Impurities in nominally pure KTaO$_3$: evidence from electron spin resonance

Impurities in nominally pure KTaO₃: evidence from electron spin resonance

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Abstract. The ESR investigation of nominally pure KTaO₃ was carried out at 4.2 K $< T <$ 77 K. Two ESR spectra were observed for the first time. The first spectrum with cubic symmetry was shown to be that of Gd^{3+} substituted for K^+. The analysis of the spectrum line intensities and widths gave no evidence about the quasi-static displacements of tantalum ions in the lattice assumed earlier. The second spectrum had axial symmetry and its source was identified as a new off-centre impurity ion Fe^+ substituted for K^+ in KTaO₃. The surrounding oxygen ion displacements were shown to be the main reason for the Fe^+ ESR spectra axiality. The estimation of these displacements Δx was carried out in the framework of crystalline-field theory and appeared to be about 0.2 Å.

1. Introduction

Nominally pure incipient ferroelectric KTaO₃ has attracted great attention in the last few years owing to its unusual properties at low temperatures ($T < 30$ K). In spite of cubic symmetry, several phenomena which are characteristic of the crystals without an inversion centre were observed: Raman scattering of the first order [1], second-harmonic generation and hyper-Rayleigh scattering [2, 3]. Unavoidable impurities and crystal imperfections, e.g. oxygen vacancies or Ta^{3+} ions were assumed to be the main reasons for these phenomena [2, 3], since at low temperatures the lattice correlation radius is large (several lattice constants) and thus the volume with defect-induced lattice symmetry breaking may be large enough even for a small defect content. On the other hand the peculiarities of the KTaO₃ low-temperature ¹⁸¹Ta NMR spectra [4] as well as dielectric relaxation measurement [5] opened up discussion about the dynamic crossover from displacive into order–disorder motion [6] or sudden quasi-static off-centre displacement of Ta ions in all the lattice which results in local non-cubic symmetry on a time scale $\Delta t > 10^{-7}$ s. The observation of Debye-like relaxation in nominally pure KTaO₃ at low temperatures [5] was assumed to be confirmation of the off-centre displacement of Ta ions despite its magnitude discrepancy with NMR data. The discussion [7, 8] about the quantum coherent state in SrTiO (as well as the possibility of such a state in KTaO₃) connected with soft-optic and acoustic phonon interaction peculiarities should be noted. Because no one obtained evidence about overall symmetry lowering, the need for a defect structure investigation on nominally pure KTaO₃ is obvious, at least as the first step for the solution of the problem of the peculiarities in the low-temperature properties. Obtaining information about unavoidable defects in pure KTaO₃ is very important also for the physics of phase transitions induced by off-centre ions in this

crystal [9]. It was shown recently that random fields of unavoidable defects can destroy long-range order induced by electric dipoles and thus change strongly the transition temperature and critical concentration of dipoles [10]. The observation of impurity photoconductivity in undoped $KTaO_3$ [11] as well as in $K_{1-x}Li_xTaO_3$ [12] also requires knowledge about the impurities in these crystals. The first investigation of symmetry-breaking defects in pure $KTaO_3$ was carried out recently using the ESR method [13]. Axial and rhombic symmetry centres of Fe^{3+} were observed. It was supposed that these centres may be the main reason for the observation for example of first-order Raman scattering and second-harmonic generation.

In this work we observed two paramagnetic centres in nominally pure $KTaO_3$ using the ESR method at $T = 4.2$ K. One of them was shown to be Gd^{3+} with cubic symmetry, which is very important because of its high sensitivity to small lattice distortions. We also discovered a new off-centre ion in $KTaO_3$, namely Fe^+ substituted for K^+. The axial symmetry of its ESR spectrum was shown to appear because of surrounding oxygen displacements. Estimation of these displacements was carried out in the framework of the crystalline-field theory. The possible origin of the low-temperature anomalies in pure $KTaO_3$ is discussed.

