# Investigations of the Defect Structure for $Cu^{2+}$ in $SrLaAlO_4$

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The defect structure for $Cu^{2+}$ in $SrLaAlO_4$ is theoretically investigated by the perturbation formulas of the spin Hamiltonian parameters ($g$ factors $g_{\parallel}$, $g_{\perp}$ and the hyperfine structure constants $A_{\parallel}$ and $A_{\perp}$) for a $3d^9$ ion in tetragonally elongated octahedra. Based on these studies, the tetragonal center may be attributed to $Cu^{2+}$ occupying the host $Al^{3+}$ site, associated with one hole delocalized at the four oxygen ligands in planar coordination. Furthermore, the four Cu,O bonds (perpendicular to the four-fold axis) are found to suffer an outward stretch of about 0.06 Å due to (i) the local tenseness in this plane, arising from the size mismatching substitution of the smaller $Al^{3+}$ by the larger $Cu^{2+}$ and (ii) the weaker electrostatic attraction of the less charged $Cu^{2+}$ acting upon the four oxygen ions containing the delocalized hole. The calculated spin Hamiltonian parameters agree well with the experimental data. The defect structure of this center is discussed.

*Key words:* Electron Paramagnetic Resonance (EPR); Defect Structure; Crystal-field and Spin Hamiltonians; $Cu^{2+}$; $SrLaAlO_4$.

## 1. Introduction

$SrLaAlO_4$ (SLA) belongs to the group of $ABCO_4$ compounds (where A = Sr, Ca; B = La, Y and C = Al, Ga or some transition-metal elements) [1] and crystallizes generally in a perovskite-like tetragonal $KNiF_4$-type structure of $I4/mmm$ space group [2]. SLA has extensively been studied due to its elastic and elasto-optic properties and applications as promising substrate for high-temperature superconducting thin films [3 – 5]. Electron paramagnetic resonance (EPR) studies were also performed on this material doped with transition-metal ions (e.g., $Cr^{3+}$, $Co^{2+}$) [6, 7], which may be helpful to understand the effect of local distortion around impurity ions. Recently, the magnetic structures and dynamics of $Cu^{2+}$ (as well as $Ni^{3+}$) were investigated, and the spin Hamiltonian $g$ factors $g_{\parallel}$, $g_{\perp}$ and the hyperfine structure constants $A_{\parallel}$ and $A_{\perp}$ were measured [8]. Until now, however, these experimental results have not been theoretically explained, and the defect structure of $Cu^{2+}$ in SLA has not been quantitatively determined (note: the above $Cu^{2+}$ center was attributed to a delocalized hole at the four oxygen ions in planar coordination in [8]). Since information about the defect structure and properties of $Cu^{2+}$ in SLA may be useful in investigations of the local behaviour and dynamics of impurities, theoretical studies on the defect structure for $Cu^{2+}$ in SLA are significant. In this paper, theoretical studies on the defect structure are carried out, based on perturbation formulas of the spin Hamiltonian parameters for a $3d^9$ ion in tetragonally elongated octahedra.

## 2. Calculation

In SLA, the $Al^{3+}$ site is surrounded by a tetragonally elongated oxygen octahedron with two longer bond lengths $R_{\parallel}$ ($\approx 2.121$ Å) parallel to the four-fold axis, and four shorter bonding lengths $R_{\perp}$ ($\approx 1.885$ Å) perpendicular to the axis [6]. When the impurity $Cu^{2+}$ ion enters the lattice of SLA, it may occupy the $Al^{3+}$ site due to similar ionic radius, and local charge mismatch may be introduced. According to the axiality of the observed spin Hamiltonian, three defect structure models seem possible: distant charge compensation with little influence on the defect structure (model I), one nearest oxygen vacancy $V_O$ (model II) and a delocalized hole at the four oxygen ions in planar coordination (model III, i. e., the defect model proposed in [8]).

For $Cu^{2+}$ ($3d^9$) in tetragonally elongated octahedra, the lower $^2E_g$ irreducible representation may be separated into the orbital singlets $^2B_{1g}(|x^2-y^2\rangle)$ and $^2A_{1g}(|z^2\rangle)$, with the former lying lowest, while the upper $^2T_{2g}$ representation would split into an orbital singlet $^2B_{2g}(|xy\rangle)$ and a doublet $^2E_g(|xz\rangle,|yz\rangle)$ [9]. The perturbation formulas of the spin Hamiltonian parameters of the $^2B_{1g}$ ground state for a $3d^9$ ion in tetragonal symmetry can be expressed as [10]

