Theoretical Investigation of the EPR *g*-factors for Yb^{3+} in $YBa_2Cu_3O_{7-\delta}$

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The EPR *g* factors $g_\parallel$, $g_\perp$ for Yb^{3+} in $YBa_2Cu_3O_{7-\delta}$ are studied with perturbation formulas based on the cluster approach of the spin-Hamiltonian parameters for a $4f^{13}$ ion in tetragonal symmetry. In these formulas, the contributions to the EPR parameters of the covalency effects, the admixture between the $J = 7/2$ and $J = 5/2$ states and the second-order perturbation terms are all included. The used crystal-field parameters are calculated with the superposition model and the local structural data of Yb^{3+} in $YBa_2Cu_3O_{7-\delta}$. The resulting EPR *g* factors for Yb^{3+} ions in the superconductor $YBa_2Cu_3O_{7-\delta}$ agree reasonably with the experimental values. The results are discussed.

Key words: Electron Paramagnetic Resonance; High-Tc Superconductor; Yb^{3+}; $YBa_2Cu_3O_{7-\delta}$.

1. Introduction

$YBa_2Cu_3O_{7-\delta}$ (Y123) has extensively been studied as a well-known high-Tc superconductor [1 – 3]. Y^{3+} can be replaced by most trivalent rare-earth ions (Re^{3+}) without significantly affecting the superconducting behavior. $YBa_2Cu_3O_{7-\delta}$ can be obtained in closely related orthorbombic and tetragonal structures depending on the oxygen content. On the other hand, electron paramagnetic resonance (EPR) studies of rare-earth (Re^{3+}) ions in high-Tc oxide superconductors have attracted much interest because they can provide valuable information on the ground state properties of Re^{3+} ions, which are further employed as sensitive probes of the spin dynamics in high-Tc superconductors [4 – 6]. For example, EPR measurements were performed on Yb^{3+} in $YBa_2Cu_3O_{7-\delta}$ [7]. From the crystal field parameters obtained from other Re^{3+} (Ho^{3+}, Dy^{3+} and Er^{3+} et al.) ions in $YBa_2Cu_3O_{7-\delta}$, and by considering only the interaction within the ground $^2H_{7/2}$ multiplets, S. K. Misra et al. have calculated the EPR *g* factors by using the conventional first-order perturbation formulas [8]. The calculated values are not suitable for the experimental findings, for instance comparing with the experimental value 3.1 the calculated ones $g_\parallel = 2.76$, 2.51 and 1.40 by the crystal field parameters taken from Ho^{3+}, Dy^{3+}, and Er^{3+}, respectively [3, 5, 8]. So, in order to explain satisfactorily the *g*-factors of Yb^{3+} in $YBa_2Cu_3O_{7-\delta}$, further refinement of the crystal field parameters and more exact calculations of *g*-factors are needed.

$YBa_2Cu_3O_{7-\delta}$ has the lattice constants $a \approx 3.8177$ Å, $b \approx 3.8836$ Å, $c \approx 11.6872$ Å [9], i.e., the lattice constant of the *c* axis is about 3 times larger than those of the *a* and *b* axes. However, since *a* is close to *b*, many authors have choosen tetragonal symmetry as a realistic approximation to study the EPR spectra of Re^{3+} ions in $YBa_2Cu_3O_{7-\delta}$ [8, 10]. We also choose the tetragonal symmetry to study the EPR *g*-factors.

In this paper, we use the second-order perturbation formulas of EPR parameters for the $4f^{13}$ ion in tetragonal symmetry. In these formulas the contributions to the EPR parameters due to 1.) the J-mixing between the ground $^2F_{7/2}$ and the excited $^2F_{5/2}$ and the second excited $^6H_{9/2}$ states via crystal-field interactions 2.) the contribution due to mixtures between the lowest Kramers doublet $\Gamma\gamma$ and the other Kramers doublets Γ_X via crystal-field and angular momentum interactions, and 3.) the covalence reduction effects are all considered. From these formulas and the crystal field parameters obtained from the crystal structure by the

aid of Newman's superposition model, the EPR parameters *g* factors for Yb^{3+} in $YBa_2Cu_3O_{7-\delta}$ are calculated. The results are discussed.