2. Measurements and spectra identification

2.1. Investigated samples

The investigated samples were stoichiometric undoped $KTaO_3$ single crystals grown by the spontaneous crystallization technique. The starting components were the salt K_2CO_3 and the oxide Ta_2O_5 of high purity, i.e. the contents of unavoidable impurities in them were less than 10–50 ppm. All the crystals were optically transparent, some of them being colourless and others having a slightly pink colour. The specimen dimensions were 1 mm×2 mm×3 mm with plates of (001) type.

ESR spectra were measured in the 9.3 GHz microwave region at 4.2 K $\leqslant T < 77$ K. ESR spectra measurements were carried out on both the colourless and the slightly pink $KTaO_3$ crystals. Up to $T = 4.2$ K no spectra of pink samples were observed. At $T = 4.2$ K we measured three ESR spectra of the colourless samples: two with axial symmetry and one with cubic symmetry. The spectra show no modifications of their parameters up to 40 K. Under the Boltzmann thermal factor effect the ESR line intensities decrease when the temperature increases and at $T > 60$ K the spectra became unobservable.

2.2. The cubic-symmetry spectrum

The cubic-symmetry spectrum contained seven lines (figure 1). The dependence of these line positions on the external magnetic field orientation are depicted in figure 2 and can be fitted by the spin Hamiltonian (SH) of cubic symmetry:

$$\mathcal{H} = g\beta\overline{HS} + \frac{b_4^0}{60}(O_4^0 + 5O_4^4) + \frac{b_6^0}{1260}(O_6^0 - 21O_6^4). \tag{1}$$

The parameters of the SH (1) are given in table 1.

Of the several ions with $S = \frac{7}{2}$ (e.g. Eu^{2+} and Gd^{3+}) the most probably candidate is Gd^{3+} since Eu^{2+} has non-zero nucleus spin, i.e. its spectrum must have hyperfine structure. Moreover the Gd^{3+} spectrum of $KTaO_3$ doped by Gd was investigated earlier [14]. It was shown that Gd^{3+} substitutes for K^+; its excess charge compensation takes place in distance
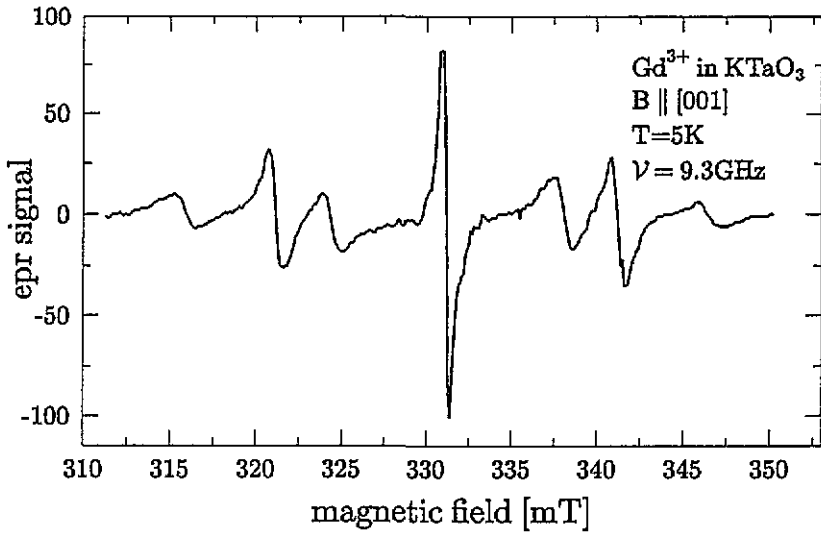
Figure 1. The Gd^{3+} ESR spectrum in nominally pure KTaO₃ ($\nu = 9.3$ GHz; $T = 5$ K).