$$\begin{aligned}
g_\parallel &= g_s + 8k\zeta_d/E_1 + k\zeta_d{}^2/E_2{}^2 + 4k\zeta_d{}^2/E_1E_2 \\
&\quad - g_s\zeta_d^2(1/E_1{}^2 - 1/2E_2{}^2) \\
&\quad + k\zeta_d{}^3(4/E_1 - 1/E_2)/E_2{}^2 \\
&\quad - 2k\zeta_d{}^3(2/E_1E_2 - 1/E_2{}^2)/E_1 \\
&\quad + g_s\zeta_d{}^3(1/E_1E_2{}^2 - 1/2E_2{}^3), \\
g_\perp &= g_s + 2k\zeta_d/E_2 - 4k\zeta_d{}^2/E_1E_2 \\
&\quad + k\zeta_d{}^2(2/E_1 - 1/E_2)/E_2 + 2g_s\zeta_d{}^2/E_1{}^2 \\
&\quad + k\zeta_d{}^3(2/E_1 - 1/E_2)(1/E_2 + 2/E_1)/2E_2 \\
&\quad - g_s\zeta_d{}^3(1/E_1{}^2 - 1/E_1E_2 + 1/E_2{}^2)/2E_2, \\
A_\parallel &= P[(-\kappa - 4/7) + (8k\zeta_d/E_1 + 6k\zeta_d/7E_2 \\
&\quad - 3k\zeta_d{}^2/7E_2{}^2 - 40k\zeta_d{}^2/7E_1E_2 + \kappa\zeta_d{}^2/E_2{}^2)], \\
A_\perp &= P[(-\kappa + 2/7) + 11k\zeta_d/7E_2 \\
&\quad + 9k\zeta_d{}^2/14E_2{}^2 - 4k\zeta_d{}^2/7E_1{}^2 \\
&\quad + 11k\zeta_d{}^2/7E_1E_2 + \kappa\zeta_d{}^2(2/E_1{}^2 + 1/2E_2{}^2)],
\end{aligned} \tag{1}$$

where $g_s$ ($\approx 2.0023$) is the spin-only value, $k$ the orbital reduction factor and $\kappa$ the core polarization constant. $\zeta_d$ and $P$ are, respectively, the spin-orbit coupling coefficient and the dipolar hyperfine structure parameter of the $3d^9$ ion in crystals. They can be written in terms of the corresponding free-ion values, i.e., $\zeta_d \approx k\zeta_d{}^0$ and $P \approx kP_0$. $E_1$ and $E_2$ are the energy separations between the excited $^2B_{2g}$ and $^2E_g$ and the ground $^2B_{1g}$ states [10]:

$$E_1 = 10Dq,\ E_2 = 10Dq - 3D_s + 5D_t. \tag{2}$$

Here $Dq$ is the cubic field parameter, and $D_s$ and $D_t$ are the tetragonal field parameters. In the following, these possible defect models are to be examined by the perturbation formulas of the spin Hamiltonian parameters (1).

Table 1. The spin Hamiltonian $g$ factors and the hyperfine structure constants (in units of $10^{-4}$ $cm^{-1}$) for the tetragonal $Cu^{2+}$ center in SLA.

| | $g_\parallel$ | $g_\perp$ | $A_\parallel$ | $A_\perp$ |
|---|---|---|---|---|
| Cal.[a] | 2.321 | 2.067 | −147 | 1 |
| Cal.[b] | 2.321 | 2.067 | −147 | 1 |
| Cal.[c] | 2.321 | 2.070 | −150 | −3 |
| Expt. [8] | 2.320 | 2.069 | −150 | < 10 |

[a] Calculations based on model I. [b] Calculations based on model II and the impurity displacement $\Delta Z$ in (6). [c] Calculations based on model III and the displacement $\Delta X$ in (7) for the four planar oxygen ligands.

### 2.1. Model I

In this model, charge compensation is considered as far enough from the impurity center, and so its influence on the defect structure is neglected. From the superposition model [11] and the geometrical relationship of this center, the tetragonal field parameters can be expressed as

$$\begin{aligned}
D_s &= (4/7)\bar{A}_2(R_0)[(R_0/R_\perp)^{t_2} - (R_0/R_\parallel)^{t_2}], \\
D_t &= (16/21)\bar{A}_4(R_0)[(R_0/R_\perp)^{t_4} - (R_0/R_\parallel)^{t_4}],
\end{aligned} \tag{3}$$

where $t_2$ and $t_4$ are the power-law exponents; we take $t_2 \approx 3$ and $t_4 \approx 5$ here [12]. $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are the intrinsic parameters, with the reference bonding length taken as the average of the metal-ligand distances, i. e., $R_0 = \bar{R} = (R_\parallel + 2R_\perp)/3$. For $3d^n$ octahedral clusters, $\bar{A}_4(R_0) \approx (3/4)Dq$ and the ratio $\bar{A}_2(R_0)/\bar{A}_4(R_0) \approx 9 \sim 12$ are regarded as valid in many crystals [12–14]. $\bar{A}_2(R_0) \approx 9\bar{A}_4(R_0)$ is adopted here. According to the optical spectra of the $[Cu(H_2O)_6]^{2+}$ cluster, the cubic field parameter $Dq \approx 1260$ $cm^{-1}$ can be obtained [15].

