Theoretical Studies on the Gyromagnetic Factors and the Hyperfine Structure Constants for the Tetragonal Copper Center in $KTaO_3$

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The gyromagnetic factors $g_{\parallel}$, $g_{\perp}$ and the hyperfine structure constants $A_{\parallel}$ and $A_{\perp}$ of the tetragonal Cu^{2+} center in $KTaO_3$ are theoretically studied in this work. Based on the analyses of the electron paramagnetic resonance results of this center, it is found that the impurity Cu^{2+} occupies the octahedral Ta^{5+} site, associated with a nearest-neighbouring oxygen vacancy V_O along the C_4 axis. Due to the electrostatic repulsion of V_O, Cu^{2+} is displaced away from V_O by $\Delta Z (\approx -0.29$ Å) along the C_4 axis. The theoretical values of the g and A factors based on the above defect structure and the impurity displacement agreee reasonably with the experimental data.

Key words: Electron Paramagnetic Resonance; Defect Structures; Crystal-field Theory; Cu^{2+}; $KTaO_3$.

1. Introduction

$KTaO_3$ is a useful host to study defects due to transition-metal ions, such as hyper-Rayleigh scattering and second harmonic generation [1 – 4]. Extensive studies have been carried out on the defect structure (e. g., impurity-vacancy centers) and interaction between impurity and ligands in some transition-metal ion (such as Cu^{2+}, Mn^{2+}, Co^{2+}) doped $KTaO_3$ by means of EPR [5 – 8]. For instance, the gyromagnetic factors $g_{\parallel}$ and $g_{\perp}$ and the hyperfine structure constants $A_{\parallel}$ and $A_{\perp}$ of a tetragonal Cu^{2+} center were measured [8]. Until now, however, the above EPR results have not been theoretically investigated, although this center was tentatively attributed to Cu^{2+} occupying the host octahedral Ta^{5+} site with some type of charge compensation in view of axiality of the spectra [8]. In this paper we study theoretically the g and A factors as well as the local structure of this center, based on a reasonable defect model.

2. Calculations

Cu^{2+} may substitute the host octahedral Ta^{5+} site in $KTaO_3$ due to its similar ionic radius, despite of its significant charge mismatch (note: some transition-metal ions such as Fe^{3+} and Ni^{3+} can also occupy the dodecahedral K^+ site [5]). Since the impurity Cu^{2+} has less charge than the host Ta^{5+}, one nearest-neighbouring oxygen vacancy (V_O) can occur along one of the [100] directions as charge compensation. As a result, the local symmetry is reduced from the original cubic one in the host to tetragonal C_{4v} in the impurity center. Thus, the studied impurity center may be denoted as the defect structure Cu^{2+}-V_O (or $[CuO_5]^{8-}$ cluster).

When a Cu^{2+} ($3d^9$) ion is under octahedral symmetry, there are only two energy levels, i. e., one lower orbital doublet ^2E_g and another higher orbital triplet $^2T_{2g}$. As the octahedron is elongated along the C_4 axis, the lower ^2E_g irreducible representation would split into two orbital singlets $^2B_{1g}(|x^2-y^2> \text{ or } \varepsilon)$ and $^2A_{1g}(|z^2> \text{ or } \theta)$, with the former being lower. Meanwhile, the upper $^2T_{2g}$ energy level would be separated into an orbital singlet $^2B_{2g}(|xy> \text{ or } \zeta)$ and a doublet $^2E_g(|xz>, |yz> \text{ or } \eta, \chi)$ [9].

The perturbation formulas of the g factors and the hyperfine structure constants for the $3d^9$ ion in tetragonally elongated octahedra may be written as [10, 11]

$$g_{\parallel} = g_0 + 8k\zeta_d/D_1 + k{\zeta_d}^2/{D_2}^2 + 4k{\zeta_d}^2/(D_1D_2)$$

$$
\begin{aligned}
&- g_0\zeta_d{}^2[1/D_1{}^2 - 1/(2D_2{}^2)] + k\zeta_d{}^3[4/(D_1D_2{}^2) \\
&- 1/D_2{}^3] - 2k\zeta_d{}^3[2/(D_1{}^2D_2) - 1/(D_1D_2{}^2)], \\
g_\perp &= g_0 + 2k\zeta_d/D_2 - 4k\zeta_d{}^2/(D_1D_2) \\
&+ k\zeta_d{}^2[2/(D_1D_2) - 1/D_2{}^2] + 2g_0\zeta_d{}^2/D_1{}^2 \\
&+ k\zeta_d{}^3(2/D_1 - 1/D_2)(1/D_2 + 2/D_1)/(2D_2), \\
A_\parallel &= P_d[-\kappa - 4k/7 + (g_\parallel - g_0) + 3(g_\perp - g_0)/7], \\
A_\perp &= P_d[-\kappa - 2k/7 + 11(g_\perp - g_0)/14], \qquad (1)
\end{aligned}
$$