spheres, and so the Gd^{3+} local symmetry is cubic. The parameters of the SH obtained in [14] and our values are represented in table 1. It is seen that all the parameters are of the same order of magnitude. The small deviation of the b_4^0-value (which is outside the experimental accuracy) is the result of more precise fitting of angular dependence than in [14]. In our opinion it appeared possible owing to the narrower lines of our spectrum; for example at $\theta = 0$, $\Delta H_{7/2,5/2} = 1.2$ mT, $\Delta H_{5/2,3/2} = 1.1$ mT, $\Delta H_{3/2,1/2} = 0.8$ mT and $\Delta H_{1/2,-1/2} = 0.5$ mT, their integral intensity ratio $I_{7/5,5/2}:I_{5/2,3/2}:I_{3/2,1/2}:I_{1/2,-1/2} = 9:13:14:16$ being close to the theoretical prediction for $S = \frac{7}{2}$ (7:12:15:16). The last fact favours the assumption that our single crystal contains a lower defect concentration than that used in [14]. Gd^{3+} is known to be very sensitive to electric fields [15], i.e. even small internal fields of defects can be expected to broaden the ESR lines strongly. The spin–spin interaction contribution to the linewidth is also larger in the samples doped by Gd^{3+} than in our nominally pure KTaO₃.

2.3. The axial-symmetry spectra

The axial-symmetry spectra were described by a SH of the form

$$\mathcal{H} = g_\parallel^{\text{eff}} \beta (S_z^{\text{eff}} H_z) + g_\perp^{\text{eff}} (S_x^{\text{eff}} H_x + S_y^{\text{eff}} H_y) \tag{2}$$

where x, y, z are along the cubic axis directions of [100] type. The parameters of the first, $g_\parallel^{\text{eff}} = 2$, $g_\perp^{\text{eff}} = 6$, $S^{\text{eff}} = \frac{1}{2}$, have been shown to coincide with those of the well known paramagnetic centre Fe^{3+} ($3d^5$; $S = \frac{5}{2}$) substituted for K^+ in KTaO₃ doped by iron [16]. Equation (2) is known to be the consequence of a large axial crystalline field constant D. The Kramers pair acts as an effective spin doublet with effective g-factor. Its value can be represented as

$$g^{\text{eff}} = [(g_\parallel \cos\theta)^2 + (S + \tfrac{1}{2})^2 (g_\perp \sin\theta)^2]^{1/2}. \tag{3}$$

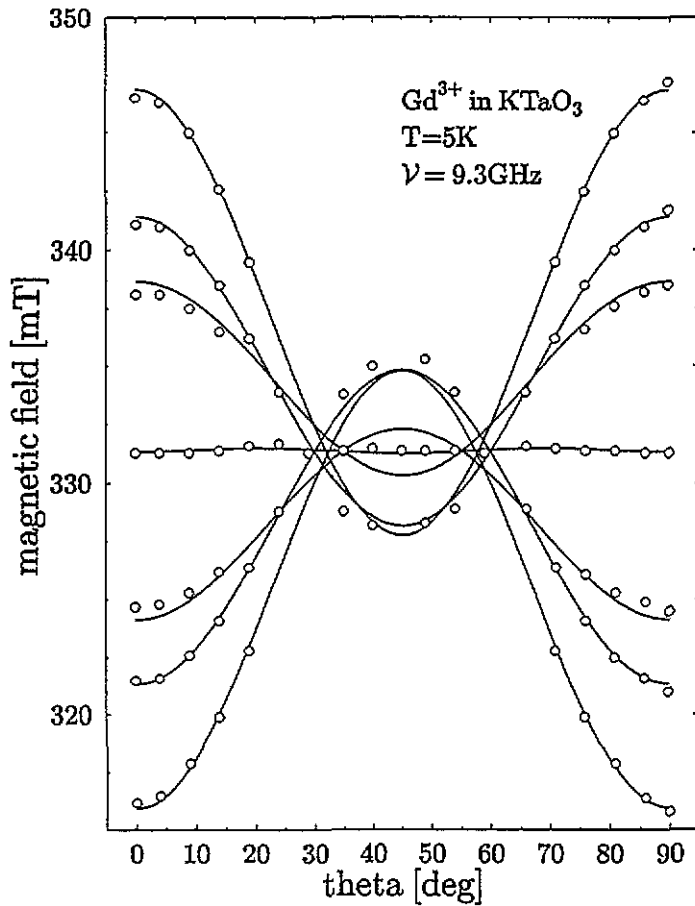Here θ is the polar angle of the external magnetic field.

