Defect Structure of the Tetragonal Cu^{2+} Center in $PbTiO_3$: Cu^{2+} Crystal

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The defect structure of the tetragonal Cu^{2+} center in $PbTiO_3$: Cu^{2+} crystal is studied by analyzing the EPR g factors and hyperfine structure constants. From the study, we suggest that an oxygen vacancy occurs in the nearest-neighbors site of Cu^{2+} due to charge compensation, and that the off-center displacement of Cu^{2+} is smaller than that of the replaced host ion Ti^{4+}. The reasonableness of the defect structure is discussed.

Key words: Defect Structure; Electron Paramagnetic Resonance; Crystal-field Theory; Cu^{2+}; $PbTiO_3$

1. Introduction

The perovskite titanate oxides $ATiO_3$ have been extensively studied because of the technological importance of the materials [1, 2]. In these studies, the role of dopant impurities receives considerable attention, because the impurities can influence the properties of the material. The transition-metal ($3d^n$) ions are often readily incorporated in these materials and thought to occupy the Ti site. Since the size and charge of the impurity ion are often different from those of the replaced host ion, the local structure in the vicinity of the impurity may be unlike that in the pure crystal. The EPR spectra of $3d^n$ ions are sensitive to the defect (or local) structure of impurity centers, so one can obtain information on the local structure of these impurity centers by analyzing their EPR data. For example, for perovskite titanate oxides $ATiO_3$, the local structures for Cr^{3+} and Fe^{3+} in $BaTiO_3$ [3, 4] and Cr^{3+} and Mn^{2+} in $PbTiO_3$ [5, 6] were studied by analyzing their EPR data. However, for Cu^{2+} in $PbTiO_3$, the local structure has not been studied, although the EPR g factors and hyperfine structure constants were measured. In this paper, we study the defect structure of the Cu^{2+} center in $PbTiO_3$: Cu^{2+} crystal.

2. Calculation

The crystal structure of $PbTiO_3$ at room temperature is tetragonal with the space group P4mm. The lattice constants are $a = 3.896$ Å and $c = 4.14$ Å [5, 8]. The Ti^{4+} ion in $PbTiO_3$ is shifted by about 0.3 Å from the center of the oxygen octahedron along the C_4 axis (see Fig. 1). Cu^{2+}in $PbTiO_3$ replaces the Ti^{4+} ion. From the observed g factors (i.e., $g_\parallel > g_\perp > g_e$ [7], where $g_e = 2.0023$) it can be expected that the ground state of Cu^{2+} is $|x^2 - y^2\rangle$. Thus, from the perturbation method, the high-order perturbation formulas of EPR parameters $g_\parallel$, $g_\perp$, $A_\parallel$, and $A_\perp$ for the $3d^9$ ion in tetragonal symmetry can be derived as

$$g_\parallel = g_e + \frac{8k\zeta}{E_1} + \frac{k\zeta^2}{E_2^2} + \frac{4k\zeta^2}{E_1E_2} - \frac{g_e\zeta^2}{4E_1^2} + \frac{g_e\zeta^2}{2E_2^2} + \frac{6k\zeta^3}{E_1E_2^2} - \frac{k\zeta^3}{E_2^3} - \frac{4k\zeta^3}{E_1^2E_2} + \frac{g_e\zeta^3}{E_1E_2^2} - \frac{g_e\zeta^3}{2E_2^3},$$

$$g_\perp = g_e + \frac{2k\zeta}{E_2} - \frac{2k\zeta^2}{E_1E_2} - \frac{k\zeta^2}{E_2^2} + \frac{2g_e\zeta^2}{E_1^2} + \frac{2k\zeta^3}{E_1^2E_2} - \frac{k\zeta^3}{2E_2^3} - \frac{g_e\zeta^3}{2E_2^3} + \frac{g_e\zeta^3}{2E_1E_2^2}, \quad (1)$$

$$A_\parallel = P\left(-\frac{4}{7} - \kappa + \frac{8k\zeta}{E_1} + \frac{6k\zeta}{7E_2} - \frac{3k\zeta^2}{7E_2^2} - \frac{40k\zeta^2}{7E_1E_2} + \kappa\frac{\zeta^2}{E_2^2}\right),$$

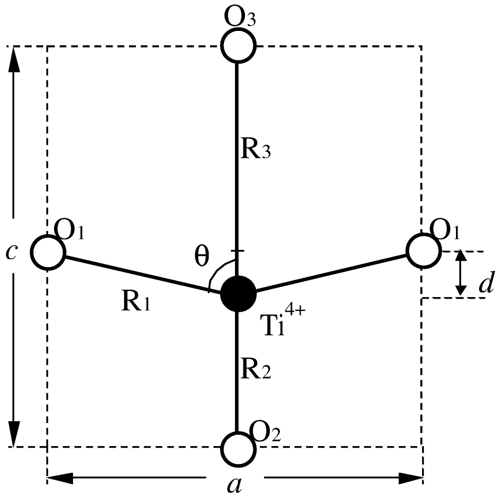

Figure 1. Structure of $PbTiO_3$.

