# Investigations on the Spin–Hamiltonian Parameters and Local Structure of the Orthorhombic Cu²⁺ Center in PbTiO₃ Crystal

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The spin–Hamiltonian parameters (the $g$ factors $g_i$ and the hyperfine structure constants $A_i$, $i = x$, $y$, $z$) and local structure of the Cu²⁺ center in PbTiO₃ are theoretically studied by using the perturbation formulae of these parameters for a $3d^9$ ion in an orthorhombically elongated octahedra. The orthorhombic center is attributed to Cu²⁺ occupying the host Ti⁴⁺ site associated with a nearest–neighbouring oxygen vacancy $V_O$ along the $c$–axis, and the impurity Cu²⁺ off-center displacement $\Delta Z_L$ ($\approx 0.18$ Å) is smaller than that of the host Ti⁴⁺ site ($\Delta Z_H \approx 0.3$ Å). Meanwhile, the planar Cu²⁺–O²⁻ bonds are found to experience the relative variation $\Delta R$ ($\approx 0.098$ Å) along the $a$- and $b$-axes, respectively, due to the Jahn–Teller effect and the size mismatching substitution of Ti⁴⁺ by Cu²⁺. The theoretical spin-Hamiltonian parameters based on the above defect structure agree well with the observed values.

## 1. Introduction

PbTiO₃ as a member of ferroelectric perovskite family is a potential material with the technological applications in ferroelectric-volatile memory devices and piezoelectric actuators [1–3]. The physical and chemical properties of perovskites may be selectively changed by doping with transition-metal (TM) ions. For understanding the properties caused by these doping ions, many electron paramagnetic resonance (EPR) spectra of PbTiO₃ doped with TM impurities have been made [4–8]. The EPR technique is a powerful tool to study the defect model and defect structure of paramagnetic impurity centers in crystals. These studies show that divalent and trivalent states of substitutional $3d^n$ ions at Ti⁴⁺ site can be charge compensated by a nearest-neighbour oxygen vacancy $V_O$, and the microstructure of these $M^{n+} - V_O$ centers has attracted the attention of many investigators [9–11]. Amongst these TM ions, Cu²⁺ ($3d^9$) ion is a model system with a single $3d$ hole, corresponding to only one ground state and one excited state under ideal octahedral crystal-fields. EPR studies for Cu²⁺ can provide important structural and electronic information of the doped materials and are of specific significance. For example, Warren et al. [12] performed EPR studies on Cu²⁺ doped in PbTiO₃, and the spin-Hamiltonian (SH) parameters (the $g$ factors $g_i$ and the hyperfine structure constants $A_i$, $i = x$, $y$, $z$) were also measured. The observed $g$ factor ($g_x \approx 2.051$, $g_y \approx 2.065$, and $g_z \approx 2.340$ [12]) of the orthorhombic center for PbTiO₃:Cu²⁺ was very close to that ($g_x \approx 2.106$, $g_y \approx 2.076$, and $g_z \approx 2.381$ [13]) for the impurity Cu²⁺ ion doped in LiNbO₃ with or-

thorhombic [CuO₅]⁸⁻ cluster. Therefore, there are good reasons to assume that the observed SH parameters of the orthorhombic center for PbTiO₃:Cu²⁺ was due to the impurity Cu²⁺ substituting Ti⁴⁺ site with one nearest neighbour oxygen vacancy $V_O$ along the $c$ axis as the compensator similar as LiNbO₃:Cu²⁺ [13].

Up to now, however, the above experimental SH parameters have not been theoretically explained, and the information about local structures of the impurity Cu²⁺ in PbTiO₃ has not been obtained yet. Considering that microscopic mechanisms of the SH parameters and information of impurity local structures can be helpful to understand the properties of these TM ion doped materials, further theoretical investigations on these SH parameters and the local structures for the Cu²⁺ center in PbTiO₃ are of scientific and technical significance. In this paper, the high (fourth) order perturbation formulae of the SH parameters for a $3d^9$ ion under orthorhombically elongated octahedra are adopted for the analysis of the above Cu²⁺ center. Based on these studies, some useful information of defect structures for Cu²⁺ in PbTiO₃ can be acquired.

