Investigation of the Electric-field Effect in EPR Spectra of Fe^{3+} in $KTaO_3$

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The displacements of Fe^{3+} (at the Ta^{5+} site) along the [001] direction in $KTaO_3$ crystal, caused by the electric field, have been studied by calculating the electric-field-induced zero-field splittings from the microscopic mechanisms and the empirical superposition model. It is found that the Fe^{3+} displacements obtained by the two methods at the same electric-field strength and temperature are close to each other. These displacements are also close to that estimated from the force-balance equation. It is suggested that the electric-field-induced zero-field splitting can be attributed primarily to the above displacement and the temperature dependence of the electric-field-induced zero-field splitting is mainly due to the change in the dielectric constant of $KTaO_3$ with temperature.

Key words: Electron Paramagnetic Resonance; Electric-field Effect; Crystal-field Theory; Fe^{3+}; $KTaO_3$.

1. Introduction

$KTaO_3$ has the cubic perovskite structure. The Fe^{3+} ion in $KTaO_3$ crystal can replace K^+ and Ta^{5+} ions and so there are two cubic Fe^{3+} centers (with inversion symmetry) in $KTaO_3$. The electric-field effect in the EPR spectra of the two cubic Fe^{3+} centers was studied in [1]. If an electric-field of $E \approx 150$ kV/cm along the [001] direction was applied, no changes were observed in the EPR spectra of Fe^{3+} at the K^+ site. However an anomalously large shift (and hence a large electric-field-induced zero-field splitting) was observed for Fe^{3+} at a Ta^{5+} site. In addition, the electric-field-induced zero-field splitting depends strongly on the temperature [1]. In general, electric-field-induced changes of EPR spectra can hardly be observed in systems of paramagnetic ions with inversion symmetry. It can be found for Fe^{3+} at a K^+ site in $KTaO_3$ [1] and $3d^n$ ions in MgO [2]. So, it is interesting to study the electric-field effect on EPR spectra for Fe^{3+} at a Ta^{5+} site in $KTaO_3$. Considering that the impurity Fe^{3+} carries less charge than the replaced Ta^{5+} ion, the coupling of the impurity to the lattice should be looser and it should more easily be shifted by the electric-field (on the other hand, because of the extra charge of Fe^{3+} at a Li^+ site, its displacement should be more difficult), and the high dielectric constant of $KTaO_3$ [3] results in a large local electric-field. We suggest that the observed zero-field splitting in an electric-field can be attributed primarily to the displacement of Fe^{3+} along the electric-field direction in (FeO_6) clusters [note: the displacement leads the symmetry of the $(FeO_6)^{9-}$ cluster to change from cubic to tetragonal, and so the zero-field splitting occurs]. Based on the suggestion, in this paper we study the electric-field-induced displacements of Fe^{3+} at various electric-field strengths and temperatures by calculating the zero-field splittings from the microscopic mechanisms and the empirical superposition model. The results are discussed.

2. Calculation

The zero-field splitting of the ^6S state ion can be studied by the microscopic mechanisms and the empirical superposition model. The microscopic origin of the zero-field splitting is complex because of the lack of orbital angular momentum in the ^6S ground state. There are many mechanisms which can contribute to zero-field splitting [4 – 9]. It is usually believed that among these mechanisms, the spin-orbit (SO)-coupling mechanism [4, 5], the relativistic (RE)

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mechanism and the covalency and overlap (CO) mechanism [8, 9] are of importance. Thus, we have

$$D = D_{SO} + D_{RE} + D_{CO}. \tag{1}$$

For SO mechanism, the high-order perturbation formula in tetragonal symmetry can be expressed as [5]

$$\begin{aligned} D_{SO} = {} & \frac{4\xi^2}{70P^2D'}(-B_{20}^2 - 21\xi B_{20}) \\ & + \frac{\xi^2}{63P^2G}(-5B_{40}^2 + 14B_{44}^2), \end{aligned} \tag{2}$$

where ξ is the spin-orbit-coupling coefficient. P, D' and G are the energy separations between the excited quarters and the ground sextet of the free ion and so they can be calculated from the Racah parameters B and C. By the point-charge-dipole model, the tetragonal field parameters B_{kl} can be written as

