Theoretical Studies of the EPR Parameters and the Local Structure of the Tetragonal Fe^+ Center in $KTaO_3$

Shao-Yi Wu[a,b], Hui-Ning Dong[b,c], and Xiu-Ying Gao[a]

[a] Department of Applied Physics, University of Electronic Science and Technology of China, Chengdu 610054, P. R. China
[b] International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, P. R. China
[c] College of Electronic Engineering, Chongqing, University of Posts and Telecommunications, Chongqing 400065, P. R. China

Reprint requests to S.-Y. W.; E-mail: shaoyi_wu@163.com

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The EPR parameters (zero-field splitting D and g factors $g_\parallel$ and $g_\perp$) and the local structure for the tetragonal Fe^+ center in $KTaO_3$ are theoretically studied by using the perturbation formulas of the EPR parameters for a $3d^7$ ion in tetragonally distorted dodecahedra. Based on these studies, we find that the impurity Fe^+ may not locate on the regular dodecahedral K^+ site but suffer a large off-center displacement ΔZ (≈ 0.43 Å) along one of the $\langle 100 \rangle$ (or C_4) axes, which is responsible for the large tetragonal distortion of the impurity center. The displacement ΔZ obtained in this work is comparable with that (≈ 0.46 Å) of a similar monovalent Li^+ on K^+ site of $KTaO_3$ obtained from the nuclear quadrupole shift and can be regarded as reasonable. The calculated g factors, particularly the anisotropy $\Delta g\,(= g_\perp - g_\parallel)$ based on the above displacement, agree with the observed values.

Key words: Defect Structures; Electron Paramagnetic Resonance (EPR); Crystal- and Ligand-fields; Fe^+; $KTaO_3$

1. Introduction

Investigations on $KTaO_3$ have attracted attention due to its unusual properties such as second harmonic generation, first-order Raman scattering and dielectric losses [1 – 4]. These properties are believed to be sensitive to the internal electric and elastic fields produced by impurities [1]. As an incipient ferroelectric which remains cubic to zero temperature, $KTaO_3$ is a useful host to study transition-metal defects [5]. Recently, the electron paramagnetic resonance (EPR) g factors $g_\parallel$ (≈ 2.02) and $g_\perp$ (≈ 2.16) for a new tetragonal Fe^+ center have been measured by EPR technique [6]. This center was attributed to an off-center Fe^+ ion substituting the host K^+, which can be regarded as the potential source of induced polar regions at low temperature and as a prospective candidate for the creation of ferroelectric long-range order in iron-doped crystals [6]. Up to now, however, the above EPR parameters have not been satisfactorily interpreted. Since (i) the EPR parameters zero-field splitting D, and g factors $g_\parallel$ and $g_\perp$ [particularly, the anisotropy $\Delta g\,(= g_\perp - g_\parallel)$] are sensitive to the immediate environment of a paramagnetic ion in crystals and (ii) the local structure, especially the off-center displacement of the impurity Fe^+, would be helpful to study the properties of $KTaO_3$ (or other similar perovskite-type ferroelectrics such as $KNbO_3$ and $BaTiO_3$), theoretical investigations on the EPR parameters and the local structure of the tetragonal Fe^+ center in $KTaO_3$ are of significance. In this paper, the EPR parameters and the local structure of Fe^+ on a K^+ site of $KTaO_3$ are studied by using the perturbation formulas of the EPR parameters for a $3d^7$ ion in tetragonally distorted dodecahedra based on the cluster approach. In these formulas, the contributions to the EPR parameters from the spin-orbit coupling of ligands, the admixture of the d orbitals of the central ion with the p orbitals of ligands as well as the low symmetry (tetragonal) distortion are included.

2. Calculations

When a $Fe^+(3d^7)$ ion enters the lattice of $KTaO_3$, it may occupy the dodecahedral K^+ site because of charge match, and then no charge compensation is needed. For a $3d^7$ ion in a cubic dodecahedral (or tetra-

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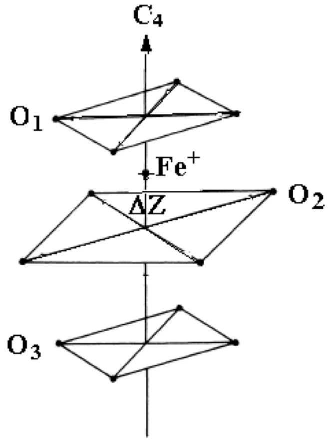