The orbital reduction factor $k$ ($\approx 0.765$) is adopted here. In the formulas of the hyperfine structure constants, we take $\kappa \approx 0.286$, which is within the range ($\approx 0.26 \sim 0.3$ [16]) for $Cu^{2+}$ in tutton salts and can be regarded as reasonable. Substituting these parameters and the free-ion values $\zeta_d{}^0 \approx 829$ $cm^{-1}$ [17] and $P_0 \approx 360 \times 10^{-4}$ $cm^{-1}$ [18] into (1), the spin Hamiltonian parameters are calculated and shown in Table 1.

### 2.2. Model II

In model II, one nearest $V_O$ is assumed to occur along the four-fold axis as the charge compensation. Due to the effective positive charge of $V_O$, the central $Cu^{2+}$ may be pushed away from the $V_O$ by an amount $\Delta Z$ along the axis. From the superposition model [11] and the local geometrical relationship due to the $\Delta Z$, the tetragonal field parameters can be obtained as

$$\begin{aligned} D_s &= (4/7)\bar{A}_2(R_0)[(3\cos^2\theta-1)(R_0/R'_\perp)^{t_2} \\ &\quad +(1/2)(R_0/R'_\parallel)^{t_2}], \\ D_t &= (8/21)\bar{A}_4(R_0)[(1/2)(35\cos^4\theta-30\cos^2\theta \\ &\quad +3-7\sin^4\theta)(R_0/R'_\perp)^{t_4}+(R_0/R'_\parallel)^{t_4}]. \end{aligned} \tag{4}$$

The superposition model parameters are the same as in model I. The local structural parameters in (2) are determined as

$$\begin{aligned} &R'_\parallel \approx R_\parallel + \Delta Z,\ R'_\perp \approx ({R_\perp}^2+\Delta Z^2)^{1/2}, \\ &\cos\theta \approx \Delta Z/R'_\perp. \end{aligned} \tag{5}$$

Here $R'_\parallel$ denotes the bonding length for the $Cu^{2+}$,$O^{2-}$ bond along the four-fold axis, $R'_\perp$ the bonding length for the other four $Cu^{2+}$,$O^{2-}$ bonds due to $\Delta Z$. $\theta$ is the angle between $R'_\perp$ and the $C_4$ axis.

Substituting these parameters (note: the other values remain unchanged) into (1) and fitting the calculated spin Hamiltonian parameters to the experimental values, one obtains the impurity displacement

$$\Delta Z \approx -0.36\ \text{Å}. \tag{6}$$

Here shift towards $V_O$ is defined as the positive direction. The corresponding spin Hamiltonian parameters are shown in Table 1.

### *2.3. Model III*

One delocalized hole may be induced at the four $O^{2-}$ ions in planar coordination (i. e., $CuO_2$ layer) due to charge compensation, as pointed out in [8]. This argument is supported by the average copper oxidation state of +2.46, which is regarded as consequence of the partial contribution from the hole rather than $Cu^{3+}$ state [8, 19]. Since the ionic radius (≈ 0.72 Å [20]) of the impurity $Cu^{2+}$ is larger than that (≈ 0.51 Å [20]) of the host $Al^{3+}$, local lattice tenseness may be introduced, and then the four Cu,O bonds are expected to stretch a little. On the other hand, due to the less charge of $Cu^{2+}$ and the partial positive charge of the hole assigning to the four oxygen ligands in the $CuO_2$, weaker copper-oxygen electrostatic attraction would make it easy for these ligands to shift slightly away from the impurity. As a result, the four $O^{2-}$ may suffer an outward displacement $\Delta X$ away from the impurity $Cu^{2+}$. Then, the planar impurity-ligand distance should be expressed as $R''_\perp \approx R_\perp + \Delta X$.