$$\begin{aligned} B_{20} = {} & -\frac{2eq\left(1+\frac{3p}{eR}\right)\langle r^2\rangle(3\cos^2\theta - 1)}{R_1^3} \\ & - eq\left(1-\frac{3p}{eR}\right)\langle r^2\rangle\left(\frac{1}{R_2^3}+\frac{1}{R_3^3}\right), \\ B_{40} = {} & -\frac{2eq\left(1+\frac{5p}{eR}\right)\langle r^4\rangle(35\cos^4\theta - 30\cos^2\theta + 3)}{R_1^5} \\ & - eq\left(1-\frac{5p}{eR}\right)\langle r^4\rangle\left(\frac{1}{R_2^5}+\frac{1}{R_3^5}\right), \\ B_{44} = {} & -\frac{-\sqrt{70}eq\left(1+\frac{5p}{eR}\right)\langle r^4\rangle\sin^4\theta}{4R_1^5}, \end{aligned} \tag{3}$$

where q $(= -2e)$ is the ligand charge and p is the dipole. R_i are the metal-ligand distances and θ is the angle between the R_1 and C_4 axis. In consideration of the Fe^{3+} displacement along the [001] direction in the $(FeO_6)^{9-}$ cluster in $KTaO_3$, we have

$$\begin{aligned} & R_1 = \sqrt{R^2+S^2},\ R_2 = R+S, R_3 = R-S, \\ & \cos\theta = \frac{S}{R_1}, \end{aligned} \tag{4}$$

where R (≈ 1.994 Å [10]) is the corresponding distance in the host crystal $KTaO_3$.

For Fe^{3+}, from the empirical d orbital we have [11]

$$\begin{aligned} & B_0 = 1130.22\ \text{cm}^{-1},\ C_0 = 4111.45\ \text{cm}^{-1}, \\ & \xi_0 = 588.946\ \text{cm}^{-1}, \\ & \langle r^2\rangle_0 = 1.89039\ \text{au}^2,\ \langle r^4\rangle_0 = 11.46485\ \text{au}^4. \end{aligned} \tag{5}$$

Introducing an adjustable parameter N to denote the average covalency reduction effect in crystal, one gets [11]

$$\begin{aligned} & B = N^4B_0,\ C = N^4C_0, \\ & \xi = N^2\xi_0,\ \langle r^n\rangle = N^2\langle r^n\rangle_0. \end{aligned} \tag{6}$$

The adjustable parameters N and p can be estimated by analyzing the optical spectra of the studied system. From the optical spectra of $KTaO_3$:Fe^{3+} [12], we have

$$N \approx 0.9,\ p \approx 0.0754eR. \tag{7}$$

The zero-field splitting due to the RE mechanism in tetragonal symmetry is [6]

$$D_{RE} = 6\xi A_{20}\langle b_2(11)\rangle/125P, \tag{8}$$

where $A_{20} = B_{20}/\langle r^2\rangle$. The value of $\langle b_2(11)\rangle$ for Fe^{3+} was approximately estimated to be -0.0243 au^2 [13].

The zero-field splitting caused by the CO mechanism in the above tetragonal symmetry can be expressed as [8, 9]

$$\begin{aligned} D_{CO} & = \frac{3}{2}\sum_{i=1}^{6} d(R_i)(3\cos^2\theta_i - 1) \\ & = 6d(R_1)(3\cos^2\theta - 1) + 3d(R_2) + 3d(R_3), \end{aligned} \tag{9}$$

where the R dependence of $d(R)$ was calculated for the $(FeO_6)^{9-}$ cluster and can be expressed approximately as [9]

$$d(R) \approx 2.29/R^5\ \text{cm}^{-1}, \tag{10}$$

where R is in Angstroms.

From the above microscopic formulas one can find that the Fe^{3+} displacement S can be obtained by fitting the calculated zero-field splitting to the observed value. The electric-field-induced shift ΔH in the resonance field of the line of $KTaO_3$:Fe^{3+} for the transition ($\pm 3/2 \rightarrow \pm 1/2$) at 77 K and 300 K was measured [1]. Since the rank-four spin-Hamiltonian parameters a and F are much smaller than the rank-two spin-Hamiltonian parameter D, we have $\Delta H = E(\pm 3/2) - E(\pm 1/2) \approx 2D$. Thus, the observed zero-field splitting D at various electric fields and temperatures can be obtained as shown in Table 1. It can be seen that under the same electric-field strength, the splitting D at 77 K is considerably larger than that at 300 K. By fitting the calculated splitting D to the observed value, the Fe^{3+} displacements S at various electric-field strengths and temperatures are obtained. They are shown in Table 1.

Table 1. The zero-field splitting D and the Fe^{3+} displacements S induced by the electric-field strengths E along the [001] direction in $KTaO_3$:Fe^{3+} at $T = 77$ K and 300 K.

