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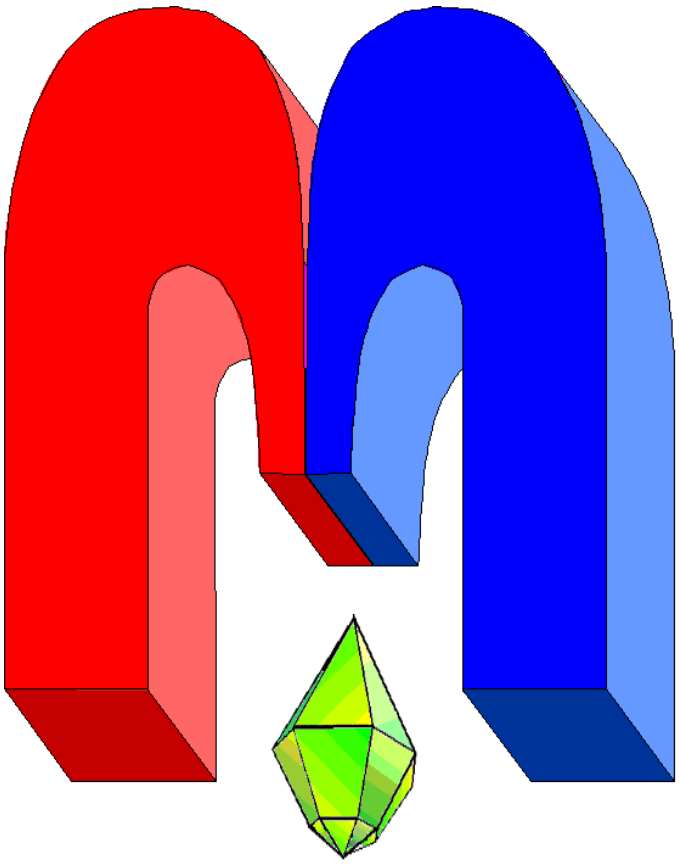

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* In Kazan State University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Photoinduced EPR in $KTa_{0.988}Nb_{0.012}O_3$ crystals

A.I. Gubaev [1], A.A. Rodionov [2], M.Kh. Salakhov [2], I.N. Subacheva [2,*], P.P. Syrnikov [3], V.A. Trepakov [3,4] and R.V. Yusupov [2]

[1] Basel University, Klingelbergstr. 50-70, Basel 4056, Switzerland

[2] Kazan State University, Kremlevskaya, 18, Kazan 420008, Russia

[3] A. F. Ioffe Physical-Technical Institute, St.-Petersburg 194021, Russia

[4] Institute of Physics, ASCR, 182 21 Prague 8, Czech Republic

**E-mail*: subirina@gmail.com

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We report the first experimental observation of the photoinduced EPR spectra in $KTa_{1-x}Nb_xO_3$ crystals ($x = 0.012$). The signal has two components: nearly isotropic with $g_{eff} = 2$ and strongly anisotropic one. Isotropic signal originates most probably from single localized photo-carriers – electrons or holes. Anisotropic spectrum is observed below 10 K and reveals a set of characteristic properties. It originates from the axial centers with axes coinciding with the C_4 axes of the crystal. Effective g-factor values are $g_{\|} = 2.106(3)$ and $g_{\perp} < 0.8$. Angle dependencies of the intensity and the width of the anisotropic signal as well as the resonance field can qualitatively be explained within the simple $J = 1$ model. The observed anisotropic photoinduced EPR spectrum is tentatively assigned to excitons or bipolarons.

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1. Introduction

Potassium tantalate ($KTaO_3$, KTO) is a popular and widely studied material, a representative of the family of the ABO_3 highly polarizable oxides, displacive-type ferroelectrics and related materials. Its resonance type dielectric permittivity strongly rises on cooling due to the lowest TO1 phonon mode softening (incipient ferroelectricity) and the KTO paraelectric central inversion cubic O_h^1 phase nearly loses stability. However, in the low temperature region of dominating quantum statistics the ferroelectric instability is inhibited and paraelectric phase is maintained due to quantum mechanical effects (quantum paraelectricity) [1]. However, polar state in KTO can be easily induced by suitable perturbation, e.g. by external uniaxial pressure [2], electric field, or doping with the off-central impurities like Li or Nb [3].

Slightly doped with niobium KTO is the subject of special interest. Because of practically equal ionic radii of Ta^{5+} and Nb^{5+} such doping brings small difference in lattice parameter, however in $KTa_{1-x}Nb_xO_3$ (KTN) at $x \geq 0.008$ the transition to ferroelectric state occurs with the critical temperature depending on the doping index x [4]. This gives very interesting possibility to study properties of quantum paraelectrics in the region of quantum mechanically displacive limit [5] where T_C appears to be equal or very close to 0 K and material is extremely sensitive to external perturbations. Special interest in this concern arises from a possibility of inducing the phase transitions in incipient ferroelectrics via optical polaron generation. Relatively recently in series of works [6] it was shown that the UV illumination of quantum paraelectrics STO and KTO at low temperatures is accompanied by "giant dielectric response" which have been attributed to the photo-polaron-induced phase transformation.

