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Photochromic centers and impurities in nominally pure $KTaO_3$ and $K_{1-x}Li_xTaO_3$

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Investigations of photochromic centers and impurities in nominally pure single crystals of $KTaO_3$ and $K_{1-x}Li_xTaO_3$ (KTL) have been carried out by the ESR method. In all investigated KTL samples ($x=0.016$, 0.02, 0.03) the axial symmetry spectrum of Fe^{3+} substituted for K^+ [$Fe_{ax}^{3+}(K)$], cubic symmetry spectrum of Fe^{3+} substituted for K^+ [$Fe_c^{3+}(K)$], and that of Ni^{3+} substituted for Ta^{5+} [$Ni_c^{3+}(Ta)$] have been observed at $T \leq 60$ K. After light illumination with $365 \leq \lambda \leq 436$ nm, several ESR spectra appeared, each one with the characteristic temperature of its annealing in the region $25 \leq T \leq 120$ K. In KTL samples simultaneously the $Fe_{ax}^{3+}(K)$ spectrum disappeared and intensities of $Fe_c^{3+}(K)$ and $Ni_c^{3+}(Ta)$ spectra decreased. In nominally pure $KTaO_3$ the spectra $Fe_{ax}^{3+}(K)$ and $Fe_{ax}^{+}(K)$, observed before illumination, disappeared after it. The gradual restoration of these aforementioned spectra in both $KTaO_3$ and KTL was observed at $T>25$ K when some of the photoinduced spectra disappeared. One of the photoinduced spectra was shown to be that of O^- in both $KTaO_3$ and KTL. A scheme of local electronic levels of impurities in the band gap of nominally pure $KTaO_3$ and KTL was proposed. This scheme and especially the shallow O^- level in it made it possible to explain some peculiarities of photosensitive phenomena observed in nominally pure $KTaO_3$ and KTL in recent years.

I. INTRODUCTION

Study of the impurities in nominally pure incipient ferroelectric $KTaO_3$ is of great importance to find the mechanics of the anomalies of many properties in the low-temperature region ($T \leq 50$ K). Recently, it was shown that the low-temperature peculiarities of thermoconductivity and dielectric permittivity are connected with impurities of iron ions.[1] These ions, as well as other impurities, were thoroughly investigated by the electron spin resonance (ESR) method.[2,3] Symmetry-breaking axial and rhombic Fe^{3+} centers substituting for Ta^{5+} and K^+ ions, as well as the axial center Fe^+ substituting for K^+, were shown to exist in $KTaO_3$ single crystals. These iron impurities were supposed to be the main reason for many low-temperature anomalies of nominally pure $KTaO_3$: Raman scattering of the first order,[4] second-harmonic generation,[5] fluorescence spectra (see Ref. 6 and references therein), photocurrent, and photoluminescence.[7] It was obvious that new photochromic centers could appear under the light beam and these centers might strongly influence the above-mentioned photosensitive properties. On the other hand, a photocurrent was observed recently in the nominally pure model disordered ferroelectric $K_{1-x}Li_xTaO_3$ (KTL),[8] which is known to be in the dipole glass state or ferroelectric phase at definite Li^+ ion concentrations.[9] The photocurrent value and its temperature dependence in KTL gave evidence about the impurity nature of the observed photocurrent. However, up to now nothing was known about impurities in nominally pure KTL and about photochromic centers in $KTaO_3$ and KTL. In this article, impurity centers induced by light in $KTaO_3$ and KTL, as well as impurities in nominally pure KTL, are investigated by the ESR method. The existence was shown of Fe^{3+} axial and cubic symmetry centers, both substituting for K^+ [$Fe_{ax}^{3+}(K)$, $Fe_c^{3+}(K)$] in nominally pure KTL. After illumination the intensity of these centers decreased and new centers which were observable only at low temperatures appeared. One of them was identified as the O^- center. A scheme of local electronic levels of impurities in the forbidden gap of nominally pure $KTaO_3$ and KTL was proposed. This scheme made it possible to explain qualitatively some peculiarities of photosensitive phenomena observed in recent years in these materials.