Substituting the above relationship into (1) and fitting the calculated spin Hamiltonian parameters to the experiment, the displacement $\Delta X$ can be obtained. Thus, we have

$$\Delta X \approx 0.06\ \text{Å or } R''_\perp \approx 1.945\ \text{Å}. \tag{7}$$

Note that the displacement direction away from the impurity ion is defined as positive. The corresponding spin Hamiltonian parameters are also shown in Table 1.

## 3. Discussion

From Table 1, we find that the calculated spin Hamiltonian parameters for the tetragonal $Cu^{2+}$ center in SLA based on model III (and also the planar shift $\Delta X$) show slightly better agreement with the observed values than those based on models I and II, suggesting that model III for the defect structure and the related parameters adopted here can be regarded as reasonable.

1.) As suggested in [8], the $Cu^{2+}$ center in SLA can be attributed to a delocalized hole on the four oxygen ions in planar coordination. Since the theoretical spin Hamiltonian parameters of model III (based on the ligand displacement $\Delta X$) agree well with the observed values, the assignment for the defect structure of $Cu^{2+}$ in SLA in [8] is theoretically verified by analyzing its EPR results in this work. The validity of this model may be illustrated further. (i) The hole at the four oxygen ions may cancel partially the negative charge of these ligands. (ii) The impurity $Cu^{2+}$ has less charge than the host $Al^{3+}$. Both points lead to weaker electrostatic attraction acting upon these ligands, and then make them movable in the $CuO_2$ plane. (iii) Size mismatching substitution of the smaller $Al^{3+}$ by the larger $Cu^{2+}$ may induce tenseness around the impurity. Thus, the outward shift of the planar ligands can be induced so as to reduce the above local tenseness. As a result, the whole planar displacement $\Delta X$ (≈ 0.06 Å) away from the impurity may be understood. Interestingly, a similar stretch of the planar bonding length in impurity centers is found in SLA doped with $Co^{2+}$, based on EPR investigations [21]. In fact, expansion of the planar impurity-ligand distances leads to a slight decrease in the difference between the bonding lengths parallel with and perpendicular to the four-fold axis, and hence in tetragonal distortion, yielding a larger (or better) value of the calculated $g_\perp$. Although the sign of the experimental $A_\parallel$ was not determined in [8], theoretical studies in this work support the negative sign of $A_\parallel$, as did some similar EPR investigations on $Cu^{2+}$ in elongated oxygen octahedra [22, 23].

2.) Models I and II are possible defect structures for the $Cu^{2+}$ centers. As for model II, the theoretical $g$ and $A$ factors are not as good as those of model III. Further, existence of the nearest $V_O$ would significantly increase the effective valence state of copper, which is inconsistent with the measured average oxidation state of $+2.46$ [9, 19]. In addition, the displacement $\Delta Z$ ($\approx -0.36$ Å) of the impurity seems to be somewhat too large, i.e., the relative variation $\Delta Z/R_\parallel$ is about 17%. Finally, no experimental treatments leading to an oxygen deficiency were reported in [8]. For model I, no charge compensation is considered in the vicinity of the impurity, which may be difficult to cancel the local charge mismatch due to $Cu^{2+}$ replacing $Al^{3+}$. Besides, this model cannot satisfactorily explain the observed average oxidation state of $+2.46$ of copper [9, 19]. Based on the above points, models I and II seem not to be as reasonable as model III and can be tentatively excluded.

3.) Based on the theoretical calculations in the present work, the spin Hamiltonian parameters (particularly the mean values) are sensitive to the value of the orbital reduction factor. The value $k$ ($\approx 0.765$) adopted in this work reveals some covalency nature of the $Cu^{2+}$,$O^{2-}$ bonds. Based on the defect model (model III), the planar impurity-ligand distance $R''_\perp$ ($\approx 1.945$ Å) is lower than the sum ($\approx 2.04$ Å) of ionic radii for $Cu^{2+}$ and $O^{2-}$, in agreement with moderate covalency and hence with the small value of $k$ ($< 1$). In spite of the covalency effect, the conventional single spin-orbit coupling coefficient formulas [10] are adopted here, since the spin-orbit coupling coefficient ($\approx 151$ cm$^{-1}$ [24]) of the oxygen ligand is much smaller than that ($\approx 829$ cm$^{-1}$ [17]) of the $Cu^{2+}$ and so the contributions from the ligand are for simplicity neglected in the calculations.

In summary, the defect structure for the tetragonal $Cu^{2+}$ center in SLA is investigated in this work. Based on the studies of the spin Hamiltonian parameters, the EPR results for this center in [8] can be attributed to model III (i. e., a delocalized hole at the four oxygen ions in planar coordination in the impurity center), and thus the previous assignment [8] is also theoretically verified.

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