$$A_\perp = P\left(\frac{2}{7} - \kappa + \frac{11k\zeta}{7E_2} + \frac{11k\zeta^2}{7E_1E_2} + \frac{9k\zeta^2}{14E_2^2} - \frac{4k\zeta^2}{7E_1^2} + \kappa\frac{\zeta^2}{2E_2^2} + \kappa\frac{2\zeta^2}{E_1^2}\right), \quad (2)$$

where $k(\approx \zeta/\zeta_0 \approx P/P_0)$ is the orbital reduction factor. ζ is spin-orbit coupling coefficient for a $3d^9$ ion in the crystal, and ζ_0 (= 829 cm^{-1} for Cu^{2+} [9]) the corresponding coefficient of a free $3d^9$ ion. P and P_0 are the dipolar hyperfine parameters in the crystal and free state, respectively (for $^{63}Cu^{2+}$, $P_0 = 388 \cdot 10^{-4}$ cm^{-1}, and for $^{65}Cu^{2+}$, $P_0 = 416 \cdot 10^{-4}$ cm^{-1} [10]). κ is the core polarization constant (for a $3d^9$ ion, κ is near 0.3 [11, 12]. We take $\kappa = 0.31$ here). The energy separations E_i are

$$E_1 = \varDelta', \; E_2 = \varDelta' - 3D_s + 5D_t. \quad (3)$$

For the above tetragonal symmetry, from the superposition model [13] the crystal-field parameters $\varDelta'$, D_s, and D_t can be written as

$$\varDelta' = \frac{40}{3}\bar{A}_4(R_0)\left(\frac{R_0}{R}\right)^{t_4}\sin^4\theta,$$

$$D_s = \frac{4}{7}\bar{A}_2(R_0)\left[(3\cos^2\theta - 1)\left(\frac{R_0}{R_1}\right)^{t_2} + \frac{1}{2}\left(\frac{R_0}{R_2}\right)^{t_2} + \frac{1}{2}\left(\frac{R_0}{R_3}\right)^{t_2}\right],$$

Table 1. EPR parameters (g-shift $\Delta g = g - g_e$ and hyperfine structure constants) for Cu^{2+} in $PbTiO_3$.

	$\Delta g_\parallel$	$\Delta g_\perp$	$A_\parallel(10^{-4}\ cm^{-1})$ $^{63}Cu^{2+}$	$A_\parallel(10^{-4}\ cm^{-1})$ $^{65}Cu^{2+}$	$A_\perp(10^{-4}\ cm^{-1})$ $^{63}Cu^{2+}$	$A_\perp(10^{-4}\ cm^{-1})$ $^{65}Cu^{2+}$
Calc.[a]	0.092	0.340	−159	−170	15	16
Calc.[b]	0.083	0.326	−163	−175	13	13
Calc.[c]	0.059	0.337	−166	−178	6	6
Expt.[7][d]	0.056(1)	0.338(1)	−155(2)	−166(2)	5.4(2.0)	5.8(2.0)

[a] Calculation using the displacement $d = 0.30$ Å and orbital reduction factor $k = 0.77$ for the Cu^{2+} center. [b] Calculation using the displacement $d = 0.24$ Å and orbital reduction factor $k = 0.77$ for the Cu^{2+} center. [c] Calculation using the displacement $d = 0.19$ Å and orbital reduction factor $k = 0.80$ for the Cu^{2+}-V_O center. [d] The signs of experimental $A_\parallel$ and $A_\perp$ are not given in [7].

$$D_t = \frac{8}{21}\bar{A}_4(R_0) \cdot \left[\frac{1}{2}(35\cos^4\theta - 30\cos^2\theta + 3 - 7\sin^4\theta)\left(\frac{R_0}{R_1}\right)^{t_4} + \left(\frac{R_0}{R_2}\right)^{t_4} + \left(\frac{R_0}{R_3}\right)^{t_4}\right], \quad (4)$$