Figure 2. The angular dependence of the Gd^{3+} resonance fields in $KTaO_3$ ($\nu = 0.3$ GHz; $T = 5$ K): O, measured data; ——, calculations.

Table 1. Parameters of the Gd^3 ($S = \frac{7}{2}$) spin Hamiltonian in $KTaO_3$.

g	b_4^0 (10^{-4} cm^{-1})	b_6^0 (10^{-4} cm^{-1})	Reference
1.9904 ± 0.0002	-7.251 ± 0.027	0.46 ± 0.027	This paper
1.99 ± 0.002	-8.14 ± 0.27	0.47 ± 0.3	[14]

The second axial spectrum of small intensity was new. The angular dependence of its line positions (figure 3) can be nicely fitted by SH (2) with the parameters

$$g_\parallel^{\text{eff}} = 2.02 \qquad g_\perp^{\text{eff}} = 4.33 \qquad S^{\text{eff}} = \tfrac{1}{2}. \qquad (4a)$$

Equations (3) and (4a) give the following real parameters:

$$g_\parallel = 2.02 \qquad g_\perp = 2.16 \qquad S = \tfrac{3}{2}. \qquad (4b)$$

The ESR spectrum with parameters close to these values ($g^{\text{eff}} \simeq 4.33$) was observed earlier [17] for $KTaO_3$ crystals strongly doped by Ni. Unfortunately Abraham *et al* did
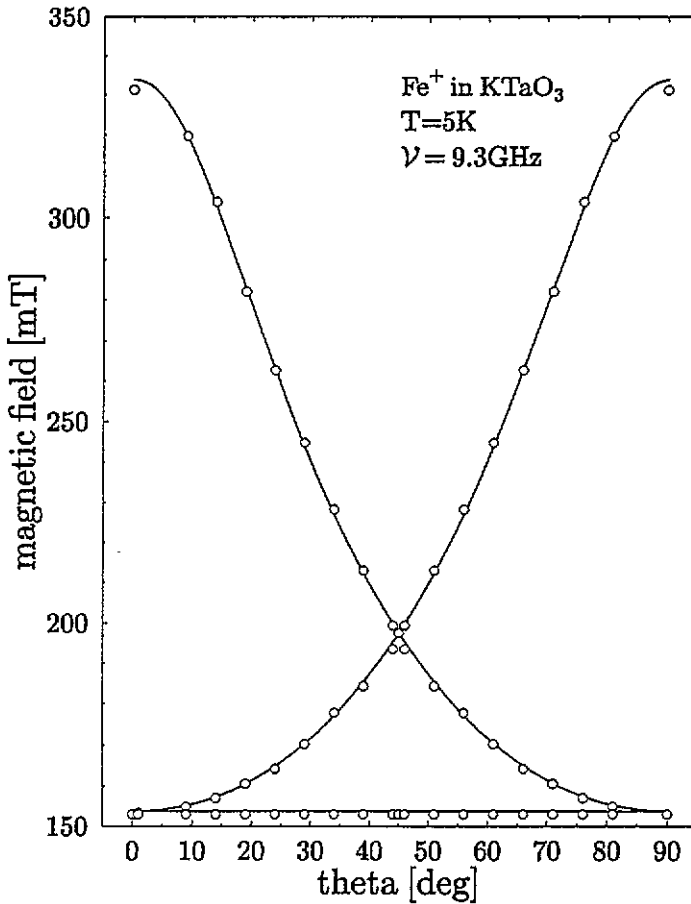
Figure 3. The angular dependence of the Fe^+ resonance fields in nominally pure $KTaO_3$ ($\nu = 9.3$ GHz; $T = 5$ K): O, measured data; ——, calculations.