E (kV/cm)	T (K)	D (10^{-4} cm^{-1}) [1]	S^a (Å)	S^b (Å)	S^c (Å)
25	77	12.7	0.019	0.016 (3)	0.021
50	77	49.4	0.038	0.032 (6)	0.042
75	77	105.5	0.056	0.046 (8)	0.064
100	77	173.6	0.071	0.059 (10)	0.085
25	300	2.7	0.009	0.007 (1)	0.006
50	300	8.0	0.016	0.013 (2)	0.013
75	300	12.0	0.019	0.016 (3)	0.019
100	300	17.4	0.023	0.019 (3)	0.025

[a] Obtained by calculating the zero-field splitting D from the microscopic mechanisms.
[b] Obtained by calculating the zero-field splitting D from the empirical superposition model.
[c] Obtained from the force-balance equation.

The empirical superposition model is a powerful tool in explaining the zero-field splitting of ^{6}S state ion in crystals [14, 15]. From the model [14], the zero-field splitting in the above tetragonal symmetry is

$$D = \bar{b}_2(R_0)\left[2\left(\frac{R_0}{R_1}\right)^{t_2}(3\cos^2\theta - 1) + \left(\frac{R_0}{R_2}\right)^{t_2} + \left(\frac{R_0}{R_3}\right)^{t_2}\right], \tag{11}$$

where the intrinsic parameter $\bar{b}_2(R_0) \approx -0.26(10)$ cm^{-1} with $R_0 \approx 2.019$ Å for the Fe^{3+}-O^{2-} combination [15]. The power-law exponent $t_2 \approx 7$ [15]. Thus, the electric-field-induced displacements S can be obtained by calculating the zero-field splittings. They are also shown in Table 1.

3. Discussion

From Table 1 one can find that the calculated Fe^{3+} displacements S from the microscopic mechanisms and the empirical superposition model at the same electric-field strength and temperature are close to each other. Since these mechanisms and models are effective in explaining the zero-field splitting of ^{6}S state ions in crystals, these placements can be regarded as reasonable.

In order to confirm further the reasonableness of these calculated Fe^{3+} displacements, we make a rough estimation for the electric-field-induced Fe^{3+} displacements by using the force-balance equation

$$q' E_{10C} = kS, \tag{12}$$

where q' $(= 3e)$ is the charge of Fe^{3+}, k is the force constant, E_{10C} is the local electric field for Fe^{3+} in $KTaO_3$ crystal. As is known [1, 16],

$$E_{10C} \approx E_{ex} + \frac{4\pi}{3}\gamma P \approx \left[1 + \frac{\gamma}{3}(\varepsilon - 1)\right] E_{ex}. \tag{13}$$

So, we have

$$S/E_{ex} \approx q'[1 + \gamma(\varepsilon - 1)/3]/k, \tag{14}$$

where E_{ex} is the external field, ε the dielectric constant, and γ the Lorentz factor. For the Ta^{5+} site in $KTaO_3$, $\gamma \approx 5$ [1, 16]. The calculation of the force constant k for the Ta^{5+},O^{2-} bond in $KTaO_3$ with perovskite structure is very difficult and we estimate approximately the force constant k by using the formula $k = 6R/\chi$ [17] in the NaCl structure, where χ is the linear compressibility. For $KTaO_3$, $R \approx 1.994$ Å [10] and $\chi \approx 1.53 \cdot 10^{-4}$/kb [18], so we obtain

$$k \approx 7.8 \cdot 10^2 \text{ N/m}. \tag{15}$$

The dielectric constant ε of $KTaO_3$ depends strongly on the temperature. At $T = 300$ K, $\varepsilon = 243$ [3], so, we have

$$S/E_{ex}(300 \text{ K}) = 2.5 \cdot 10^{-4} \text{ Å/kV}, \tag{16}$$

and at $T = 77$ K, $\varepsilon = 830$ [3], we have

$$S/E_{ex}(300 \text{ K}) = 8.5 \cdot 10^{-4} \text{ Å/kV}. \tag{17}$$

Thus, the Fe^{3+} displacements S at various electric-field strengths and both temperatures can be calculated. They are also collected in Table 1. It can be seen that at the same electric-field strength and temperature, the Fe^{3+} displacement estimated by the simple force-balance equation is close to those obtained by calculating the electric-field-induced zero-field splitting from both methods. So, although there are some approximations in the estimation and calculation, the analogy of Fe^{3+} displacements obtained from the three methods suggests that these displacements may be reasonable.

Under the same electric-field strength, the temperature dependences of the Fe^{3+} displacement and hence of the zero-field splitting are caused by the change of dielectric constant of $KTaO_3$ with the temperature. So, the larger electric-field-induced zero-field splitting at 77 K than that at 300 K can be reasonably explained.

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