where t_2 and t_4 are the power-law exponents. We take $t_2 = 3$ and $t_4 = 5$ because of the ionic nature of the bonds [13–15]. $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are the intrinsic parameters with the reference distance R_0. The ratio $\bar{A}_2(R_0)/\bar{A}_4(R_0)$ is in the range of 9–12 for $3d^n$ ions in many crystals [14–17]. We take $\bar{A}_2(R_0)/\bar{A}_4(R_0) = 9$ here. For a $3d^n$ ion in an octahedron, $\bar{A}_4(R_0) = 3/4D_q$ [13–15], where D_q is the cubic field parameter which can be estimated from the optical spectra of the studied system. No optical spectra data for $PbTiO_3$:Cu^{2+} were reported. We estimate $\bar{A}_4(R_0)$ from Cu^{2+} in the similar crystal $LiNbO_3$. From the optical spectra of $LiNbO_3$: Cu^{2+} [18], we yield for $(CuO_6)^{10-}$ octahedra, $D_q = 820$ cm^{-1}, and hence $\bar{A}_4(R_0) = 615$ cm^{-1} with $R_0 = 2.153$ Å. The structural parameters R_i and θ are shown in Figure 1. Thus, we have

$$R_1 = \sqrt{\left(\frac{a}{2}\right)^2 + d^2}, \quad \cos\theta = \frac{d}{R_1},$$
$$R_2 = \frac{c}{2} - d, \quad R_3 = \frac{c}{2} + d. \quad (5)$$

If we assume that in $PbTiO_3$:Cu^{2+}, the immediate environment of Cu^{2+} is the same as that of the replaced Ti^{4+} ion, then from the structural data a, c and d of the host $PbTiO_3$, and by adjusting the reduction factor k, we find that the calculated $\Delta g_\parallel$, $\Delta g_\perp$, $A_\parallel$, and $A_\perp$

do not agree with the observed values. The best results obtained by taking $k = 0.77$ are shown in Table 1.

One possibility of improving the calculated results is the following (which was used by some authors in studies of EPR data for $3d^n$ ions Cr^{3+} and Mn^{2+} in $PbTiO_3$ [5, 6]). The Cu^{2+} ion does not occupy the exact position of Ti^{4+} but is shifted along C_4 axis. Thus, by adjusting the off-center displacement d, we find that with $d = 0.24$ Å the calculated results are only slightly improved (see Table 1). Another possibility is that the local lattice constants a_{loc} and c_{loc} are slightly greater than the corresponding host values because the ionic radius [19] of Cu^{2+} is slightly greater and the charge is less than those of the replaced Ti^{4+} ion. However, even if we increase the values of a and c within a factor of 10% and adjust the parameters k and d, little improvement is found for the calculated EPR parameters. So, other possibility should be considered.

Since the charge of the Cu^{2+} ion is less than that of the replaced Ti^{4+} ion, an oxygen vacancy (V_O) may occur on the nearest-neighbor site of Cu^{2+} (so the Cu^{2+} center is called Cu^{2+}-V_O center) due to charge compensation. A similar Fe^{3+}-V_O center was found in $PbTiO_3$ [20–22], and M^{n+}-V_O (where M denotes a $3d^n$ ion, such as Fe^{3+}, Mn^{2+}, Co^{2+} and Cu^{2+}) centers in other perovskite oxides $KTaO_3$, $KNbO_3$, $BTiO_3$ and $SrTiO_3$ [14, 21–25]. So, the Cu^{2+}-V_O center in $PbTiO_3$:Cu^{2+} is possible. The tetragonal symmetry of the Cu^{2+}-V_O center in $PbTiO_3$ suggests that the V_O should be on an O_2 or O_3 site along the C_4 axis. Thus, in (4) the terms related to R_2 or R_3 should vanish. Since the effective charge of V_O is positive, the Cu^{2+} ion should be displaced away from V_O owing to electrostatic repulsion, and so the off-center displacement d of Cu^{2+} should differ from that of Ti^{4+}. By adjusting the parameters k and d, we find that when V_O is on an O_2 site and $d = 0.19$ Å and $k = 0.80$ are used, all the calculated EPR parameters show good agreement with the observed values. Comparisons between the calculated and experimental EPR parameters are shown in Table 1.

3. Discussion

The signs of $A_{\parallel}$ and $A_{\perp}$ for the isotopes $^{63}Cu^{2+}$ and $^{65}Cu^{2+}$ in $PbTiO_3$ were not reported. From the above calculations we suggest that for both isotopes $A_{\parallel}$ is negative and $A_{\perp}$ is positive.

As has been mentioned above, the positive effective charge of V_O should repulse the Cu^{2+}ion along C_4 axis, which results in a smaller off-center displacement d of Cu^{2+} than that ($= 0.30$ Å) of Ti^{4+}. So, the above local displacement $d = 0.19$ Å is reasonable. In addition, similar M^{n+}-V_O centers were reported in $PbTiO_3$ and also in the perovskite oxides $KTaO_3$, $KNbO_3$, $BTiO_3$ and $SrTiO_3$, so we suggest that the observed Cu^{2+} center in $PbTiO_3$ is a Cu^{2+}-V_O center with a smaller off-center displacement of Cu^{2+}. This point remains to be further checked.

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