Fig. 1. Local structure of the tetragonal Fe$^+$ center in KTaO$_3$. The impurity Fe$^+$ substituting the host K$^+$ ion undergoes an off-center displacement ΔZ along the C_4 axis.

hedral) field, the ground state ^{4}F of sevenfold orbital degeneracy is split into a singlet ^{4}A$_2$ and two triplets ^{4}T$_1$ and ^{4}T$_2$, with the ^{4}A$_2$ state lying lowest [7]. Since the impurity Fe$^+$ is much smaller than the replaced K$^+$ ion, the former may be unstable on the regular K$^+$ site and then take an off-center displacement ΔZ along one of the $\langle 100\rangle$ (or C_4) axes. Similar off-center displacements of impurity ions replacing larger host cations in crystals were also obtained by using the shell-model interionic potential method [8, 9]. As a result, the axial displacement ΔZ can reduce the local symmetry of the impurity center from cubic to tetragonal (see Fig. 1), which is consistent with the experimental g factor axiality [6]. In the following, the displacement ΔZ for this impurity center is to be determined by using the perturbation formulas of the EPR parameters for a 3d^7 ion in tetragonally distorted dodecahedra based on the cluster approach.

From the cluster approach, the spin-orbit coupling coefficients ζ and ζ' and the orbital reduction factors k and k' for the 3d^7 ion in dodecahedra (or tetrahedra) can be written as [10]

$$\begin{aligned}
\zeta &= N_\mathrm{t}{}^2[\zeta_\mathrm{d}{}^0 + (\sqrt{2}\lambda_\pi\lambda_\sigma - \lambda_\pi{}^2/2)\zeta_\mathrm{p}{}^0],\\
\zeta' &= N_\mathrm{t}N_\mathrm{e}[\zeta_\mathrm{d}{}^0 + (\lambda_\pi\lambda_\sigma/\sqrt{2} + \lambda_\pi{}^2/2)\zeta_\mathrm{p}{}^0],\\
k &= N_\mathrm{t}{}^2[1 - \lambda_\pi{}^2/2 + \sqrt{2}\lambda_\pi\lambda_\sigma\\
&\qquad + 2\lambda_\sigma S_\mathrm{dp}(\sigma) + 2\lambda_\pi S_\mathrm{dp}(\pi)],\\
k' &= N_\mathrm{t}N_\mathrm{e}[1 + \lambda_\pi{}^2/2 + \lambda_\pi\lambda_\sigma/\sqrt{2}\\
&\qquad + 4\lambda_\pi S_\mathrm{dp}(\pi) + \lambda_\sigma S_\mathrm{dp}(\sigma)].
\end{aligned} \tag{1}$$

Here $\zeta_\mathrm{d}{}^0$ and $\zeta_\mathrm{p}{}^0$ are, respectively, the spin-orbit coupling coefficient of the d electrons of a free 3d^7 ion and that of the p electrons of a free ligand ion. $S_\mathrm{dp}(\sigma)$ and $S_\mathrm{dp}(\pi)$ are the group overlap integrals for the σ and π orbitals, respectively. N_γ ($\gamma = e$ and t, which denote the irreducible representations of the T_d group) are the normalization factors. λ_j ($j = \sigma$ and π) are the orbital mixing coefficients. They satisfy the normalization conditions

$$\begin{aligned}
N_\mathrm{t} &= [1 + \lambda_\sigma{}^2 + \lambda_\pi{}^2 + 2\lambda_\sigma S_\mathrm{dp}(\sigma) + 2\lambda_\pi S_\mathrm{dp}(\pi)]^{-1/2},\\
N_\mathrm{e} &= [1 + 3\lambda_\pi{}^2 + 6\lambda_\pi S_\mathrm{dp}(\pi)]^{-1/2}.
\end{aligned} \tag{2}$$

Utilizing the perturbation method, the formulas of the EPR parameters D, $g_\parallel$ and Δg of the ground state ^{4}A$_2$ for the 3d^7 ion in tetragonally distorted dodecahedra (or tetrahedra) are derived. Thus, we have [10]

$$\begin{aligned}
D &= \frac{35}{9}D_\mathrm{t}\zeta'^2[1/E_1{}^2 - 1/E_3{}^2] - 35BD_\mathrm{t}\zeta\zeta'/(E_2E_3{}^2),\\
g_\parallel &= g_s + 8k'\zeta'/(3E_1) - 2\zeta'(2k'\zeta - k\zeta' + 2g_sk)/(9E_1{}^2)\\
&\quad + 4\zeta'^2(k - 2g_s)/(9E_3{}^2) - 2\zeta^2(k + g_s)/(3E_2{}^2)\\
&\quad + k'\zeta\zeta'[4/(9E_1E_3) - 4/(3E_1E_2) + 4/(3E_2E_3)]\\
&\quad - 140k'\zeta'D_\mathrm{t}/(9E_1{}^2),\\
\Delta g &= g_\perp - g_\parallel = 210k'\zeta'D_\mathrm{t}/(9E_1{}^2),
\end{aligned} \tag{3}$$