II. THE SAMPLES AND EXPERIMENTAL DETAILS

The measurements were carried out on single-crystal samples of nominally pure $KTaO_3$ and $K_{1-x}Li_xTaO_3$ (KTL), $x=0.016$, 0.02, and 0.03. $KTaO_3$ and KTL ($x=0.02$) single crystals were grown by the spontaneous crystallization technique and two other KTL samples were produced by the controlled nucleation method.[10] The starting components were K_2CO_3 and Ta_2O_5 of high purity, i.e., the content of unavoidable impurities in them was less than 10–50 ppm. All the crystals were of high optical quality. The specimen dimensions were $1\times2\times3$ mm^3 with the plates of [001] type.

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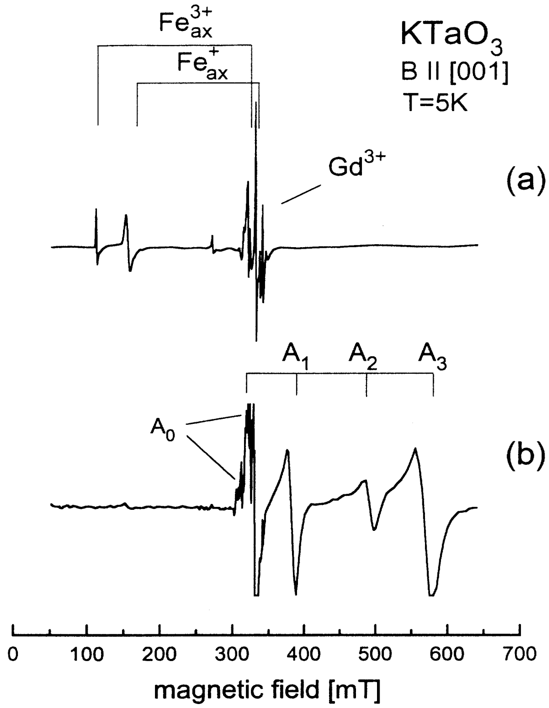

FIG. 1. ESR spectra in the nominally undoped $KTaO_3$ crystal before (a) and after (b) illumination. A_0, A_1, A_2, and A_3 correspond to the photoinduced spectra.

ESR spectra were recorded in the X-band microwave region at $4.2 < T < 77$ K. The Oxford Instruments ESR-9 cryosystem was used. An arc lamp of 200 W power served as the source of the light beam. Optic filters made it possible to extract the lines with wavelength λ of 365, 405, 436, 546, and 577 nm. The samples were illuminated in the resonator through a system of optical lenses and a special window in the resonator wall. The duration of illumination was about 2 min.

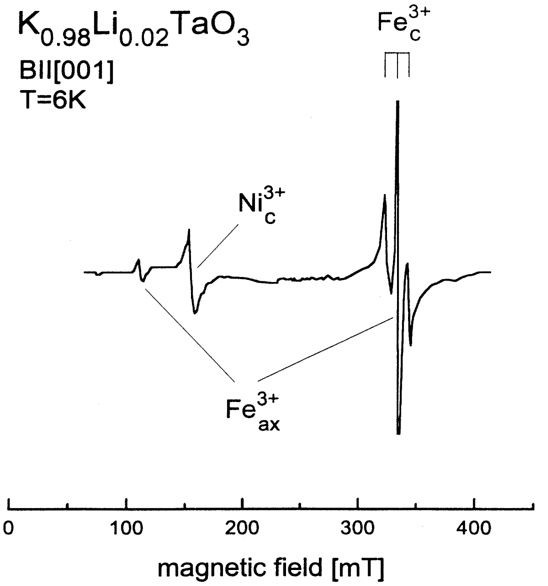

FIG. 2. ESR spectra in the nominally undoped $K_{0.98}Li_{0.02}TaO_3$.