## 2. Calculations

In PbTiO₃ crystal, both the host Pb²⁺ and Ti⁴⁺ ions suffer large displacements from their corresponding oxygen planes by about 0.47 and 0.3 Å at room temperature, resulting in a colossal tetragonality of 6.5% along with a 0.75 C/m² spontaneous polarization [14, 15]. When the impurity Cu²⁺ ion enters the lattice of PbTiO₃, it may occupy the Ti⁴⁺ site due to similar ionic radius, despite of its significant charge mismatch. Since Cu²⁺ has less charge as compared with the replaced Ti⁴⁺, one nearest neighbour oxygen vacancy $V_O$ may occur along the $c$-axis as compensator, forming [CuO₅]⁸⁻ cluster. For the Jahn–Teller ion Cu²⁺, the planar ligands can suffer a relative bond length variation due to the Jahn–Teller effect

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via vibration interaction by compressing and stretching the $Cu^{2+}$–$O^{2-}$ bonds along the $a$- and $b$-axes, respectively, which can bring forward moderate orthorhombic distortion to the impurity center. Meanwhile, the charge mismatching substitution of $Ti^{4+}$ by $Cu^{2+}$ may also lead to some modifications of the planar bond lengths. On the other hand, the impurity $Cu^{2+}$ off-center displacement $\Delta Z_L$ would be dissimilar to that ($\Delta Z_H \approx 0.3$ Å [15]) for the host $Ti^{4+}$ site.
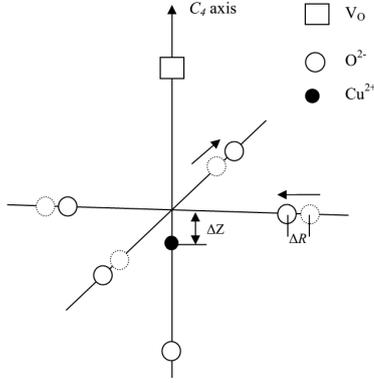


Fig. 1. Projective view of the impurity $Cu^{2+}$ center in $PbTiO_3$ crystal with one oxygen vacancies adjacent along $C_4$ axis.

As a result, the local structure of the impurity center can be described by the $[CuO_5]^{8-}$ cluster and the impurity off-center displacement (characterized by $\Delta Z_L$) and the relative planar bond length variation (characterized by $\Delta R$) (see Fig. 1). Consequently, the impurity-ligand bond lengths are divided into three groups, i.e., the planar ones labeled as "$R_1$" and "$R_2$" along the $a$- and $b$-axes due to the bond length variation $\Delta R$ and the off-planar one labeled as "$R_3$" along the $c$-axis. The angles between the planar bond lengths $R_1$ and $R_2$ and the $c$-axis are defined as $\theta_1$ and $\theta_2$, respectively. The local bond lengths and bond angles are determined as

$$R_1 \approx [(R_\perp - \Delta R)^2 + \Delta Z_L^2]^{1/2},$$

$$R_2 \approx [(R_\perp + \Delta R)^2 + \Delta Z_L^2]^{1/2}, R_3 \approx R_\parallel - \Delta Z_L,$$

$$\cos\theta_1 \approx \Delta Z_L / R_1, \quad \cos\theta_2 \approx \Delta Z_L / R_2. \quad (1)$$

Thus, the impurity-ligand bonding lengths are unlike the host Ti–O distances $R_\parallel \approx 2.076$ Å and $R_\perp \approx 1.952$ Å [15] parallel and perpendicular to the $c$-axis for the center of the oxygen octahedron in the host $PbTiO_3$.

For a $Cu^{2+}$ ($3d^9$) ion in orthorhombically elongated octahedra, its lower orbital doublet $^2E_g$ would be separated into two singlets $^2A_{1g}(\theta)$ and $^2A'_{1g}(\varepsilon)$, with the latter lying lowest [16, 17]. Meanwhile, the higher cubic orbital triplet $^2T_{2g}$ would be split into three singlets $^2B_{1g}(\zeta)$, $^2B_{2g}(\eta)$ and $^2B_{3g}(\xi)$ [16, 17]. Considering that the spin–orbit parameter $\zeta_p^0$ ($\approx 150$ cm$^{-1}$ [18]) of ligand $O^{2-}$ is much smaller than that $\zeta_d^0$ ($\approx 829$ cm$^{-1}$ [19]) of the central ion $Cu^{2+}$, the contributions to SH parameters due to

the spin–orbit parameter of ligand via covalence effect is small and can be omitted, as in the conventional crystal-field theory. Then, the high order perturbation formulae of the SH parameters based on the conventional crystal-field model [18] containing merely the central ion orbital and spin–orbit coupling contributions can be reasonably adopted here. Thus, we have

$$g_x = g_s + \frac{2k\varsigma}{E_2} + k\varsigma^2 \frac{2E_3 - E_1 - 4E_2}{E_1 E_2 E_3}$$