not identify it unambiguously. They supposed that it can be that of Ni^{3+} or Fe^{3+}. In our opinion, neither the Ni^{3+} [18] nor the Fe^{3+} [16] axial spectra parameters fit the spectrum observed by us. Really, the angular dependence of the ESR line resonance field (figure 3) looks like that of Ni^{3+} ($3d^7$; $S = \frac{3}{2}$) but its parameters are somewhat different: $g_{\parallel}^{\text{eff}} = 2.216$; $g_{\perp}^{\text{eff}} = 4.423$. On the other hand, both Fe^+ ($3d^7$) and Fe^{5+} ($3d^3$) have the same spin $S = \frac{3}{2}$ as Ni^{3+}; thus it could be that $g_{\perp}^{\text{eff}} \simeq 4.3$ for both of them. Let us check this possibility. Allowing for the Fe^{5+} charge state, we can suppose that Fe^{5+} substitutes for Ta^{5+}. In the octahedral-symmetry crystalline field the orbital singlet level $L = 0$, $S = \frac{3}{2}$ is known to be the lowest [19]. The field of axial symmetry splits the fourfold degeneracy level and results in g-factor anisotropy, their values being of the following form [19]:

$$g_{\parallel} = g_s - \frac{8\lambda}{\Delta_0} \qquad g_{\perp} = g_s - \frac{8\lambda}{\Delta_1}. \tag{5}$$

Here $g_s = 2.0042$, λ is the energy of the spin-orbit interaction, and Δ_0 and Δ_1 are the energy distances from the ground to the excited states.

It is clear that $\delta g_{\parallel} = g_{\parallel} - g_s$ and $\delta g_{\perp} = g_{\perp} - g_s$ must have the same negative sign ($\lambda > 0$ for $3d^3$ ions). This is in strong contradiction to ours: $\delta g_{\parallel} > 0$; $\delta g_{\perp} > 0$ (see equation 4(*b*)). Thus only Fe^+ ($3d^7$, $S = \frac{3}{2}$) substituted for K^+ can cause the observed ESR spectrum.

Since both the K^+ and the Fe^+ charge states coincide, the axial symmetry of the ESR spectrum can be the consequence of the Fe^+ off-centre shift which appears owing to the large difference between the K^+ and Fe^+ ionic radii ($R_{K^+} - R_{Fe^+} \approx 0.45$ Å).

Observation of the same axial spectrum at $T = 77$ K with the parameters (4*a*) in iron-doped $KTaO_3$ was reported earlier [20] and both Fe^+ and Fe^{5+} were assumed to be its possible sources.

3. Discussion and conclusions

3.1. Gd^{3+} paramagnetic centres

The Gd^{3+} centres in $KTaO_3$ were shown to be very sensitive to the electric fields [15]. Because of this, one could suppose that its sensitivity also to quasi-static Ta ion shifts, if any, is of the order of the ESR time scale ($\Delta t > 10^{-10}$ s). Since there is overall cubic symmetry conservation of pure $KTaO_3$ in all temperature regions, including $T < 30$ K, the invariability of all the lines resonance field positions is not surprising, but one could expect at least a contribution from the Ta ion shifts to the linewidth.

If most Ta ions are chaotically shifted from lattice sites at $T < 30$ K [4], the intensities of the fine transition, especially ($\pm\frac{7}{2}$, $\pm\frac{5}{2}$) lines, were essentially different from theoretical prediction because of their broadening almost up to disappearance. Meanwhile we have observed all the fine transition lines with the ratio of integral intensities close to the theoretical prediction for an ideal lattice. Thus our ESR data gave no evidence of Ta ion displacements at low temperatures.