III. ESR SPECTRA BEFORE ILLUMINATION

A. Nominally pure $KTaO_3$

For the sake of comparison of ESR spectra before and after illumination we begin with a brief description of $KTaO_3$ spectra. These samples were investigated by us earlier.[2,3] The ESR spectra of Fe^{3+}_{ax}(K) and Fe^{+}_{ax}(K) as well as the cubic symmetry centers of Gd^{3+}_{c}(K) were observed [see Fig. 1(a)]. The intensity of the spectra was small. Due to the Boltzmann thermal factor effect the ESR line intensities decreased when the temperature increased and at $T > 60$ K the spectra became unobservable.

TABLE I. Paramagnetic defects in the investigated $KTaO_3$ and $K_{1-x}Li_xTaO_3$ samples.

Paramagnetic center	T (K)	g factor	Fine structure (10^{-4} cm^{-1})	Reference
$KTaO_3$				
Fe^{3+}_{ax}(K)	5	$g_{\parallel}$: 1.997(2) $g_{\perp}$: 6.005(2)		11,12
Fe^{+}_{ax}(K)	5	$g_{\parallel}$: 2.00(2) $g_{\perp}$: 4.33(1)		Present paper, 3
Gd^{3+}_{c}(K)	5	1.990(1)	b_4: $-7.25(2)$ b_6: 0.46(2)	3
$K_{1-x}Li_xTaO_3$				
Fe^{3+}_{ax}(K)	5	$g_{\parallel}$: 1.997(2) $g_{\perp}$: 6.005(2)		11,12
Fe^{3+}_{c}(K)	5	1.990(2)	b_4: 19(1)	3
Ni^{3+}_{c}(Ta)	5	4.28(1)		Present paper

B. Nominally pure KTL

In all investigated KTL samples ($x=0.016$, 0.02, and 0.03) the same ESR spectra were observed at $T=6$ K. The axial and cubic symmetry spectra of the Fe^{3+} substituted for K^+ were observed (see Fig. 2), their parameters being the same as in $KTaO_3$ doped by iron ions.[11] For example, we observed the cubic symmetry spectrum of iron with spin $S=5/2$ and cubic crystalline field constant $a=38\times10^{-4}$ cm^{-1}. A similar spectrum was found earlier in $KTaO_3$ doped with iron and titanium.[12] We observed also an almost new spectrum containing a simple line with isotropic g factor $g=4.28$ and linewidth $\Delta H=6$ mT. The spectrum with such parameters is known to belong to ions in the $3d^7$ state in an octahedral symmetry crystalline field.[13] The most probable candidate may be Ni^{3+} substituted for Ta^{5+} in the oxygen octahedra of $KTaO_3$ with the excess charge compensation in distant spheres. In this case only one line was observed, its effective isotropic g factor being equal[13] to

$$g_{\text{eff}}=\tfrac{5}{3}g_s-\tfrac{2}{3}g_l\ , \qquad (1)$$

where $g_s=2.0042$, $g_l=-3/2$, and thus $g_{\text{eff}}=4.33$. The smaller observed value ($g=4.28$) may be the result of covalency effects contributing to the g factor.

Let us make a remark that after illumination of KTL samples we have observed an axial symmetry spectrum with the same parameters as in $KTaO_3$ doped by Ni ions, which was identified earlier as the axial symmetry Ni^{3+} spectrum.[12] In our opinion this confirms the existence of Ni ions in nominally pure KTL crystals.

It is interesting to note that in different KTL specimens the ESR spectral intensities were different; the larger ones were in the specimen with $x=0.02$, the smallest ones are related to KTL with $x=0.03$. The parameters of the ESR spectra of paramagnetic defects in the $KTaO_3$ and KTL samples under consideration are collected in Table I.

