Study of the Electron Paramagnetic Resonance Parameters for Copper Ions in Lead Titanate Crystal

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Z. Naturforsch. **66a,** 559 – 561 (2011) / DOI: 10.5560/ZNA.2011-0018
Received January 13, 2011 / revised April 21, 2011

The electron paramagnetic resonance parameters (g factors $g_{\|}, g_{\perp}$ and hyperfine structure constants $A_{\|}, A_{\perp}$) of $PbTiO_3$: Cu^{2+} are calculated from the complete diagonalization method and the perturbation theory method. The calculated results obtained by the complete diagonalization method are close to that obtained by the perturbation theory method, and in good agreement with the experimental values. In the complete diagonalization method, the complete diagonalization procedure is established based on the $3d^9$ electron system in tetragonal field. From the calculation of the electron paramagnetic resonance parameters, the local defect structure of the $[CuO_6]^{-10}$ cluster can be determined as D_{4h} with $R_x = R_y = 0.1952$ nm, $R_z = 0.2076$ nm.

Key words: Electron Paramagnetic Resonance (EPR); Complete Diagonalization Method (CDM); $PbTiO_3$: Cu^{2+}.

PACS numbers: 76.30Fc; 71.55.-i; 61.72.Ww

1. Introduction

The $PbTiO_3$ (PTO) crystal is a kind of ferroelectric and piezoelectric material with perovskite structure [1]. Doping of this crystal can change its nature significantly [2 – 5]. For example, the dielectric properties usually depend on the oxygyen octahedral structure, and it is found that PTO's dielectric property will be changed when Fe^{3+} ions are doped in it [4]. Eichel et al. [6] and Dimza et al. [7] reported the experimental electron paramagnetic resonance (EPR) spectra of PTO: Cu^{2+}, and obtained the EPR parameters from experiments under different conditions. Ravi [8] and other researchers have used the perturbation theory method (PTM) to calculate the EPR parameters of paramagnetic ion doped crystal materials, the calculated values are in agreement with those obtained by experiment. But when we use the PTM to calculate the EPR parameters, there is no way to calculate all order perturbation values. This article uses the complete diagonalization method (CDM) and PTM to calculate the EPR parameters values of PTO: Cu^{2+} crystalline material and compares these two methods.

Cu^{2+} is a $3d^9$ configuration ion. When paramagnetic ions Cu^{2+} are doped to PTO, Cu^{2+} will replace the position of Ti^{4+} ions. Since both Cu^{2+} ions and the replaced ions are different in charges and ionic radii, the ligand ions will make a certain displacement. Since $g_{\|} > g_{\perp} > 2.0023$ [7], the ground state is the $^2b_{1g}$ state, and Cu^{2+} ions are located in the elongated distorted octahedral site (D_{4h}).

2. Calculation

The Hamiltonian including the electron-electron repulsion, the spin-orbit interaction, and the crystal-field potential is given by $H = H_e + H_{CF} + H_{SO}$. For a $3d^9$ configuration ion, a cubic crystal field will split the 5-fold degenerate energy level into an orbital doublet ^2e_g and triplet $^2t_{2g}$. In the tetragonal crystal field, the doublet ^2e_g level splits into two nondegenerate orbital singlets $^2a_{1g}$ and $^2b_{1g}$, and the $^2t_{2g}$ splits into a doublet ^2e_g and a singlet $^2b_{2g}$. We let the three orbital singlets $^2a_{1g}$, $^2b_{1g}$, $^2b_{2g}$, and a doublet ^2e_g be the basis functions of Sugano strong field. The spin-orbit coupling matrix elements of the $3d^9$ ions can be calculated by $\langle\psi|H_{SO}|\psi\rangle$, where $H_{SO} = \sum_{i=1}^{n} H_{SO}(i) = \sum_{i=1}^{n} \zeta_d \boldsymbol{l}(i) \cdot \boldsymbol{s}(i)$, and ζ_d is the spin-orbit coupling coefficient. According to the covalence reduction effect for $3d^n$ ions

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in crystals, $\zeta_d = N^2\zeta_0$, in which N is the average covalency factor, and ζ_0 is the corresponding value of the free $3d^n$ ion. For a free Cu^{2+} ion, $\zeta_0 = 829\,cm^{-1}$ [9].

