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# Paramagnetic dipole centers in $KTaO_3$: Electron-spin-resonance and dielectric spectroscopy study

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Electron-spin-resonance (ESR) and dielectric spectroscopy techniques have been applied to study the dipole centers connected with $Mn^{2+}$ and $Fe^{3+}$ impurity ions substituted for $K^+$ in the incipient ferroelectric $KTaO_3$. It was shown that the reorientations of paramagnetic dipole complexes $Fe^{3+}$-$O_I$ ($O_I$ is the interstitial oxygen) give rise to dielectric losses near $T \simeq 185$ K at the frequency 1 kHz. Their activation energy $E_r = 0.34$ eV was obtained both from dielectric and ESR measurements. The peak of dielectric losses at $T \simeq 55$ K was observed in $KTaO_3$ doped by low concentrations of $Mn^{2+}(n \approx 0.01$ at. %). At $n \gtrsim 0.3$ at. % a pronounced peak of dielectric susceptibility similar to that in $KTaO_3$:Li was revealed in addition to the aforementioned losses peak. The studies of electric field and temperature dependence of $Mn^{2+}$ ESR intensities with respect to the local Lorentz field had shown that the dipole moment 1.4 $e$Å can be associated with $Mn^{2+}$ ion. The origin of this dipole moment was shown to be off-center displacement $\Delta \simeq 0.9$ Å of $Mn^{2+}$ from the $K^+$ site in one of six [001]-type directions. The relaxation rate of these dipoles after the polarizing electric field switching off was directly measured by the ESR method. It was described by Arrhenius law with activation energy $E_r = 0.104$ eV, which is close to the value obtained from dielectric measurements. Possible sources of dielectric losses in nominally pure $KTaO_3$ single crystals in the vicinity of $T \approx 40$ K are analyzed and discussed on the basis of both present work data and earlier results collected from the literature.

## I. INTRODUCTION

The study of impurity dipoles in the incipient ferroelectrics like $KTaO_3$ attracts much attention of scientists because the dipoles were shown to influence strongly host material properties (up to ferroelectric phase transition appearance).[1,2] The ferroelectric phase transition in $KTaO_3$ with off-center impurities (like $Li^+$ and $Nb^{5+}$) manifests itself both by maxima in dielectric susceptibility and by losses at low temperatures. On the other hand, the low-temperature losses (LTL) can be the result of reorientational motion of impurity dipole complexes like $Me^{n+}$-$V_A$, where $Me^{n+}$ represents the dopant ion and $V_A$ is the anion vacancy (see, e.g., Ref. 3 and references therein).

Last year the dielectric anomalies were observed even in nominally pure $KTaO_3$ single crystals; they were shown to be a sample-dependent phenomena similar to optical properties (like first-order Raman scattering, second harmonic generation, etc.).[4–7] It was shown recently[8] that the origin of the aforementioned optical properties can be light-induced centers like $Ta^{4+}$ near oxygen vacancy. However, the reasons of LTL with peak at $T \approx 40$ K and the nature of several other dielectric spectra maxima observed earlier[9,10] are still not clear, mainly because of the absence of dielectric and defect structure measurements on the same samples. The attempt to perform simultaneously dielectric, optical absorption, photoluminescence, and electron-spin-resonance (ESR) measurements in nominally pure and weakly doped $KTaO_3$ was not successful due to actual absence of ESR measurements. On the other hand, the large number of noncubic paramagnetic centers ($Fe^{3+}$, $Fe^+$, $Mn^{2+}$, $Ta^{4+}$) observed recently in nominally pure $KTaO_3$ (Refs. 11 and 12) hints on several impurities as the sources of dielectric spectra anomalies.

In the present work we performed ESR and dielectric spectra measurements on several $KTaO_3$ single crystals, both nominally pure and weakly doped by Li (1 at. %), Fe and Mn (0.01-1.0 at. %). Quantitative analysis of obtained spectra made it possible to find out that the impurities of iron create the reorientable dipole complexes $Fe^{3+}$-$O_I$ ($O_I$ is interstitial oxygen ion), contributing to dielectric losses at $T \sim 185$ K. $Mn^{2+}$ impurities were shown to create electric dipoles with a dipole moment $d \simeq 1.4$ $e$Å, originated from $Mn^{2+}$ displacement $\Delta \approx 0.9$ $e$Å from $K^+$ site similar to that of $Li^+$.

We discuss the reasons of dielectric losses in pure $KTaO_3$ near $T \simeq 40$ K. From our analysis it follows that several types of dipole centers (which are unavoidable impurities in nominally pure $KTaO_3$) of small concentration ($\lesssim 0.01$ at. %) can be the sources of the aforementioned losses.