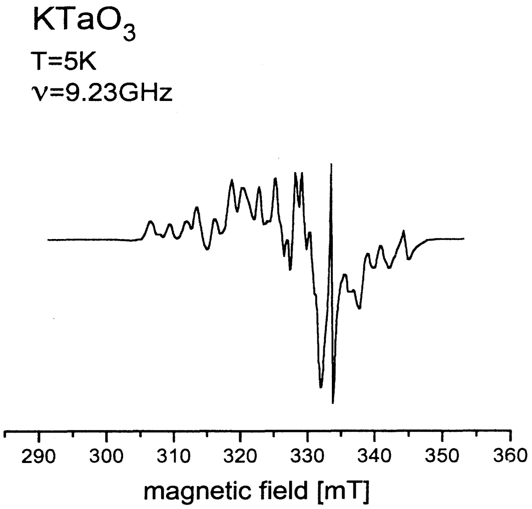

FIG. 3. ESR spectrum of O^- center in $KTaO_3$ after illumination.

IV. PHOTOINDUCED ESR SPECTRA IN $KTaO_3$ AND KTL

A. Illuminated $KTaO_3$

After illumination by the light beam with $\lambda=365$ nm at $T=5$ K new ESR spectra appeared and simultaneously the spectra of $Fe_{ax}^{3+}(K)$ and $Fe_{ax}^{+}(K)$ centers disappeared;

TABLE II. Photochromic centers in nominally pure $KTaO_3$ and $K_{1-x}Li_xTaO_3$ and their spectral parameters.

Paramagnetic center	T (K)	g factor	Hyperfine constant (10^{-4} cm^{-1})	Annealing temperature (K)
$K_{1-x}Li_xTaO_3$				
Ni_I^{3+}	25	$g_\parallel$: 2.111(2)		125
		$g_\perp$: 2.232(2)		
Ni_{II}^{3+}	25	$g_\parallel$: 2.155(2)		
		$g_\perp$: 2.086(2)		
O^-	8	$g_\parallel$: 2.110(2)	A: 21(2)	50
		$g_\perp$: 2.012(5)		
$KTaO_3$				
A_1[a]	5	$g_\parallel$: 2.05(1)		25
		$g_\perp$: 1.725(2)		
A_2[a]	5	$g_\parallel$: 2.10(1)		35
		$g_\perp$: 1.345(2)		
A_3[a]	5	$g_\parallel$: 2.081(2)		35
		$g_\perp$: 1.169(2)		
O^-	5	$g_\parallel$: 2.110(2)	A: 21(2)	50
		$g_\perp$: 2.012(5)		

[a] Unidentified centers, possibly Ta^{4+}.

the $Gd_c^{3+}(K)$ spectrum was conserved. For the sake of comparison, all the spectra before and after illumination are depicted in Figs. 1(a) and 1(b), respectively.

We can extract two different groups of lines among those after illumination. The first one is in the region of magnetic fields 305–338 mT [see Fig. 1(b) and Fig. 3, where we denoted this group by A_0]. The width of the lines of this group is about 0.5 mT and they may be the components of the hyperfine structure of the spectrum. The second group of lines in the higher magnetic field region has more intensive and wider lines with $\Delta H_{pp} \approx 15$–20 mT. We divided this group into three subgroups denoted here as A_1, A_2, and A_3 in Fig. 1(b). The line positions have axial symmetry along [001] type directions. The parameters of their spectra are listed in Table II.

After heating the samples to $T=25$ K, the lines A_1 disappeared and the small intensive $Fe_{ax}^{3+}(K)$ spectrum was restored. The lines of A_2 and A_3 spectra disappeared and the intensity of the A_0 spectrum became about two times less after sample heating to $T=35$ K. In the samples heated to $T=50$ K all the photoinduced spectra disappeared and spectra of $Fe_{ax}^{3+}(K)$ and $Fe_{ax}^{+}(K)$ centers were almost restored, their parameters being the same as before illumination.