$$+ g_s\varsigma^2 \frac{4E_2^2 E_3^2 - E_1^2 E_3^2 - E_1^2 E_2^2}{2E_1^2 E_2^2 E_3^2}$$

$$- k\varsigma^3 \left[ \frac{E_1(E_3^2 - E_2^2) + E_3(4E_2^2 - E_1^2)}{2E_1^2 E_2^2 E_3^2} - \frac{E_3 - E_2}{2E_2^2 E_3 E_4} \right]$$

$$+ g_s\varsigma^3 \frac{E_1^2 E_3^2 + 2E_1^2 E_2^2 - E_1^2 E_2 E_3 + 2E_2 E_3^3 - 2E_2^2 E_3^2 - 2E_1 E_2^2 E_3}{4E_1^2 E_2^2 E_3^3},$$

$$g_y = g_s + \frac{2k\varsigma}{E_3} + k\varsigma^2 \frac{2E_2 - E_1 - 4E_3}{E_1 E_2 E_3}$$

$$+ g_s\varsigma^2 \frac{4E_2^2 E_3^2 - E_1^2 E_2^2 - E_1^2 E_3^2}{2E_1^2 E_2^2 E_3^2}$$

$$- k\varsigma^3 \left[ \frac{E_1(E_2^2 - E_3^2) + E_2(4E_3^2 - E_1^2)}{2E_1^2 E_2^2 E_3^2} - \frac{E_2 - E_3}{2E_2 E_3^2 E_4} \right]$$

$$+ g_s\varsigma^3 \frac{E_1^2 E_2^2 + 2E_1^2 E_3^2 - E_1^2 E_2 E_3 + 2E_2^3 E_3 - 2E_2^2 E_3^2 - 2E_1 E_2 E_3^2}{4E_1^2 E_3^2 E_3^2},$$

$$g_z = g_s + \frac{8k\varsigma}{E_1} + k\varsigma^2 \frac{E_1 - 2E_2 - 2E_3}{E_1 E_2 E_3}$$

$$+ g_s\varsigma^2 \frac{4E_2^2 E_3^2 - E_1^2 E_3^2 - 2E_1^2 E_2^2}{4E_1^2 E_2^2 E_3^2}$$

$$- k\varsigma^3 \frac{12E_1 E_2 E_3 - (E_1^2 + 4E_2 E_3)(E_2 + E_3)}{2E_1^2 E_2^2 E_3^2}$$

$$+ g_s\varsigma^3 \frac{2E_2^2 + 2E_3^2 - E_1 E_3 - E_1 E_2}{4E_1 E_2^2 E_3^2},$$

$$A_x = P \left[ -\kappa - \frac{2}{7} + (g_x - g_s) - \frac{3(g_y - g_s)}{14} \right],$$

$$A_y = P \left[ -\kappa - \frac{2}{7} + (g_y - g_s) - \frac{3(g_x - g_s)}{14} \right],$$

$$A_z = P \left[ -\kappa + \frac{4}{7} + (g_z - g_s) - \frac{6(g_x + g_y - 2g_s)}{14} \right]. (2)$$

Here $g_s$ ($\approx 2.0023$) is the spin-only value. $k$ ($\approx N^2$) is the orbital reduction factor, characteristic of the covalence effect of the studied system. $\zeta$ and $P$ are, respectively, the spin–orbit coupling coefficient and the dipolar hyperfine structure parameter for the $3d^9$ ion in crystals. Because of the covalence reduction effect for $3d^n$ ions in crystals, we have [20, 21]:

$$\varsigma \approx N^2 \varsigma_d^0, \quad P \approx N^2 P_0. \quad (3)$$

Here, for a free $Cu^{2+}$ ion, the dipolar hyperfine structure parameter $P_0$ ($\approx 388 \times 10^{-4}$ cm$^{-1}$ [22]). The isotropic

core polarization constants satisfies the relationship $\kappa \approx -2\chi/(3\langle r^{-3}\rangle)$ [23]. Here $\chi$ is characteristic of the density of unpaired spins at the nucleus of the central ion, and $\langle r^{-3}\rangle$ is the expectation value of the inverse cube of the radial wave function of the $3d$ orbital in crystals in terms of the related free-ion value $\langle r^{-3}\rangle_0$ multiplying the covalence factor $N$. From the data $\langle r^{-3}\rangle_0 \approx 8.252$ a.u. [16] and $\chi \approx -3.12$ a.u. [23] for $Cu^{2+}$ in some oxides, the value $\kappa \approx 0.29$ may be estimated and used for the studied system here.