2. Calculation

$YBa_2Cu_3O_{7-\delta}$ has the layered perovskite-type structure which belongs to the P_{mmm} space group. The Y^{3+} ion is sandwiched by two CuO_2-planes, which are closely related to the superconductivity, and located apart from CuO-chain site through the BaO layer [9]. For a free Yb^{3+} ion, the electronic configuration is $4f^{13}$ with a $^2F_{7/2}$ ground state and a $^2F_{5/2}$ excited state. When Yb^{3+} ion is located on the Y^{3+} site of $YBa_2Cu_3O_{7-\delta}$, the crystal field splits of the degeneracies of the $^2F_{7/2}$ and $^2F_{5/2}$ states into four and three Kramers doublets, respectively. The lowest lying doublet is Γ_6 or Γ_7, corresponding to the average $\bar{g} \approx 2.667$ or 3.429 to the first order [11]. According to the average value of $\bar{g}[= (g_x + g_y + g_z)/3 \approx 3.433]$ for Yb^{3+} ions in $YBa_2Cu_3O_7$ superconductor, the lowest lying doublet of the system should be Γ_7. Because of the $J-$mixing between the $J = 7/2$ and $J = 5/2$ states via crystal-field interaction, the basis function of the ground doublet $\Gamma\gamma$ can be obtained by diagonalizing a 14×14 energy matrix for the $4f^{13}$ ion in tetragonal symmetry. Thus, we have

$$
\begin{aligned}
|\Gamma\gamma(\text{or }\gamma')\rangle = & \\
& \sum_{M_{J1}} C(^2F_{7/2}; \Gamma\gamma(\text{or }\gamma')M_{J1})|^2F_{7/2}M_{J1}\rangle \\
& + \sum_{M_{J2}} C(^2F_{5/2}; \Gamma\gamma(\text{or }\gamma')M_{J2})|^2F_{5/2}M_{J2}\rangle,
\end{aligned} \tag{1}
$$

where the subscripts γ and γ' denote the two components of the Γ irreducible representation. M_{J1} and M_{J2} are half-integers in the ranges $-7/2$ to 7/2 and $-5/2$ to 5/2, respectively.

Since the other $(4+3-1=6)$ Kramers doublets Γx (which are obtained by diagonalizing the 14×14 energy matrix) may mix with the ground $\Gamma\gamma$ doublet via the crystal-field interaction H_{CF} and angular momentum $\hat{J}$, and so contribute to the EPR parameters, the calculation of the EPR parameters for an $4f^{13}$ ion in tetragonal symmetry should include the second-order contribution. Thus, the perturbation formulas of EPR parameters can be written as

$$
\begin{aligned}
& g_\parallel = {g_\parallel}^{(1)} + {g_\parallel}^{(2)}, \quad {g_\parallel}^{(1)} = 2g_J\langle\Gamma\gamma|\hat{J}_z|\Gamma\gamma\rangle, \\
& {g_\parallel}^{(2)} = 2\sum_X{}' \frac{\langle\Gamma\gamma|\hat{H}_{CF}|\Gamma_X\gamma_X\rangle\langle\Gamma_X\gamma_X|\hat{J}_Z|\Gamma\gamma\rangle}{E(\Gamma_X) - E(\Gamma)}, \\
& g_\perp = {g_\perp}^{(1)} + {g_\perp}^{(2)}, \\
& {g_\perp}^{(1)} = g_J < \Gamma\gamma|\hat{J}_+|\Gamma\gamma'\rangle, \\
& {g_\perp}^{(2)} = 0,
\end{aligned} \tag{2}
$$

where the Lande factors g_J and g'_J (note: the nondiagonal elements g'_J occur in the expansions of (3) for the interactions between different ^{2S+1}L configurations) for various states can be obtained from [11, 12]. Since none of the six Γx has a non-zero matrix element with the ground $\Gamma\gamma$ for both H_{CF} and the *x* or *y* component of $\hat{J}$, in above formulas ${g_\perp}^{(2)} = 0$.

The perturbation Hamiltonian for a rare earth ion in the crystal under an external magnetic field can be written as

$$
\hat{H}' = \hat{H}_{SO} + \hat{H}_{CF} + \hat{H}_Z, \tag{3}
$$

where $\hat{H}_{SO}$ is the spin-orbit coupling interaction and $\hat{H}_{CF}$ is the crystal field Hamiltonian.