Polaronic problem is a subject of permanent interest in connection with the role of the polarons in the structural transitions in perovskite-like compounds. However, formation of polaronic states was established in rather limited number of objects. Thus, in $LiNbO_3$ [7] and $BaTiO_3$ [8], the compounds

similar to KTO, the formation of the hole O^- polarons and the electronic polarons associated with Nb and Ti was established by electron paramagnetic resonance (EPR) studies. Therefore, observation of the mentioned above optically-induced effects in quantum paraelectrics has once again revived the interest to the polaronic problems in ABO_3 perovskites and possibility of polaron-induced phase transformations.

The present work is a logic continuation of our previous study [9] in which an intense photoinduced (PI) optical absorption was found both in KTO and KTN. In KTN the maximum of the wide PI absorption (PIA) band is at 0.69 – 0.80 eV depending on Nb concentration. The PIA spectrum of KTO is different: the absorption occurs above 1.14 eV.

The properties of the PI centers in KTO were successfully studied with EPR: intense lines of 3 axial centers were assigned to the self-trapped electrons on Ta ion [10] or holes on oxygen [11], associated with definite defects of the crystal. Interestingly, while an intense long-lived PIA is observed both in KTO and KTN, nothing was known about photoinduced EPR (PI-EPR) of KTN. Moreover, one can find the statements that no PI-EPR occurs in KTN. In order to clarify this seeming contradiction we have performed the study of PI-EPR of KTN with $x = 0.012$ (KTN-1.2) and the first experimental observation of PI-EPR in KTN and its unusual properties are presented in this paper.

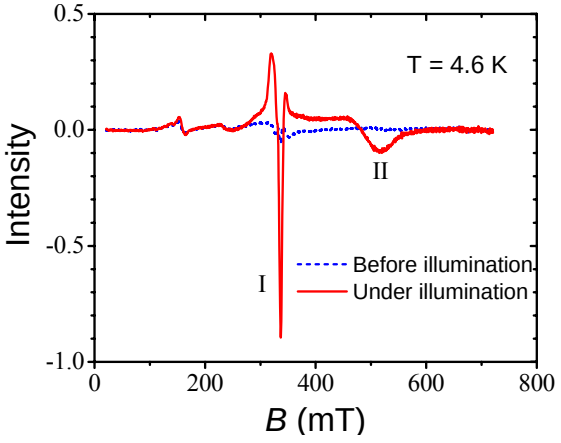

Figure 1. EPR spectra of the KTN-1.2 crystal at $T = 4.6$ K before UV-light illumination and under a stationary illumination with arbitrary orientation of $\mathbf{B}_0$ in C_4-C_2-C_4 plane, $\mathbf{B}_1 \parallel C_4$.

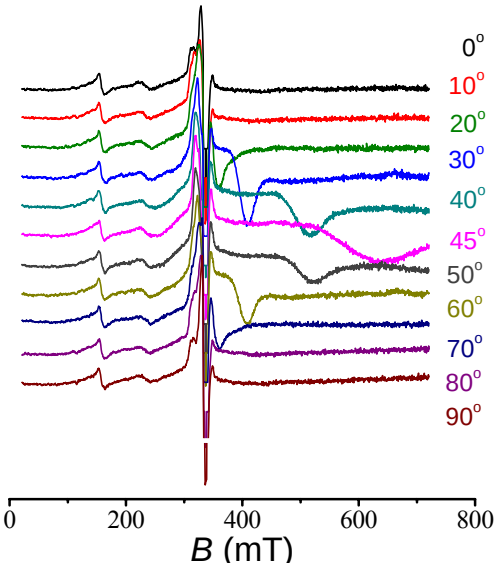

Figure 2. Angular dependence of the KTN-1.2 sample EPR spectra under UV-light illumination at $T = 4.0$ K when $\mathbf{B}_1 \perp \mathbf{B}_0$, $\mathbf{B}_1 \parallel C_4$, $\mathbf{B}_0$ is in C_4-C_2-C_4 plane, $\theta = 0$ corresponds to $\mathbf{B}_0 \parallel C_4$.

