be approximately adopted here, with only $\bar{A}_4(R_0)$ and $\bar{A}_6(R_0)$ adjustable. The free ion parameters of the Coulomb repulsion ($F^2 \approx 97476$ cm^{-1}, $F^4 \approx 70733$ cm^{-1} and $F^6 \approx 47742$ cm^{-1}), the two-body interaction parameters ($\alpha \approx 16.66$ cm^{-1}, $\beta \approx -473$ cm^{-1} and $\gamma \approx 1489$ cm^{-1}) and the spin-orbit coupling coefficient ($\zeta_{4f} \approx 2345$ cm^{-1}) in the energy matrix were obtained in [22]. Considering the admixture (or covalency) between the 4f orbitals of the central Er^{3+} ion and the 2p orbitals of the O^{2-} ligands for the Er^{3+}-O^{2-} bond in Pr_2CuO_4:Er^{3+}, the orbital reduction factor $k \approx 0.979$ for the similar Er^{3+}-O^{2-} bond in MgO: Er^{3+} [13, 15, 16] can also be applied in this work.

By substituting these parameters into (1) and (2) and fitting the calculated EPR *g* factors to the observed values, we obtain $\bar{A}_4(R_0) \approx 47.5$ cm^{-1} and $\bar{A}_6(R_0) \approx 13.6$ cm^{-1} for Pr_2CuO_4:Er^{3+}. The corresponding $g_\parallel$ and $g_\perp$ for Er^{3+} in Pr_2CuO_4 are given and compared with the observed values in Table 1. For comparisons, the theoretical results by considering only the first-order perturbation contributions are also calculated and shown in Table 1.

3. Discussion

From Table 1, one can find that the calculated $g_\parallel$ and $g_\perp$ for Er^{3+} in Pr_2CuO_4, based on the second-order perturbation formulas of *g* factors for $4f^{11}$ ions in tetragonal symmetry, agree well with the observed values, suggesting that the perturbation formulas adopted in this work are suitable. In addition, the parameters $\bar{A}_4(R_0) \approx 47.5$ cm^{-1} and $\bar{A}_6(R_0) \approx 13.6$ cm^{-1} for the $(ErO_8)^{13-}$ cluster obtained in this work are also comparable with those $\bar{A}_4(R_0) \approx 23.1 \sim 44.7$ cm^{-1} and $\bar{A}_6(R_0) \approx 15.2 \sim 29.3$ cm^{-1} [15]) for the $(ErO_8)^{13-}$ clusters in zircon-type compounds and can be regarded as reasonable.

Table 1. The EPR *g*-factors for the tetragonal Er^{3+} center in Pr_2CuO_4 superconductor.

	Cal.[a]	Cal.[b]	Expt. [11]
$g_\parallel$	15.84	17.80	17.94 (5)
$g_\perp$	0.04	0.04	≤ 0.2

[a] Calculated results by considering only the first-order perturbation contributions.; [b] Calculated results by considering both the first- and second-order perturbation contributions.

According to our calculations, the contributions to $g_\parallel$ arising from the second-order perturbation terms, having the absolute value of about 2, amount to about 12% of those from the first-order perturbation terms. Therefore, in order to explain the *g* factors for Er^{3+} centers in crystals to a better extent, the second-order perturbation contributions should be taken into account.

Interestingly, the large anisotropy $\Delta g (= g_\parallel - g_\perp \approx 17.9)$ of the observed *g* factors for Pr_2CuO_4:Er^{3+} can be attributed to considerable tetragonal distortion near the Pr^{3+} site occupied by the impurity Er^{3+}, which seems related to the properties of this superconductor. So, the theoretical studies on the EPR *g* factors for the Er^{3+} center in this paper may be helpful for the investigations on the electronic and magnetic properties of the CuO_2 plane in Pr_2CuO_4. The above theoretical methods can also be applied to other tetragonal Er^{3+} centers in high-T_c electron superconductors.

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