where g_s ($= 2.0023$) is the spin-only value. The denominators E_i ($i = 1 \sim 3$) are the energy separations between the excited states ^{4}T$_2$, ^{2}T$_{2\mathrm{a}}$ and ^{2}T$_{2\mathrm{b}}$ and the ground state ^{4}A$_2$. D_t is the tetragonal crystal-field parameter.

According to the superposition model [11] and the geometrical relationship of the studied Fe$^+$ center (i. e., [FeO$_{12}$]$^{23-}$ cluster, see Fig. 1), the tetragonal field parameter D_t in (3) can be written as

$$\begin{aligned}
D_\mathrm{t} = -\frac{4}{21}\bar{A}_4(R_0)\Big[\sum_{i=1}^{3}(35\cos^4\theta_i - 30\cos^2\theta_i\\
+ 3 - 14\sin^4\theta_i/3)(R_0/R_i)^{t4}\Big]
\end{aligned} \tag{4}$$

with

$$R_1 = \left[\left(\frac{R_0}{\sqrt{2}}\right)^2 + \left(\frac{R_0}{\sqrt{2}} - \Delta Z\right)^2\right]^{1/2},$$

$$R_2 = (R_0^2 + \Delta Z^2)^{1/2},$$

$$R_3 = \left[\frac{R_0^2}{2} + \left(\frac{R_0}{\sqrt{2}} + \Delta Z\right)^2\right]^{1/2},$$

$$\theta_1 = \mathrm{tg}^{-1}\left(\frac{R_0}{R_0 - \sqrt{2}\Delta Z}\right),$$

$$\theta_2 = \frac{\pi}{2} + \mathrm{tg}^{-1}\left(\frac{\Delta Z}{R_0}\right),$$

$$\theta_3 = \frac{\pi}{2} + \mathrm{tg}^{-1}\left(\frac{R_0}{R_0 + \sqrt{2}\Delta Z}\right), \tag{5}$$

where R_i ($i = 1 \sim 3$) are the distances between the ith group of O^{2-} ligands and the impurity Fe^+. θ_i are the angles between R_i and the C_4 axis (note: the structural parameters for the four nearest oxygen ligands of the impurity Fe^+ are labeled by "O_1", see Fig. 1). The intrinsic parameter $\bar{A}_4(R_0) \approx (27/16)Dq$ (where R_0 is the reference bonding length or impurity-ligand distance, and Dq is the cubic field parameter) [11]. The power-law exponent t_4 is taken as 5 due to the ionic nature of the bonds [11, 12]. Thus, the tetragonal distortion (or the axial displacement ΔZ) of the studied system is related to the tetragonal field parameter D_t and hence to the EPR parameters (particularly the anisotropy Δg).

Since the ionic radius of the impurity Fe^+ is different from that of the replaced K^+ ion, the impurity-ligand distance R_0 can be reasonably obtained from the empirical formula $R_0 \approx R_H + (r_i - r_h)/2$ [13], where R_H ($= a/\sqrt{2} \approx 2.820$ Å, here a is the lattice constant [14]) is the K^+-O^{2-} distance in pure $KTaO_3$ and $r_i - r_h$ (≈ -0.45 Å [6]) is the ionic radius difference between the impurity Fe^+ and the host K^+ ions. Thus we have $R_0 \approx 2.595$ Å. By using the distance R_0 and the Slater-type SCF functions [15, 16], the group overlap integrals $S_{dp}(\pi) \approx 0.002$ and $S_{dp}(\sigma) \approx -0.008$ can be calculated.