B. Illuminated KTL

In all the KTL specimens illuminated with $\lambda=365$ nm at $T=6$ K a new spectrum with lines in the magnetic field region 305–338 mT appears, which looks like the A_0 spectrum in $KTaO_3$ [Fig. 4(a) and Fig. 3]. However, its intensity in KTL with $x=0.016$ was much less (about 10–20 times) than that in $KTaO_3$ and in KTL with $x=0.02$ and 0.03. After illumination the spectrum of $Fe_{ax}^{3+}(K)$ disappeared; meanwhile the intensity of cubic symmetry spectra of $Fe_c^{3+}(K)$ and $Ni_c^{3+}(Ta)$ decreased about 3 and 1.5 times, respectively.

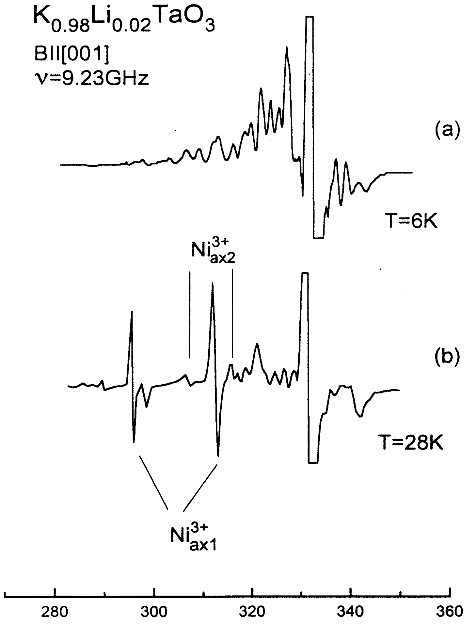

FIG. 4. ESR spectra of the photoinduced centers in $K_{0.98}Li_{0.02}TaO_3$ after illumination at $T=6$ K (a) and $T=28$ K (b).

After heating the sample to $T=50$ K the spectra of Fe^{3+} ions were restored; the photoinduced lines disappeared but for the isotropic line with $g=2.00$ which was conserved up to $T\approx300$ K. We investigated the photoinduced spectra intensity dependence on the λ value. The intensity appeared to decrease beginning from $\lambda=405$ nm (3.06 eV); at $\lambda=436$ nm (2.84 eV) it decreased about three times and at $\lambda=546$ nm (2.27 eV) the photoinduced spectrum almost disappeared. We have to note that the band gap in $KTaO_3$ is equal to 3.5–3.6 eV.[7]

We observed another photoinduced spectrum in KTL with $x=0.02$ at $20 \le T \le 120$ K [Fig. 4(b)] which annealed at $T > 125$ K. The spectrum was intensive and had axial symmetry along [001] type directions; its position angular dependencies were described by the following g factors: $g_\parallel=2.232$, $g_\perp=2.111$. As was mentioned previously, these g factor values coincide with those of axial symmetry Ni^{3+} centers in $KTaO_3$ doped by Ni ions.[12] We have to note this spectrum peculiarity: it was observed only at $T > 20$ K and at $T \le 12$ K it was absent. Moreover, we carried out several cycles of sample heating and cooling: we heated it up to $T=50$ K and then cooled it to $T=12$ K and the spectrum always appeared only at $T > 20$ K and never at $T < 12$ K. Unfortunately, it appeared impossible to carry out measurements at $12 < T < 20$ K because of the strong dielectric permittivity changes which made the technical condition of temperature stabilization insufficient for ESR spectra recording. In the region $20 < T < 120$ K the spectrum was unchanged. To check the influence of the saturation effect on this ESR spectrum, we decreased the microwave power down to 0.5 μW, but even at this power the spectrum at $T < 12$ K did not appear. We have observed also weaker signals of a second center of axial symmetry (see Fig. 4). It was supposed to belong to a Ni^{3+} ion with Li^+ as the nearest neighbor.