The denominators $E_i$ ($i = 1$–4) stand for the energy separations between the excited $^2A_{1g}(\theta)$, $^2B_{1g}(\zeta)$, $^2B_{2g}(\eta)$ and $^2B_{3g}(\xi)$ and the ground $^2A'_{1g}(\varepsilon)$ states, respectively. They are determined from the energy matrix for a $3d^9$ ion under orthorhombic symmetry in terms of the cubic field parameter $D_q$ and the orthorhombic field parameters $D_s$, $D_t$, $D_\xi$ and $D_\eta$:

$$E_1 \approx 4D_s + 5D_t, \quad E_2 \approx 10D_q,$$
$$E_3 \approx 10D_q - 3D_s + 5D_t + 3D_\xi - 4D_\eta,$$
$$E_4 \approx 10D_q + D_s + 10D_t - 3D_\xi + 4D_\eta. \tag{4}$$

From the superposition model [24] and the local geometrical relationship of the studied impurity center, the orthorhombic field parameters are determined as follows:

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

$$D_\xi = \frac{2}{7}\bar{A}_2(R_0)\sum_{i=1,2}(-1)^i \sin^2\theta_i \left(\frac{R_0}{R_i}\right)^{t_2},$$

$$D_t = -\frac{8}{21}\bar{A}_4(R_0)\frac{1}{4}\sum_{i=1,2}(35\cos^4\theta_i - 30\cos^2\theta_i$$
$$+3 - 7\sin^4\theta_i)\left(\frac{R_0}{R_i}\right)^{t_4},$$

$$D_\eta = \frac{5}{42}\bar{A}_4(R_0)\sum_{i=1,2}\sin^2\theta_i(7\cos^2\theta_i - 1)\left(\frac{R_0}{R_i}\right)^{t_4}. \tag{5}$$

Here $t_2 \approx 3$ and $t_4 \approx 5$ [10, 14, 25–28] are the power-law exponents due to the dominant ionic nature of the bonds. $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are the intrinsic parameters, with the reference bond length $R_0$ taken as the average of the metal–ligand distances (i.e., $R_0 = (R_\parallel + R_\perp)/3 \approx 1.993$ Å). For $3d^n$ ion in octahedral crystal-fields, the relationships $\bar{A}_4(R_0) \approx (3/4)D_q$ and the ratio $\bar{A}_2(R_0)/\bar{A}_4(R_0)$ is in the range 8–12 for $3d^n$ ions in many crystals [10, 22, 26–28], we take the average value $\bar{A}_2(R_0) \approx 10\bar{A}_4(R_0)$ here. Thus, the SH parameters (especially the axial and perpendicular anisotropies $\Delta g = g_z - (g_x + g_y)/2$ and $\delta g = g_y - g_x$) are correlated to the orthorhombic field parameters and hence to the local structure of the impurity center. For the studied orthorhombic $[CuO_5]^{8-}$ cluster here, the cubic field parameter $D_q \approx 820$ cm$^{-1}$ and the covalence factor $N \approx 0.80$ can be obtained from the tetragonal $Cu^{2+}$ center in $PbTiO_3$:$Cu^{2+}$ based on the EPR analysis [10].

The calculated and experimental spin-Hamiltonian $g$ factors and the hyperfine structure constants (in $10^{-4}$cm$^{-1}$) for $PbTiO_3$:$Cu^{2+}$.

| | $g_x$ | $g_y$ | $g_z$ | $A_x$ | $A_y$ | $A_z$ |
|---|---|---|---|---|---|---|
| Cal. | 2.0547 | 2.0650 | 2.3336 | 7.991 | 10.874 | −116.457 |
| Exp. [12] | 2.051 | 2.065 | 2.340 | 7.74 | 9.34 | 112.05 |

The local structure bond lengths $R_1$ and $R_2$ and $R_3$ (in Å), the angles $\theta_1$ and $\theta_2$ (in °), the cubic field parameter $D_q$ and the orthorhombic field parameters $D_s$, $D_t$, $D_\xi$ and $D_\eta$ (in cm$^{-1}$) for $Cu^{2+}$ center in $PbTiO_3$.

| $R_1$ | $R_2$ | $R_3$ | $\theta_1$ | $\theta_2$ | $D_q$ | $D_s$ | $D_t$ | $D_\xi$ | $D_\eta$ |
|---|---|---|---|---|---|---|---|---|---|
| 1.904 | 2.099 | 1.813 | 84.6 | 85.1 | 820 | −2640 | −115 | −606 | −32 |