Moreover, in our opinion the Debye type of dielectric relaxation in nominally pure $KTaO_3$ [5] may be explained by the contribution of impurities with electric dipole moments which we observed in this work, namely axial centres of Fe^{3+} and Fe^+. The Debye-type dielectric relaxation was observed recently in $KTaO_3$ doped by Fe^{3+} and Mn^{2+} [21] and made it possible to determine the frequency of impurity reorientation, barrier heights, etc. It is obvious that measurements of NMR, ESR and dielectric relaxation of the same sample are extremely desirable to solve the problem of the peculiarities of the low-temperature properties in undoped $KTaO_3$ single crystals. This problem includes the possibility of Ta ion displacements as well as quantum coherent state appearance.

3.2. Evidence for new off-centre Fe^+ ions

Evidence for new off-centre Fe^+ ions substituted for K^+ in $KTaO_3$ is of a great importance since Fe^+ ions look like Li^+ ions which are known to be shifted also in one of the [100]-type directions and to induce a ferroelectric phase transition at a definite ion concentration range [9]. This similarity makes it possible to assume the same geometry for lattice reconstruction near an Fe^+ ion (figure 4) as was shown for Li^+ [22] and for Fe^{3+} substituted for K^+ in $KTaO_3$ [23]. The Fe^+ and O^{2-} neighbouring ion displacements could lead to tetragonal distortion of the cubic field and thus could be the reason for the ESR spectrum and g-factor axiality. These displacement values can be estimated from a comparison of the observed and calculated g-factor components. For this, let us begin with the calculation of Fe^+ (^4F; $L = 3$; $S = \frac{3}{2}$) levels in the crystal. The calculation can be carried out as usual for d ions

in the framework of the crystalline-field model by solving the secular equation of seventh order:

$$\| V_{mm'} - E\delta_{mm'} \| = 0 \qquad (m, m' = 3, 2, 1, 0, -1, -2, -3). \tag{6a}$$

Here V_{mm} are matrix elements of wavefunctions of the ^4F term, V being represented in conventional form for the $3d^3$ or $3d^7$ form:

$$V(r_1, r_2, r_3) = \sum_{i=1}^{N} eq_i \left(\frac{1}{|r_1 - R_i|} + \frac{1}{|r_2 - R_i|} + \frac{1}{|r_3 - R_i|} \right). \tag{6b}$$

Where r_k $(k = 1, 2, 3)$ and R_i are the radius vectors of holes and ions, respectively, surrounding the paramagnetic centre and q_i is the ion charge.

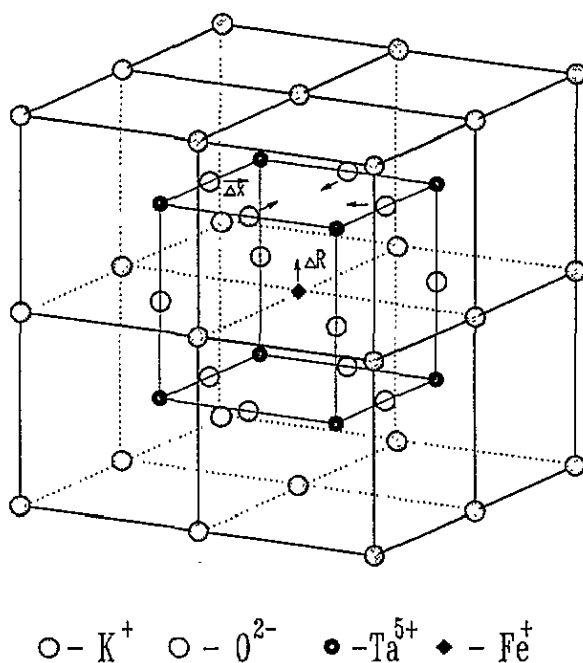$$\bigcirc - K^+ \quad \circ - O^{2-} \quad \bullet - Ta^{5+} \quad \blacklozenge - Fe^+$$

Figure 4. Part of the KTaO₃ structure with the schematic diagram of lattice reconstruction near the Fe⁺ ion substituted for K⁺.