V. DISCUSSION

Let us begin with the photoinduced spectrum in the magnetic field region 305–338 mT, (g factor region 1.97–2.15), which was observed in $KTaO_3$ and in all KTL specimens. We suppose that it belongs to O^- hole centers. The grounds for this assumption are the following.

It is known that in oxygen-octahedra materials, e.g., $BaTiO_3$ and $SrTiO_3$, many photoinduced phenomena are connected with O^- centers, which are paramagnetic and thus can be studied by ESR (see, e.g., Ref. 14, and references therein). ESR spectra of this hole center had g factors in the region 1.99–2.11 in most materials. As a matter of fact, O^- centers appeared to be shallow ones with the hole ionization energy not higher than $T\approx120$ K; however, in some other types of materials with lower symmetry this energy may be higher.[15] The shallow local electronic levels usually have extended wave functions with large radius of the electron or hole state. Thus such centers have to be very sensitive to magnetic fields produced by surrounding ions with nonzero nuclear spins. As a result a strong hyperfine structure has to be characteristic of the O^- ESR spectrum. It is obvious that the spectrum A_0 in $KTaO_3$ as well as the similar spectrum in KTL specimens [see Figs. 3 and 4(a)] possess all the aforementioned features of O^- center ESR spectrum.

However, our specimen was more complex than those observed earlier in $BaTiO_3$.[14] It is our spectrum complexity (the great number of lines with the distance between them comparable with their width) which prevents us from describing its angular dependencies with sufficient accuracy. This complexity is the consequence of high nuclear spins of lattice cations: $I(^{181}Ta)=7/2(100\%)$, $I(^{39}K)=3/2(93\%)$, where the numbers in brackets represent the natural isotope abundance. These result in many weakly resolved hyperfine lines and thus the spectrum is complex. Nevertheless, it appeared possible to carry out the analysis of at least one type of O^- centers with axial symmetry along [001] type directions. The superfine structure of the spectrum seems to consist of seven lines. The approximate values of parameters describing the spectrum of the O^- center are collected in Table II. We hope that spectrum measurements at higher frequencies, e.g., in the K or Q region, will make it possible to describe the spectrum in more detail.

One of the most interesting problems is the origin of O^- centers. In $BaTiO_3$ the capture of holes by oxygen ions near the impurities under the light beam was supposed to be the main reason for O^- appearance.[14] The authors considered several impurities, e.g., Al^{3+} substituted for Ti^{4+} or Na^+ substituted for Ba^{2+}. In our opinion, typically O^- does not create shallow levels. Recently, one possible mechanism was proposed[8,16] in the framework of a model of oxygen ion displacements near an impurity which isovalently substituted for the lattice cation. Among such types of impurities the off-center ions are the best known ones. Calculations have shown[16] that in this case the local impurity O^- level is located above the top of the valence band at an energy in the range $T \leq 100$ K.

In KTL Li^+ and in $KTaO_3$ Fe^+ ions substituted for K^+ are known to be off-center impurities.[3,9] However, the magnitude of surrounding oxygen ion displacements, which determines the O^- level position, is the main problem now. A large value of the oxygen ion shift near the axial Fe^{3+} center substituted for K^+ (Ref. 17) is argued now in more recent work.[18]