$\hat{H}_{SO}$ can be written as

$$
\hat{H}_{SO} = \zeta(\hat{L} \cdot \hat{S}), \tag{4}
$$

where ζ is the spin-orbit coupling coefficient. For a free Yb^{3+} ion, $\zeta = 2950$ cm^{-1}. $\hat{L}$ and $\hat{S}$ are the orbital and spin momentum operators, respectively. The crystal-field interaction $\hat{H}_{CF}$ can be expressed in terms of the tensor operators C_k^q:

$$
\begin{aligned}
\hat{H}_{CF} = & B_2^0C_2^0 + B_4^0C_4^0 + B_4^4(C_4^4 + C_4^{-4}) \\
& + B_6^0C_6^0 + B_6^4(C_6^4 + C_6^{-4}),
\end{aligned} \tag{5}
$$

where the B_k^q are crystal field parameters. The Zeeman interaction $\hat{H}_Z$ can be written as $\hat{H}_Z = g_J\mu_\beta\hat{H} \cdot \hat{J}$, with their original meanings [11, 12].

According to the superposition model of Newman [13], the crystal field parameters B_k^q in (2) can be expressed as

$$
B_k^q = \sum_{j=1}^{n} \bar{A}_k(R_0)(R_0/R_j)^{t_k}K_k^q(\theta_j, \phi_j), \tag{6}
$$

where the $K_k^q(\theta_j, \phi_j)$ are coordination factors which can be obtained from the local structural parameters of the studied $(YbO_8)^{13-}$ cluster. t_k is the power law exponent (here taken as that obtained from the similar $(YbO_8)^{13-}$ cluster in zircon-type crystals, i. e., $t_2 \approx 7$,

Table 1. EPR *g*-factors for Yb^{3+} in $YBa_2Cu_3O_{6+x}$ superconductor.

	Cal.[a]	Cal.[b]	Cal.(tot.)	Expt. [5]
$g_\parallel$	2.4985	0.6048	3.103	3.1
$g_\perp$	3.6051	0	3.6051	3.6[c]

[a] Calculated by using the first-order perturbation formula. [b] Calculated by using the second-order perturbation formula. [c] Here $g_\perp = (g_x + g_y)/2$.

$t_4 \approx 12$, $t_6 \approx 11$, [14]), $\bar{A}_k(R_0)$ is the intrinsic parameter depend on the ligands, R_0 is the reference distance (here $R_0 \approx 2.343$ Å [14]) and R_j is the impurity-ligand distance. Considering the covalency reduction effect, the orbital angular momentum $\hat{L}$ in (3) should be multiplied by an orbit reduction factor k. We take $k \approx 0.948$ here. Generally, $R_j \neq R_H$ (which is the cation-anion distance in the host crystal) because of the different ionic radii of Yb^{3+} and the replaced Y^{3+} ion. R_j can be reasonably estimated from the approximate formula [14, 15]

$$R_j = R_H + (r_i - r_h)/2, \tag{7}$$

where r_i and r_h are the ionic radii of the impurity and the host, respectively. For $YBa_2Cu_3O_{7-\delta}$:Yb^{3+}, $r_i \approx 0.858$ Å, $r_h \approx 0.893$ Å [16]. And from [9] we have $R_H \approx 2.4245$ Å. $\bar{A}_k(R_0)$ is taken as the adjustable parameter obtained by fitting the calculated EPR parameters with the observed values.

Thus, from the above formulas and parameters we find that, to reach good fits between calculated and experimental EPR g factors $g_\parallel$, $g_\perp$ of Yb^{3+} in $YBa_2Cu_3O_{7-\delta}$, these parameters are

$$\begin{aligned} \bar{A}_2(R_0) &\approx 674.2 \text{ cm}^{-1}, \\ \bar{A}_4(R_0) &\approx 29.7 \text{ cm}^{-1}, \\ \bar{A}_6(R_0) &\approx 16.2 \text{ cm}^{-1}, \end{aligned} \tag{8}$$

The comparisons between the calculated and experimental EPR parameters are shown in Table 1.

3. Discussion

From the Table 1 it can be seen that the calculated EPR parameters for Yb^{3+} in the $YBa_2Cu_3O_{6+x}$ superconductor agree well with the observed values. So, these *g*-factors can be explained satisfactorily with the above formulas and parameters, suggesting that these formulas and parameters are reasonable.

The contribution to $g_\parallel$ due to the second-order perturbation terms is about 19%. In our calculation we also find that the contribution to EPR parameters from the admixture between the $^2F_{7/2}$ and $^2F_{5/2}$ multiplets and the covalence effects is not more than 5%. Therefore, in order to obtain the exact calculated results of *g*-factors for Yb^{3+} ions in crystals, the second-order perturbation contribution should be taken into account.

Strictly speaking, the local symmetry at the Y^{3+} (and hence Yb^{3+}) site is of orthorbombic point symmetry. In our calculation we take it as tetragonal symmetry. As the calculated EPR *g*-factors are consistent with the observed values, this approximation and the results can be regarded as valid.

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