The KTN single crystalline samples with $x = 0.004$, 0.007, 0.012 and 0.020 were grown from ultrapure initial components (99.999%) at the A. F. Ioffe Physical Technical Institute. We have studied the $KTa_{0.988}Nb_{0.012}O_3$ (KTN-1.2) sample. It was oriented using the cleaved (001) planes. The measurements were performed with the standard X-band Bruker ESP300 spectrometer in the cavity operating in TEM_{012} mode with $\mathbf{B}_1 \perp \mathbf{B}_0$, where $\mathbf{B}_1$ is a microwave magnetic field component and $\mathbf{B}_0$ is an applied constant field. In such configuration the magneto-dipole transitions selection rule is $\Delta M_J = \pm 1$. Temperature was controlled with a commercial Oxford Instruments system. Sample was glued with (001) face to the end of the fused silica rod which in combination with an optical fiber served as a waveguide for optical illumination. Rotating around the rod axis allowed us to measure the spectrum angular dependence in the C_4-C_2-C_4 crystal plane. For illumination the Philips XBO xenon arc lamp was used, the wavelength selection was performed with a dichroic mirror that cut the wavelengths longer than 450 nm.

2. Experimental results

In Fig. 1 the EPR spectra of the KTN-1.2 crystal are shown that were measured before the UV-exposure and under a stationary illumination. Sample had an arbitrary orientation of $\mathbf{B}_0$ in C_4-C_2-C_4 plane. Weak intensity lines with $g_{eff} > 2$ that are present in both spectra are due to the presence of small amount of iron ions in the cavity and will not be considered here. As one can clearly see, there are two types of the EPR spectra that arise under sample UV-illumination. Relatively narrow signal at $g_{eff} \approx 2$ (type I in Fig. 1) originates most probably from the photo-excited self-trapped electrons and holes with $S = ½$: under illumination with a photon energies higher than the material bandgap the electron-hole pairs are created and the elementary charges localize either via the polaron formation or on the traps associated with the crystal defects. Signal around $g_{eff} \approx 2$ was also found in the PI-EPR spectra of the pure KTO crystals. Another type of the PI-EPR signal is represented in Fig. 1 by a wide asymmetric band with a maximum of the microwave absorption at ~ 500 mT (type II). Such spectrum was not observed earlier either in KTO or in KTN crystals and in this paper we will consider mainly the properties of this signal.

In Fig. 2 the angular dependence of the KTN-1.2 sample EPR spectrum in the C_4-C_2-C_4 crystal plane under UV-light illumination at $T = 4.0$ K is presented. Type I spectrum doesn't reveal any substantial angular dependence. This supports its preliminary assignment to the self-trapped charge carriers. On the other hand, it should be mentioned that the optimal conditions for the type I and II signal measurements are different. Data shown in Figs. 1 and 2 are recorded with the highest value of the B_0 modulation achievable (ΔB_0 ~ 24 Gs), which is nicely suitable for the wide spectrum of type II. At the same time, the narrower type I spectrum may be severely distorted with such ΔB_0 value and should be studied separately.

In Fig. 3 the resonance field angular dependence of the type II spectrum is shown. The field values in Fig. 3 correspond to zero crossing by the signals shown in Fig. 2. If one takes the minimum position of the EPR spectrum as a true value of resonance field, the obtained dependence would be slightly steeper that the one shown in Fig. 3. Thus the dependencies obtained with these two approaches of resonance field defining reveal the same qualitative properties and just slightly differ quantitatively.

Already at the first glance to the data one would notice a set of quite specific properties of the type II signal: i) this component has a strong angular dependence of the resonance field; ii) the spectra of this component are reproduced with a periodicity of 90°; in the spectra two magnetically inequivalent axial centers are revealed at θ values close to 45° with the axes along the C_4 axes of the crystal; at $\theta = 45°$ ($\mathbf{B}_0 \| C_2$) these centers are equivalent; iii) resonance field of the type II spectrum is minimal at $\theta = 0°$ (90°, or with $\mathbf{B}_0 \| C_4$), and increases quite steeply with the departure of θ from 0°; iv) integral intensity of this signal is minimal at $\theta = 0°$ and rises fast with its departure from 0°; v) type II spectrum width is minimal at $\theta = 0°$ and increases severely with θ increase, the lineshape of this signal is rather asymmetric. Effective g-factor values are $g_{\|} = 2.106(3)$ and $g_{\perp} < 0.8$. Items iii – v above are the characteristic properties of the EPR

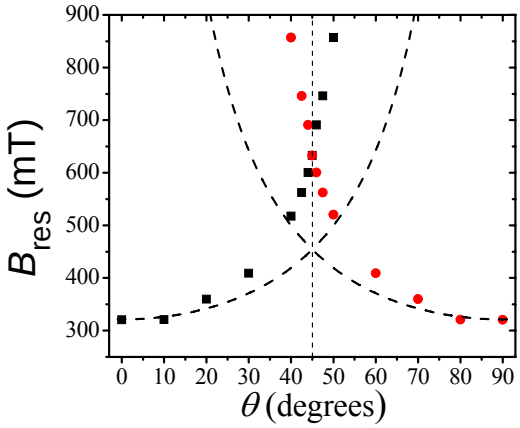

Figure 3. Angular dependence of the resonance field B_{res} for the KTN-1.2 PI-EPR spectrum. Dashed curves – result of approximation with the function $B_{res} = B_{res}^0 / \cos\theta$ where $B_{res}^0 = 312.4$ mT corresponds to the least value of the resonance field.