Using the Sugano strong field bases, the crystal field potential matrix elements in tetragonal symmetry are derived as:

$$\begin{aligned}
\langle a_{1g}|H_{CF}|a_{1g}\rangle &= -6Dq + 2Ds + 6Dt,\\
\langle b_{1g}|H_{CF}|b_{1g}\rangle &= -6Dq - 2Ds + Dt,\\
\langle b_{2g}|H_{CF}|b_{2g}\rangle &= 4Dq - 2Ds + Dt,\\
\langle e_g|H_{CF}|e_g\rangle &= 4Dq + Ds - 4Dt.
\end{aligned} \tag{1}$$

According to the Newman's superposition model [10], the crystal field parameters Dq, Ds, and Dt for the studied system can be expressed as:

$$\begin{aligned}
Dq &= \frac{4}{3}\bar{A}_4(R_0)\left(\frac{R_0}{R_\perp}\right)^{t_4},\\
Ds &= -\frac{4}{7}\bar{A}_2(R_0)\left[\left(\frac{R_0}{R_\parallel}\right)^{t_2} - \left(\frac{R_0}{R_\perp}\right)^{t_2}\right],\\
Dt &= -\frac{16}{21}\bar{A}_4(R_0)\left[\left(\frac{R_0}{R_\parallel}\right)^{t_4} - \left(\frac{R_0}{R_\perp}\right)^{t_4}\right].
\end{aligned} \tag{2}$$

$\bar{A}_4(R_0)$ and $\bar{A}_2(R_0)$ are the intrinsic parameters, $\bar{A}_2(R_0) \approx n\bar{A}_4(R_0)$, $n \approx 9 \sim 12$ [10, 11] for $3d^n$ ions. Here we take $\bar{A}_2(R_0) = 12\bar{A}_4(R_0), \bar{A}_4(R_0) = 615\,cm^{-1}$ [10, 11]. For PTO: $Cu^{2+}, R_\parallel^H \approx 0.2076$ nm, $R_\perp^H \approx 0.1952$ nm [2, 3, 5–7], corresponding reference bond length $R_0 = (2R_\parallel^H + 4R_\perp^H)/6 \approx 0.1993$ nm. t_2 and t_4 are the power-law exponents for $3d^n$ ions, $t_2 \approx 3$, $t_4 \approx 5$ [10, 11]. The impurity-ligand distances $R_\perp$ can be calculated from the approximate formula [12]

$$R_\perp \approx R_\perp^H + \frac{r_i - r_h}{2}, \tag{3}$$

where r_i and r_h are the ionic radii of impurity and that of the replaced host ion, respectively. In the PTO: $Cu^{2+}, r_i(Cu^{2+}) \approx 0.072$ nm, $r_h(Ti^{4+}) \approx 0.068$ nm, and $r_h(Pb^{2+}) \approx 0.12$ nm [13]. The value of $R_\perp$ is determined by (3), and remains invariant in the fitting calculation. For fitting the calculated $g_\parallel$, $g_\perp$, $A_\parallel$, and $A_\perp$ to the observed values, we take $N, R_\parallel$ (or $\triangle R_\parallel$) as adjustable parameters.

Neglecting the contribution of the ligand spin-orbit coupling and diagonalizing the complete energy matrix (10×10), we obtained the ground state to be b_{1g} which is consistent with the fact that the eigenvectors are Kramers degenerate. The formulas of g factors for a $3d^9$ ion in tetragonal symmetry can be expressed as:

$$\begin{aligned}
g_\parallel &= 2\langle +|kl_z + 2.0023s_z|+\rangle,\\
g_\perp &= 2\langle +|kl_x + 2.0023s_x|-\rangle,
\end{aligned} \tag{4}$$