Thus, there are only two unknown parameters, i.e., the impurity $Cu^{2+}$ displacement $\Delta Z$ along the $c$-axis due to electrostatic repulsion of the $V_O$ and the planar bond length variation $\Delta R$ along the $a$- and $b$-axes in Eq. (1) of the SH parameters. Substituting these parameters into Eq. (1) and fitting the calculated SH parameters to the experimental values, one can obtain

$$\Delta Z \approx 0.18 \text{ Å and } \Delta R \approx 0.098 \text{ Å.} \tag{6}$$

The corresponding theoretical results are collected in Table I. Meanwhile, the obtained local structural parameters $R_1$, $R_2$, $R_3$, the angles $\theta_1$, $\theta_2$ and the orthorhombic field parameters (i.e., $D_s$, $D_t$, $D_\xi$ and $D_\eta$) are listed in Table II.

## 3. Discussion

It can be seen from Table I that the calculated SH parameters for the $Cu^{2+}$ center in $PbTiO_3$ based on the local structure distortion obtained in this work show reasonable agreement with the experimental data. Thus, the defect model of $PbTiO_3$:$Cu^{2+}$ are therefore confirmed and the defect structure data (i.e., the impurity off-center displacement $\Delta Z_L$; the planar bond length variation $\Delta R$) are obtained from the calculations.

(1) The experimental orthorhombic SH parameters for $PbTiO_3$:$Cu^{2+}$ are conveniently described by the axial and perpendicular anisotropies $\Delta g$ and $\delta g$. According to Eqs. (1), (2) and (5), the anisotropies arise mainly from the axial (i.e., the crystal-field parameters $D_s$ and $D_t$ due to the $V_O$ and the impurity off-center displacement $\Delta Z_L$) and perpendicular (i.e., the $D_\xi$ and $D_\eta$ due to the planar bond length variation $\Delta R$) orthorhombic distortions of the ligand octahedron. Thus, the observed $\Delta g$ ($\approx 0.282$) and $\delta g$ ($\approx 0.014$) can also be reasonably attributed to the impurity off-center displacement $\Delta Z_L$ ($\approx 0.18$ Å) due to the electrostatic repulsion of the effectively positive $V_O$ and the planar bond length variation $\Delta R$ ($\approx 0.098$ Å) due to the Jahn–Teller and size mismatch effect. Interestingly, similar impurity off-center

displacements ($\approx 0.15-0.3$ Å) were also reported for various transition-metal ions (e.g., $Pt^{3+}$, $Cu^{2+}$, $Ru^{3+}$, $Ni^{3+}$) on the octahedral $Ti^{4+}$ site in $PbTiO_3$ based on the EPR analysis [10, 18, 29, 30].

(2) From Table I, one can see the absolute values of hyperfine structure constants $A_i$ ($i = x, y, z$) are in good agreement with the experimental findings and the signs for the calculated $A_z$ is negative, but the observed values given by Warren et al. are positive [12]. Actually, experimental determination of the signs of hyperfine structure constants for $3d^n$ ions in crystals is very difficult, many experiments give them as absolute ones. The signs of the hyperfine structure constants $A_i$ suggested here are the same as those for $Cu^{2+}$ doped in many crystals based on the EPR analysis [13, 22, 26] and can be regarded as reasonable. In addition, previous studies of hyperfine structure constants for $Cu^{2+}$ ions in various crystals suggest that the constant $\kappa$ ($\approx 0.25-0.35$) [10, 13, 21, 22]. The value of $\kappa$ ($\approx 0.29$) for $PbTiO_3$:$Cu^{2+}$ obtained in this work lies within the range and can be considered to be suitable.

## 4. Conclusion

The orthorhombic $Cu^{2+}$ center in $PbTiO_3$ can be described as the substitutional $Cu^{2+}$ on the $Ti^{4+}$ site in $PbTiO_3$, associated with one nearest neighbour $V_O$ along the $c$-axis. Based on this model assumption, the planar bond lengths are found to suffer the relative variation of about 0.098 Å by compressing and stretching the $Cu^{2+}$–$O^{2-}$ bonds along the $a$- and $b$-axes, respectively, due to the Jahn–Teller effect and the charge mismatching substitution. In addition, the impurity $Cu^{2+}$ off-center displacement $\Delta Z_L$ ($\approx 0.18$ Å) is different from the host $\Delta Z_H$ ($\approx 0.30$ Å) $Ti^{4+}$ ion.

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