Since no optical spectra of dodecahedral (or tetrahedral) Fe^+-O^{2-} clusters were reported, we can approximately calculate the normalization factors N_t, N_e (which are related to the covalency factor β by the relationship $N_t^4 \approx N_e^4 \approx \beta \approx B/B_0 \approx C/C_0$ [17, 18]) and the cubic field parameter Dq from

$$10Dq \approx f(\mathrm{L})g(\mathrm{M}), 1 - \beta \approx h(\mathrm{L})k(\mathrm{M}), \tag{6}$$

where $f(\mathrm{L})$ or $h(\mathrm{L})$ is the characteristic parameter of the ligand, and $g(\mathrm{M})$ or $k(\mathrm{M})$ the characteristic parameter of the central metal ion. For the Fe^+-O^{2-} cluster in this work, the values $g(Fe^+)$ and $k(Fe^+)$ can be extrapolated from those of the isoelectronic Co^{2+} and Ni^{3+} ions. According to the data $g(Co^{2+}) \approx 9000$ cm^{-1}, $g(Ni^{3+}) \approx 18000$ cm^{-1}, $k(Co^{2+}) \approx 0.24$, $k(Ni^{3+}) \approx 0.49$ [17, 18], one can obtain for Fe^+

$$g(Fe^+) \approx 5100\ \mathrm{cm}^{-1}, k(Fe^+) \approx 0.17. \tag{7}$$

Table 1. The EPR parameters for the impurity Fe^+ on the K^+ site of $KTaO_3$.

	D [cm^{-1}]	$g_\parallel$	Δg $(= g_\perp - g_\parallel)$
Cal.[a]	26.99	1.82	0.49
Cal.[b]	215.05	−0.47	3.92
Cal.[c]	8.75	2.04	0.15
Expt. [6]	8.31[d]	2.02	0.14

[a] Calculation by using the displacements $\Delta Z \approx 0.6$Å and $\Delta X \approx 0.2$ Å based on the simple crystal-field model in [24]; [b] Calculation by using the displacements $\Delta Z \approx 1.154$ Å and $\Delta X \approx 0.6$ Å based on the GGA studies in [5]; [c] Calculation by using the displacements $\Delta Z \approx 0.43$ Å and $\Delta X \approx 0$ based on the studies of the EPR parameters in this work; [d] The experimental D was not given in [6]. This value is estimated from the approximate relationship $D \approx \zeta_d{}^0 \Delta g/6$ [25].

Thus, the spectral parameters $Dq \approx 510$ cm^{-1} and $\beta \approx 0.8$ can be calculated from (6) and $f(O^{2-}) \approx h(O^{2-}) \approx 1.0$ [17, 18]. So the Racah parameters B and C for the studied system can be determined from the free-ion parameters $B_0 \approx 869$ cm^{-1} and $C_0 \approx 3638$ cm^{-1} of Fe^+ [19]. According to the value (≈ 0.946) of N_t or N_e obtained from β, the mixing coefficients $\lambda_\pi \approx 0.16$ and $\lambda_\sigma \approx -0.230$ are calculated from (2). By substituting the free-ion values $\zeta_d{}^0 \approx 356$ cm^{-1} [19] for Fe^+ and $\zeta_p{}^0 \approx 151$ cm^{-1} [20] for O^{2-} into (1), the parameters $k \approx 0.838$, $k' \approx 0.885$, $\zeta \approx 309$ cm^{-1} and $\zeta' \approx 317$ cm^{-1} are obtained.

Substituting the above parameters into (3) and fitting the calculated anisotropy Δg to the observed value, one can determine the axial displacement of the impurity Fe^+, i. e.,

$$\Delta Z \approx 0.43\ \text{Å}. \tag{8}$$

The corresponding theoretical $g_\parallel$ and Δg are shown in Table 1.

The local structure (or impurity displacement) for Fe^+ in $KTaO_3$ was also investigated by other methods in the previous works. For example, Glinchuk et al. [21] obtained the displacement ΔZ (≈ 0.6 Å) for Fe^+ and another inward displacement ΔX (≈ 0.2 Å) for the four oxygen ions (labeled as "O_1" in Fig. 1) nearest to the Fe^+ ion, based on the simple crystal-field model. In addition, Leung [5] found the large displacements ΔZ (≈ 1.154 Å) and ΔX (≈ 0.6 Å) based on the generalized gradient approximation (GGA) studies.

The inward displacement ΔX of the four nearest oxygen ions was regarded as due to the approaching Fe^+ and hence to its increasing electrostatic attraction. For comparisons, the theoretical EPR parameters by using the above ΔZ and ΔX in [5, 21] are also calculated and collected in Table 1.

3. Discussion

From Table 1 one can find that the calculated g factors based on the displacement ΔZ of the impurity Fe^+ in this work agree reasonably with the observed values, whereas those based on the values of ΔZ and ΔX in [5, 21] do not. In particular, the displacements in [5] yield even opposite (negative) signs of the theoretical $g_\parallel$ and more than 20 times larger Δg values than observed, suggesting that the estimated tetragonal distortion (or the value of D_t) is somewhat too large due to the significant displacements ΔZ and ΔX in the previous works [5, 21]. Therefore the displacement ΔZ for Fe^+ obtained by analyzing the EPR data seems to be more suitable. There are several points that may be discussed here.