where $|+\rangle$ and $|-\rangle$ are the diagonalized wavefunctions of ground states, k is the orbital reduction factor, $k = N^2, l_z$, and l_x the operators of the orbital angular momentum, s_z and s_x the operators of the spin angular momentum. According to the work of [14], the forms for the Cu^{2+} hyperfine structure constant A are given by

$$\begin{aligned}
A_\parallel &= P\left[\left(-\kappa - \frac{4}{7}\right) + (g_\parallel - g_s) + \frac{3}{7}(g_\perp - g_s)\right],\\
A_\perp &= P\left[\left(-\kappa + \frac{2}{7}\right) + \frac{11}{14}(g_\perp - g_s)\right],
\end{aligned} \tag{5}$$

where $g_s(\approx 2.0023)$ is the free-electron spin g-value. P is the dipole hyperfine coupling constant. κ, the core polarization constant. For PTO: Cu^{2+}, $P = N^2P_0, P_0(Cu^{2+}) \approx 388 \cdot 10^{-4}\,cm^{-1}$ [15].

According to the high-order perturbation method [16], the third-order perturbation formulas of g factors for a $3d^9$ ion in tetragonal symmetry can be expressed as [12]:

$$\begin{aligned}
g_\parallel &= g_s + \frac{8N^2\zeta}{E_1} - \frac{(g_s + N^2)\zeta^2}{E_2^2} - \frac{4N^2\zeta^2}{E_1E_2},\\
g_\perp &= g_s + \frac{2N^2\zeta}{E_2} - \frac{(g_s/2 - N^2)\zeta^2}{E_2^2} - \frac{2g_s\zeta^2}{E_1^2}.
\end{aligned} \tag{6}$$

The energy separations E_1 and E_2 can be written as $E_1 = E(b_{2g}) - E(b_{1g}) = 10Dq, E_2 = E(e_g) - E(b_{1g}) = 10Dq + 3Ds - 5Dt$. In the calculation, the fitting parameters are taken as $N = 0.8265, R_\parallel = 0.213$ nm, $\kappa = 0.2937$.

The original tetragonal symmetry of the PTO crystal is distorted to D_{4h} after Cu^{2+} is doped. According to the calculation, Cu^{2+} may replace the Ti^{4+}, and the bond lengths become $R_x = R_y = 0.1952$ nm, $R_z = 0.2076$ nm.

The calculated EPR parameters together with the experimental values are shown in Table 1.

The A factor is an absolute value in the experiment.

Table 1. EPR parameters of PTO : Cu^{2+}.

	$g_\parallel$	$g_\perp$	$A_\parallel(10^{-4}\,cm^{-1})$	$A_\perp(10^{-4}\,cm^{-1})$
PTM	2.343	2.058	−133	9
CDM	2.340	2.058	−133	9
Exp. [7]	2.340	2.058	131.0	9

3. Discussion

It can be seen easily from Table 1 that the values of $g_{\|}, g_{\perp}$, and $A_{\perp}$ calculated by CDM are in good agreement with the experimental values; the absolute value of $A_{\|}$ is also in agreement with the experimental one, but the sign is negative. In fact, the sign of the hyperfine structure constants is very difficult to determine. Thus, many experiments give it as a positive one. From the above calculation, we take the sign of $A_{\|}$ as negative, which is consistent with the values in many other materials given in [14]. The EPR parameters obtained by PTM are also in good agreement with the observed values (see Table 1).

In this paper, we use two methods to calculate the EPR parameters of PTO: Cu^{2+}, one is the perturbation theory method (PTM), whereas the other is the complete diagonalization method (CDM). We used the $3d^9$ electron system in tetragonal field to build diagonalization procedure. As seen from Table 1, the results obtained by CDM are very close to that obtained by PTM, and agree well with the experimental values. We can determine the bond lengths to $R_x = R_y = 0.1952$ nm, $R_z = 0.2076$ nm and the local defect structure of PTO: Cu^{2+} to be D_{4h} from the EPR parameters calculation.

Acknowledgement

This work is supported by the Key Program of Scientific Research Foundation of Education Bureau of Sichuan Province, China (Grant No. 10ZA002).

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