The calculations were carried out with a model of 12 neighbouring oxygen ions, eight tantalum ions and six potassium ions (see figure 4), which were considered as point charges, R_i being dependent on ΔR and Δx (ΔR and Δx are the Fe⁺ and O²⁻ displacements, respectively). The calculations of $V_{mm'}$ showed that

$$V_{12} = V_{31} = V_{30} = V_{32} = V_{3-3} = V_{21} = V_{20} = V_{2-1} = V_{2-3} = V_{1-1}$$

$$= V_{1-2} = V_{0-1} = V_{0-2} = V_{-1-2} = V_{-1-3} = V_{-2-3} = 0 \qquad V_{mm'} = V_{m'm}. \tag{7}$$

Because of the relatively small number of non-zero matrix elements it appeared possible to find the solution of equations (6a). The levels of the ^4F term in the cubic environment ($\Delta R = 0$; $\Delta x = 0$) of 12 O^{2-}, eight Ta^{5+} and six K^+ ions can be written in the form

$$E_1(^4A_{1g}) = 3E_0 + 2F_4\left(\frac{a}{\sqrt{2}}\right) - \frac{80}{9}F_4\left(\frac{a\sqrt{3}}{2}\right) + 3F_4(a)$$

$$E_{2,3,4}(^4T_{2g}) = 3E_0 + \frac{1}{3}F_4\left(\frac{a}{\sqrt{2}}\right) - \frac{40}{27}F_4\left(\frac{a\sqrt{3}}{2}\right) + \frac{1}{3}F_4(a)$$

$$E_{5,6,7}(^4T_{1g}) = 3E_0 - F_4\left(\frac{a}{\sqrt{2}}\right) + \frac{120}{27}F_4\left(\frac{a\sqrt{3}}{2}\right) - F_4(a)$$

$$(8)$$

$$E_0 = 72F_0\left(\frac{a}{\sqrt{2}}\right) - 120F_0\left(\frac{a\sqrt{3}}{2}\right) - 18F_0(a).$$

Here $F_k(R)$ are the matrix elements of r^k which is positive, and a is the lattice constant.

It is seen that the contributions of O^{2-}, K^+ and Ta^{5+} to the cubic crystalline-field splitting have the opposite signs; without the Ta^{5+} ion contribution the lowest level is $E(^4T_{1g})$ and, without O^{2-} and K^+ ions, the lowest level is $E(^4A_{1g})$. It follows from (8) and from the approximation $F_4(R) \simeq \langle r^4 \rangle / a^5$ that the level positions can be rewritten in the form

$$E_1(^4A_{1g}) \simeq 3E_0 - 5\frac{\langle r^4 \rangle}{a^5}e^2$$

$$E_{2,3,4}(^4T_{2g}) \simeq 3E_0 - 0.8\frac{\langle r^4 \rangle}{a^5}e^2 \qquad (9)$$

$$E_{5,6,7}(^4T_{1g}) \simeq 3E_0 + 2.5\frac{\langle r^4 \rangle}{a^5}e^2.$$

So the lowest level, i.e. the ground-state energy, is the singlet $E_1(^4A_{1g})$.