where $g_0(\approx 2.0023)$ is the pure spin value, k the orbital reduction factor, and κ the core polarization constant. ζ_d and P_d are, respectively, the spin-orbit coupling coefficient and the dipolar hyperfine structure parameter of the $3d^9$ ion in crystals. The denominators D_1 and D_2 are the energy separations between the excited $^2B_{2g}$ and ^2E_g and the ground $^2B_{1g}$ states [10, 11], i. e., $D_1 = 10Dq$ and $D_2 = 10Dq - 3D_s + 5D_t$. Here Dq is the cubic field parameter, and D_s and D_t are the tetragonal field parameters.

As mentioned before, one nearest-neighbouring V_O is located along the C_4 axis as the charge compensation. Because of the effective positive charge of the V_O, the impurity Cu^{2+} would be expected to shift away from V_O by an amount ΔZ along the axis under electrostatic repulsion. From the superposition model [12] and the local geometrical relationship due to ΔZ, the tetragonal field parameters can be determined as follows:

$$
\begin{aligned}
D_s &= (4/7)\bar{A}_2[(3\cos^2\alpha - 1)(R_0/R_2)^{t_2} \\
&\quad + (1/2)(R_0/R_1)^{t_2}], \\
D_t &= (8/21)\bar{A}_4[(1/2)(35\cos^4\alpha - 30\cos^2\alpha \\
&\quad + 3 - 7\sin^4\alpha)(R_0/R_2)^{t_4} + (R_0/R_1)^{t_4}].
\end{aligned} \qquad (2)
$$

Here $\bar{A}_2$ and $\bar{A}_4$ are the intrinsic parameters, with the reference bonding length (or the effective impurity-ligand distance) R_0. For $3d^n$ octahedral clusters, $\bar{A}_4 \approx (3/4)Dq$ and the ratio $\bar{A}_2/\bar{A}_4 \approx 9 \sim 12$ are regarded as valid in many crystals [12–14]. $\bar{A}_2(R_0) \approx 12\bar{A}_4(R_0)$ is adopted here. t_2 and t_4 are the power-law exponents, and we take $t_2 \approx 3$ and $t_4 \approx 5$ here [12]. The local structural parameters $R_1(\times 1)$ and $R_2(\times 4)$ in (2) can be expressed as

$$
\begin{aligned}
&R_1 \approx R_0 + \Delta Z, \quad R_2 \approx (R_0{}^2 + \Delta Z^2)^{1/2}, \\
&\cos\alpha \approx \Delta Z/R_2.
\end{aligned} \qquad (3)
$$

Table 1. The gyromagnetic factors and the hyperfine structure constants for the tetragonal Cu^{2+}-V_O center in $KTaO_3$.

	Cal.	Expt.[a] [8]
$g_\parallel$	2.289	2.228 (2)
$g_\perp$	2.052	2.056 (5)
$A_\parallel$ (10^{-4} cm^{-1})	−167	−173 (2)
$A_\perp$ (10^{-4} cm^{-1})	−51	−45 (3)

[a] Note that the signs of the experimental A factors were not determined in [8]. Based on the theoretical calculations in this work and various observed results for Cu^{2+} in some elongated oxygen octahedra [18, 20, 21], we suggest that these signs may be negative.

Here R_1 denotes the impurity-ligand bonding length for the Cu^{2+},O^{2-} bond along the C_4 axis, and R_2 the bonding length for the other four Cu^{2+},O^{2-} bonds due to the displacement ΔZ. α is the angle between the R_2 and C_4 axis.