The observed changing of the ESR spectra under the light beam could pour some light on this problem. Actually, a shallow O^- center may be considered as a trapped hole induced by light in a valence band. This, their number has to depend on the number both of holes and of the oxygen ions which are able to trap the holes. In KTL the most probable source of such oxygen ions is the oxygen ions near off-center Li^+ ions. The concentration of such above mentioned oxygen carriers is the same order of magnitude in all KTL samples ($x=0.016$, 0.02, and 0.03). But the intensities of their O^- ESR spectra are strongly different (see Sec. IV), so one can suppose that the bottleneck of the phenomenon may be the number of holes in the valence band. Since the energy of light waves in our measurements was less than the lattice band gap, the number of holes is determined by impurities which are able to trap the electrons from the valence band under the light beam. Axial centers of Fe^{3+} substituted for K^+ may be the electron trap because their ESR spectrum disappeared in illuminated KTL. However, the integrated intensity of their spectrum is less than that of O^-; thus it has to be other electron traps. Cubic symmetry Fe^{3+}(K) is the most probable candidate because its intensity decreased under illumination. The decrease of the ESR line of Ni_c^{3+}(Ta), as well as the appearance of Ni_{ax}^{3+}(Ta) after illumination in the sample with $x=0.02$ may be the consequence of changing Fermi level position.

In nominally pure $KTaO_3$ the intensities of O^- and Fe^{3+} spectra were approximately the same as those in KTL. This fact supports the conclusion that Fe_{ax}^{3+}(K) is also an electron trap in $KTaO_3$. Since the Fe_{ax}^{3+}(K) spectrum, similarly as for Fe_{ax}^{+}(K), disappeared under illumination, the latter can also be electron traps and the source of oxygen ions, which are able to trap the holes and to transform into O^- paramagnetic centers. However, in $KTaO_3$ as well as in KTL, the integrated intensity of the O^- spectrum is larger than that of the iron spectra. Thus one can suppose that there are electron traps of another origin as well as other sources of oxygen ions, which transform into O^- under illumination. Maybe the A_1, A_2, and A_3 lines in the ESR spectra of $KTaO_3$ [see Fig. 1(b)] manifest these unknown defects which become paramagnetic after recharging under illumination. We cannot exclude the existence of some defects in the Ta sublattice, which produce local levels in the band gap. Under illumination these peculiar Ta^{5+} might trap electrons and transform into the paramagnetic center Ta^{4+} ($5d^1$, $S=1/2$), its ESR spectrum g factor being less than

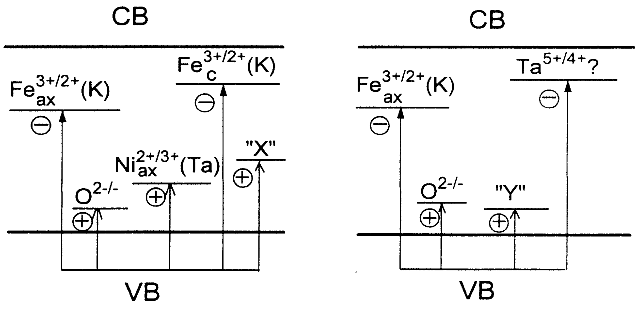

FIG. 5. Scheme of local electronic levels of impurities in the band gap of $K_{1-x}Li_xTaO_3$ (a) and $KTaO_3$ (b). The arrows describe possible electrons (⊖) and holes (⊕), light excitation (△), and trapping (↑). X and Y are levels of unidentified trapping centers with annealed temperature 30 K and 25 K, respectively.

2.00. To confirm this supposition and to clear up the nature of A_1, A_2, and A_3 spectra, additional ESR and electron-nuclear double resonance (ENDOR) measurements are desirable.