spectra that originate from the "forbidden" magnetic dipole transitions with $\Delta M_J \neq \pm 1$ (in the configuration $\mathbf{B}_1 \perp \mathbf{B}_0$). The simplest model of an object that would have such transitions is the center with $J = 1$. The Hamiltonian of an axial center with $J = 1$ is [12]

$$\hat{H} = D\left\{\hat{J}_z^2 - \tfrac{1}{3}J(J+1)\right\} + g_{\|}\beta H_z \hat{J}_z + g_{\perp}\beta\left(H_x\hat{J}_x + H_y\hat{J}_y\right). \quad (1)$$

Within this model, if D value is small, the allowed transitions $|M_J = 0\rangle \leftrightarrow |\pm 1\rangle$ should be observed which is not the case. With the high value of D the ground state is the $M_S = \pm 1$ doublet for which the resonance field angular dependence is $B_{res} = B_{res}^0 / \cos\theta$. This dependence is shown in Fig. 3 with the dashed line. The deviation of the observed behavior from the predicted one is obvious in most of the studied range, at $\theta \geq 20^\circ$: the experimental dependence is much steeper. As far as the intensity of the spectra is concerned, the probability of the transitions increases from zero with a departure of θ from 0^o due to the admixing of $|M_J = 0\rangle$ state to $|M_J = \pm 1\rangle$ by $\hat{J}_x$ and/or $\hat{J}_y$ operators in Hamiltonian (1). Thus, angular dependencies of the resonance field and intensity of the spectrum are qualitatively explained within the simplest $J = 1$ model.

The possible reason for the observed discrepancy can in principle be readily proposed. The simplest objects formed by the photo-generated charge carriers that possess the $J = 1$ state are either excitons or bipolarons. In both cases the energy level structure contains the triplet $J = 1$ state and the singlet $J = 0$ that are separated in energy by the exchange integral $\tilde{J}$. As it has been shown in [13] for the case of self-trapped exciton in silver chloride, the angular dependence of the resonance fields can be considerably modified due to the presence of close-lying $J = 0$ singlet state.

The increasing with θ width of the spectrum is another feature specific for the non-Kramers centers. In general, spectrum broadening can be related to the relaxation, to interaction with neighboring spins and to the crystal field splitting due to the sample imperfections (inhomogeneous broadening). The intensity of the EPR spectrum is small, thus we study a strongly diluted spin system and can neglect the spin-spin interactions. Both, the relaxation and spin-spin interactions should not lead to a strong angle dependence of the linewidth which is observed. Thus, taking also into account a pronounced spectra asymmetry of the observed type II spectrum, we can assign the width angular dependence to interaction with random strains, which can be accounted for by adding $E\left(\hat{J}_x^2 - \hat{J}_y^2\right)$ term to Hamiltonian (1) with a distribution of E values.

Another interesting observation is the value of $g_{\|eff} = 2.106$. For the forbidden pure spin transition $|+1\rangle \leftrightarrow |-1\rangle$ the effective g-factor value should be $g_{\|eff} \approx 4$. One of the possible reasons for such difference may be the reduction of g-values by strong spin-orbit coupling on tantalum ion (which for Ta^{4+} centers in $LiTaO_3$ was estimated as ~ 2200 cm^{-1} [14]). Indeed, for a d^1 ion in the octahedral surrounding the g-factor component values can be expressed as

$$g_{\|} = g_e - \frac{8\lambda}{\Delta}, g_{\perp} = g_e - \frac{2\lambda}{\delta}. \quad (2)$$

Here $g_e = 2.0023$, λ is the spin-orbit constant, Δ and δ are the values of the electronic level splittings in an octahedral and tetragonal fields, respectively.

Summarizing, the first observation of the PI-EPR spectra in KTN crystals is reported for the sample with Nb concentration of 1.2%. Properties of the PI spectra in KTN differ significantly from those in KTO and reveal characteristic peculiarities that allow their preliminary assignment to the non-Kramers PI objects. These objects are most probably either excitons or bipolarons. Supporting our observations, the PIA spectra of KTN crystals in the near-IR were assigned recently to Nb^{4+} pair polarons [9]. Angle dependence of the PI-EPR spectra can qualitatively be understood within the

model of $J = 1$ paramagnetic center. To achieve the quantitative agreement a more sophisticated model should be employed, e.g. with an account of the singlet $J = 0$ state in the energy level diagram. Elaborating an adequate model needs additional experimental data and is a matter of the current research.

Acknowledgments

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