For the studied Cu^{2+} center in $KTaO_3$, since the ionic radius $r_i(\approx 0.72$ Å [13]) of the impurity Cu^{2+} is larger than the radius $r_h(\approx 0.68$ Å [13]) of the host Ta^{5+}, the reference bonding length R_0 may be estimated from the empirical formula $R_0 \approx R_H + (r_i - r_h)/2$ [14, 15], where $R_H(= a/2 \approx 1.994$ Å [16]) is the host Ta^{5+},O^{2-} distance in the pure crystal. Thus we have $R_0 \approx 2.014$ Å here. The intrinsic parameter $\bar{A}_4 \approx 615$ cm^{-1} is obtained for the similar Cu^{2+} octahedron in Cu^{2+} doped $LiNbO_3$ [17] and can be applied here. The orbital reduction factor is taken as $k \approx 0.61$ in (1). Then, the spin-orbit coupling coefficient can be expressed in terms of k, i. e., $\zeta_d \approx k\zeta_d{}^0$, where $\zeta_d{}^0(\approx 829$ cm^{-1} [9]) is the corresponding free-ion value. In the formulas of the hyperfine structure constants, the dipolar hyperfine structure parameter is $P_d \approx 416 \cdot 10^{-4}$ cm^{-1} for ^{65}Cu [18], and the core polarization constant is taken as $\kappa \approx 0.375$. This value is close to the range ($\approx 0.26 \sim 0.3$ [19]) for Cu^{2+} in Tutton's salts and that (~ 0.3) for $3d^n$ ions in crystals [9], and can be regarded as suitable. Substituting these parameters into (1) and fitting the calculated g and A factors to the experimental values, we obtain the impurity displacement

$$
\Delta Z \approx -0.29 \text{ Å}. \qquad (4)
$$

Note that the displacement direction towards V_O is defined as positive. The corresponding theoretical results are shown Table 1.

3. Discussion

According to Table 1, we find that the calculated g and A factors based on the impurity displacement in (4) agree reasonably with the experimental data. Thus the observed EPR results in [8] are interpreted in this work, and the defect structure (i. e., Cu^{2+}-V_O) for this center in $KTaO_3$:Cu^{2+} is also presented.

1.) The sign of the displacement $\Delta Z < 0$ of the impurity Cu^{2+} is consistent with the expectation based on the electrostatic interaction between Cu^{2+} and the V_O. So, the displacement direction of the impurity can be regarded as reasonable. The displacement of Cu^{2+} away from V_O obtained in this work is supported by the displacement scheme for impurity ions on B sites in ABO_3 type perovskites proposed by Donnerberg [22]. Interestingly, similar negative displacement $\Delta Z (\approx -0.14$ Å) for Mn^{2+} on Ti^{4+} sites in $SrTiO_3$ and that (≈ -0.25 Å) for Fe^{3+} on Nb^{5+} site in $KNbO_3$ are also obtained from the theoretical analysis of the gyromagnetic factors [23] and the shell-model simulations (and the embedded-cluster calculations) [22], respectively.

2.) As regards the hyperfine structure constants, the signs of the experimental $A_{\|}$ and $A_{\perp}$ values were not given in [8]. However, the theoretical studies of the present work yield negative signs of the A factors due to the relatively larger magnitude of κ compared with that of the g-shifts $\Delta g [= g_i - g_0$, where i denotes $\|$ and $\perp$; see (1)]. This point is also supported by the experimental results for Cu^{2+} in some elongated oxygen octahedra [18, 20, 21]. Therefore, the signs of the A factors for the Cu^{2+} center in $KTaO_3$ is theoretically determined.

3.) There are some assumptions in the above calculations. Firstly, the displacements of the five oxygen ions in this center are not considered, due to the larger distances away from V_O than that (i.e., R_0) between Cu^{2+} and V_O, and hence much smaller electrostatic interactions. In addition, the approximation of the parameters adopted in this work would also induce some mistakes. Finally, the contributions of the spin-orbit coupling coefficient of the ligands as well as the ligand p and s orbitals are ignored. This point has been illustrated in recent studies on impurity ions in crystals, where the spin-orbit coupling coefficient of the ligand is comparable to or much larger than that of the central metal ion [24–27]. For the studied $[CuO_5]^{8-}$ cluster, however, the above contributions can be regarded as negligible because of the much smaller spin-orbit coupling coefficient (≈ 136 cm^{-1} [28]) of the ligand oxygen than that (≈ 829 cm^{-1} [9]) of the central Cu^{2+}.

4.) The impurity Cu^{2+} could also occupy the dodecahedral K^+ site in $KTaO_3$, as reported for some other transition-metal ions (e. g., Fe^{3+}, Ni^{3+}) in this host. However, the ground orbital triplet $^2T_{2g}$ of a dodecahedral Cu^{2+} would be separated in tetragonal fields and lead to possible magnetic resonance transitions between the spin levels of a resultant orbital singlet. In this case, the experimental g factors would be expected deviate much from g_0, and their magnitudes should be lower than 2.0 [29], which is inconsistent with the experimental results. Further, the relaxation time in this case would also be too short for EPR spectra to be observed at room temperature. Therefore, occupation of the impurity Cu^{2+} on the dodecahedral K^+ site in $KTaO_3$ may be excluded, at least for the experimental results in [8].

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