Under tetragonal distortion ($\Delta R \neq 0$; $\Delta x \neq 0$) the lowest level $E(^4A_{1g})$ conserved its value, and threefold degenerate levels split into singlet and doublet levels. The distances Δ_0 and Δ_1 between the ground state $E_1(^4A_{1g})$ and the excited singlet and doublet levels, respectively (which we are interested in for calculation of the g-factor components calculation (see (5)), can be represented as

$$\Delta_0 = E_2 - E_1 + \frac{\Delta x}{a}\frac{5}{3}F_4\left(\frac{a}{\sqrt{2}}\right)$$

$$\Delta_1 = E_2 - E_1 - \frac{\Delta x}{a}\frac{10}{3}F_4\left(\frac{a}{\sqrt{2}}\right) \qquad (10)$$

$$E_2 - E_1 = -\frac{5}{3}F_4\left(\frac{a}{\sqrt{2}}\right) + \frac{200}{27}F_4\left(\frac{a\sqrt{3}}{2}\right) - \frac{5}{3}F_4(a)$$

or approximated by

$$\Delta_0 \simeq E_2 - E_1 + 9.35 \frac{\Delta x}{a} \frac{\langle r^4 \rangle}{a^5} e^2$$

$$\Delta_1 \simeq E_2 - E_1 - 18.7 \frac{\Delta x}{a} \frac{\langle r^4 \rangle}{a^5} e^2 \qquad (11)$$

$$E_2 - E_1 \simeq 4.2 \frac{\langle r^4 \rangle}{a^5} e^2.$$

Let us remark that in accordance with the calculation the splitting of $E(^4T_{1g})$ is proportional to both $F_4(a/\sqrt{2})$ and $F_2(a/\sqrt{2})$, i.e. it is larger (for the same $\Delta x/a$) than that of $E(^4T_{2g})$ level. We must emphasize that the splitting of both the $E(^4T_{1g})$ and the $E(^7T_{2g})$ levels depends only on $\Delta x/a$, i.e. on the oxygen ion displacement for the considered geometry of lattice reconstruction near the off-centre ion (see figure 4). This conclusion is in agreement with the result of earlier work [23] devoted to the axial crystalline-field constant calculation for the Fe^{3+} centre. Thus the appearance of an axial g-factor is due to oxygen displacements rather than to Fe^+ off-centre displacement.

Equations (5) and (11) could allow one to determine the displacement value of oxygen ions near Fe^+, but unfortunately the energy distance Δ_0 between the ground $^4A_{1g}$ and excited singlet of $^4T_{2g}$ levels appears to be too large compared with the possible value in the KTaO₃ structure. Here obviously hybridization of the paramagnetic ion electrons with those of the ligand is essential. This decreases the effective value of the spin–orbit interaction and, consequently, the g-factor deviation from its spin value of 2.00. It seems plausible to expect the contributions of such covalency preferentially to $g_\parallel$ since the iron and oxygen ion displacement to one another is in the Z direction.

We may estimate some values for the oxygen displacements using triplet splitting for Fe^+ in SrTiO₃ [24], where the g-factors are observed to be nearly the same. Supposing that the splitting in the $^4T_{2g}$ triplet is equal to 500–600 cm⁻¹ (this corresponds to a $^4T_{1g}$ splitting of nearly 1500–2000 cm⁻¹) and assuming $\langle r^4 \rangle \simeq 30a_0^4$, where a_0 is the Bohr radius, we obtained $\Delta x/a \simeq 5 \times 10^{-2}$, i.e. $\Delta x \approx 0.2$ Å. The value of the off-centre ion displacement may be about three times larger [23,25], i.e. $\Delta R \simeq 0.6$ Å. This value is a little larger than the difference between the Fe^+ and K^+ ionic radii.

Undoubtedly, for a better description of the experimental data, one should use a more precise model than the simple crystalline field that we employed here and, in addition, measurements of the absorption optical spectra for Fe^+ in KTaO₃ are necessary.

The discovery in this work of new off-centre ions in KTaO₃ with Fe^+ substituted for K^+ may be considered as the source of induced polar regions at low temperatures and as a prospective candidate for the creation of ferroelectric long-range order in crystals doped by iron, if the Fe^+ concentration n is large enough to satisfy the inequality $nr_c^3 > 1$. Thus the investigation of these centres in KTaO₃ doped by iron is extremely desirable.

Acknowledgment

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