1. The axial displacement ΔZ for the impurity Fe^+ is consistent with the experimental g factors of axial (tetragonal) symmetry. The off-center displacement along the C_4 axis was also found for Li^+ on a K^+ site of $KTaO_3$ [22, 23], where the ionic radius of the impurity Li^+ is much smaller than that of the host K^+. More interestingly, the magnitude (≈ 0.43 Å) of the off-center displacement of the impurity Fe^+ in this work is comparable with that (≈ 0.46 Å) for Li^+ on the K^+ site of $KTaO_3$ obtained from the nuclear quadrupole shift [23, 24].

2. The displacements $\Delta Z \approx 0.43$ Å (and $\Delta X \approx 0$) obtained in this work are smaller than those ($\Delta Z \approx 0.6$ Å and $\Delta X \approx 0.2$ Å) based on the simple crystal-field model in [21], and those ($\Delta Z \approx 1.154$ Å and $\Delta X \approx 0.6$ Å) based on the GGA studies [5]. On the one hand, the estimated values of ΔZ and ΔX based on the simple crystal-field model may not be conclusive due to oversimplification of the adopted model in [21]. On the other hand, the large (~ 1 Å) off-center displacements of K-substituting impurities (e. g., Fe^{3+}, Co^{2+}) in $KTaO_3$ seem not suitable for Fe^+ in this work because of strong metal-oxygen covalent bonding obtained in [5], since the covalency effect for the Fe^+-O^{2-} cluster is not strong, i. e., the covalency factor β (≈ 0.8) is close to unit. Meanwhile, the estimated displacement ΔX (≈ 0.6 Å) in [5] did not yield good convergence in the GGA studies, either. In fact, the increasing electrostatic attraction acting on the four nearest O^{2-} ions due to the approaching Fe^+ ion along the C_4 axis would be largely canceled by the increasing electrostatic repulsion among the four O^{2-} ions. As a result, the inward displacement ΔX for the four nearest O^{2-} ions is expected to be negligible, i. e., $\Delta X \approx 0$. Thus, the tetragonal distortion of the studied Fe^+ center results mainly from the displacement ΔZ of the impurity Fe^+. Considering that the EPR parameters (e. g., Δg) are sensitive to the local structure (particularly the axial shift of the impurity), the Fe^+ in $KTaO_3$ does not necessarily undergo an as large axial displacement as those in [5, 21] to meet the tetragonal distortion of the studied system, and so the relatively small ΔZ in this work can be understood. This point remains to be further checked with experiments.

3. The experimental value of the zero-field splitting D was not given in [6]. However, the validity of the calculated D can be illustrated by the empirical relationship between D and the anisotropy Δg, i. e., $D \approx \zeta_d{}^0 \Delta g/6$ [25]. Obviously, the large theoretical D value is consistent with the large tetragonal distortion due to the axial displacement of Fe^+. According to (3) – (5), one can find that large ΔZ lead to large D_t (or tetragonal distortion) and hence to large values of Δg and D.

4. There are some errors in the calculated EPR parameters and the displacement ΔZ due to (i) approximation of the theoretical model and the related parameters (e. g., Dq and β) for the studied impurity center; (ii) neglecting of the displacements of the oxygen ligands; (iii) absence of the experimental zero-field splitting D. Fortunately, the displacement ΔZ is sensitive to Δg (see 3.) and can also be reasonably obtained by analyzing the observed Δg. As mentioned before, the displacement ΔX of the four nearest O^{2-} ions may be very small (those of the farther O^{2-} ions should be even smaller) and has little influence on the final results of the EPR parameters or ΔZ. In view of these points, the theoretical results and conclusion in this work seem valid.

In summary, the EPR parameters for $KTaO_3$:Fe^+ are theoretically explained, and information about the local structure of the off-center impurity Fe^+ in $KTaO_3$ is also obtained in this work. The studies of the off-center displacement for Fe^+ occupying the K^+ site in $KTaO_3$ is significant because it is similar to Li^+ which may also shift along the C_4 axis and induce ferroelectric phase transitions [6, 22]. So, the Fe^+-doped $KTaO_3$ can be regarded as the source of induced polar regions at low temperature and as a prospective candidate for the creation of ferroelectric long-range order in iron-doped crystals [6, 22].

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