The information obtained, including that about ESR spectra intensities changing in dependence on λ values, made it possible to depict the scheme of local electronic level positions in the band gap of KTL [Fig. 5(a)] and $KTaO_3$ [Fig. 5(b)]. These schemes and the observations of the O^- ESR spectrum in nominally pure KTL and $KTaO_3$ confirm the main ideas of the explanation of photocurrent and photoluminescence peculiarities given in Ref. 8. In particular, the existence of O^- as hole centers in illuminated samples only at low temperatures ($T<70$ K) made it possible to explain the observation of low-temperature photoconductivity in KTL (Ref. 8) and $KTaO_3$ (Ref. 7) as well as the transformation of blue into yellow photoluminescence observed at the same low temperatures earlier.[7] The photocurrent smaller by several tens of magnitude observed in Ref. 8 and the approximately proportionally smaller O^- spectrum intensity in the same KTL sample with $x=0.016$ speak in favor of a crucial role of O^- levels in photoconductivity. Two other local electronic levels supposed in Ref. 8, namely, Fe_{ax}^{3+}(K) and Fe_c^{3+}(K), also were observed in this work [see the scheme in Fig. 5(a)] in the same KTL sample where photocurrent was measured.[8] Relative to the nonidentified electronic levels scheme proposed in Ref. 7, we can identify not only the shallow acceptor O^- level but also Fe_{ax}^{3+}(K) as a donor level. Cubic symmetry Fe_c^{3+}(K) and Fe_c^{3+}(Ta) were supposed[8] to be the donor and the second acceptor levels, respectively, in $KTaO_3$. Two cubic symmetry centers Fe_c^{3+}(Ta) and Fe_c^{3+}(K) were observed in nominally pure $KTaO_3$ single crystals investigated in Ref. 1. In our $KTaO_3$ samples there were no cubic iron centers. Thus for true identification of acceptor and donor levels, ESR investigations of the same $KTaO_3$ samples in which photocurrent and photoluminescence measurements were carried out[7] are desirable. The necessity of ESR and photosensitive phenomena investigation in more detail on the same KTL and $KTaO_3$ samples is obvious.

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[1] B. Salce, J. L. Gravil, and L. A. Boatner, J. Phys. Condens. Matter **6**, 4077 (1994).

[2] A. P. Pechenyi, M. D. Glinchuk, C. B. Azzoni, A. Paleari, and F. Scardina, Phys. Rev. B (to be published).

[3] M. D. Glinchuk, V. V. Laguta, I. P. Bykov, J. Rosa, and L. Jastrabik, J. Phys. Condens. Matter **7**, 1 (1995).

[4] H. Uwe, K. B. Lyons, H. L. Garter, and P. A. Fleury, Phys. Rev. B **33**, 6436 (1986).

[5] S. Jandl, P. Grenier, and L. A. Boatner, Ferroelectrics **107**, 73 (1990).

[6] H. Vogt, Phys. Rev. B **41**, 1184 (1990); J. Phys. Condens. Matter **3**, 3697 (1991).

[7] E. Yamaishi, Shanichi Ohno, and K. Ohi, Jpn. J. Appl. Phys. **27**, 583 (1988); E. Yamaishi, K. Watanabe, and K. Ohi, J. Phys. Soc. Jpn. **57**, 2201 (1988).

[8] R. S. Klein, G. E. Kugel, M. D. Glinchuk, R. O. Kuzian, and I. V. Kondakova, Phys. Rev. B **30**, 9721 (1994).

[9] B. E. Vugmeister and M. D. Glinchuk, Rev. Mod. Phys. **62**, 993 (1990).

[10] J. J. Van der Klink and J. J. Rytz, J. Cryst. Growth **56**, 673 (1982).

[11] M. D. Glinchuk and I. P. Bykov, Phase Transitions **40**, 1 (1992).

[12] D. M. Hannon, Phys. Rev. **164**, 366 (1967).

[13] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon Press, Oxford, 1970).

[14] E. Possenriede, P. Jacobs, and O. F. Schirmer, J. Phys. Condens. Matter **4**, 4719 (1992).

[15] B. Henderson and J. E. Wertz, *Defects in the Alkaline Earth Oxides* (Taylor and Francis, London, 1977).

[16] M. D. Glinchuk, R. O. Kuzian, and A. A. Karmazin, Physica B (to be published).

[17] Zhou Yi-Yang, Phys. Rev. B **42**, 917 (1990); Zheng Wen-Chen, *ibid.* **45**, 3156 (1992).

[18] H. Donnerberg, M. Exner, and C. R. A. Catlow, Phys. Rev. B **47**, 14 (1993).