## II. SAMPLES AND EXPERIMENTAL DETAILS

The measurements were carried out on single-crystal samples of $KTaO_3$, both nominally pure and slightly doped

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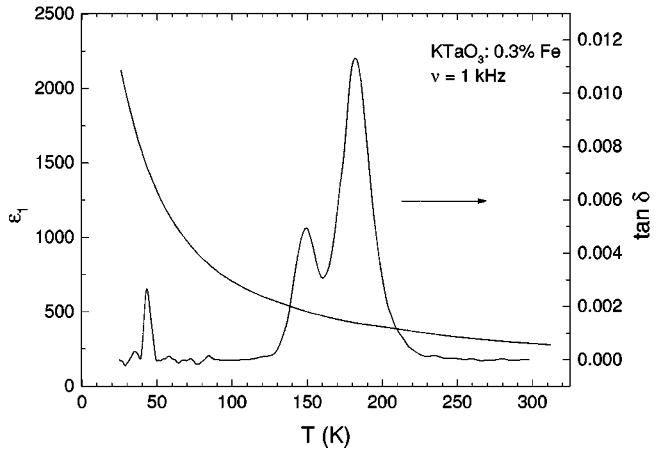

FIG. 1. Dielectric susceptibility ($\varepsilon_1$) and dielectric loss ($\tan\delta = \varepsilon_2/\varepsilon_1$) taken at 1 kHz vs temperature for $KTaO_3$:Fe.

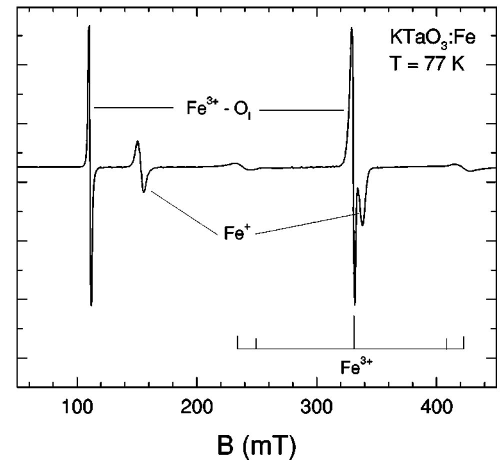

FIG. 2. ESR spectra for $KTaO_3$:Fe at $T = 77$ K and $\mathbf{B} \| [001]$.

with Li (1 at. %), Fe (0.1–1.0 at. %), and Mn (0.01 and 0.3 at. %). Two different methods have been used to grow $KTaO_3$ crystals: the spontaneous crystallization technique, and the Czochralski method. As the starting components $K_2CO_3$ and $Ta_2O_5$ of high purity were used. The sample dimensions were $(1\times2\times2)\mathrm{mm}^3$, with the surfaces parallel to crystallographic (001) planes. The major faces were electroded using Engelhard flexible silver paste.

ESR spectra were recorded in the *X*-band microwave region. The Oxford Instruments ESR-9 cryosystem allowed us to perform measurements in the temperature range 4.2–290 K with accuracy of 0.1–0.2 K. Dielectric spectra were measured within 10–290 K and 400 Hz–2 MHz ranges using a HP 4192 LF Impedance Analyzer. The permittivity was determined by measuring the capacitance and loss tangent as functions of temperature and frequency.

## III. EXPERIMENTAL RESULTS: THE COMPARISON OF ESR AND DIELECTRIC DATA

### A. $KTaO_3$:Fe

The results of the measurements of dielectric susceptibility real part ($\varepsilon_1$) and dielectric losses ($\tan\delta$), respectively, are depicted in Fig. 1. It is seen that $\varepsilon_1$ increases very similar to the case of undoped $KTaO_3$.[2] Spectrum of dielectric losses has maxima at $T \simeq 185$ K, 150 K, and 40 K. Measurements of frequency dependence of the observed peaks position had shown that relaxation time $\tau$ for dielectric losses near $T \simeq 185$ K can be described by Arrhenius law with activation energy $E_r = 0.34$ eV and $\tau_0 = 3\cdot10^{-14}$ s. Similarly a relaxation peak near 150 K can be characterized by $E_r = 0.30$ eV and $\tau_0 = 1\cdot10^{-14}$ s. These values coincide with those obtained earlier on ceramic samples[10]. Authors of Ref. 10 assumed that the reorientation of the center $Fe^{3+}$-$V_O$ is the source of dielectric losses at $T \simeq 185$ K, while 150 K peak appears due to $Fe^{2+}$ reorientations. Peak at $T \simeq 40$ K was observed earlier in several works (see, e.g., Ref. 4 and references therein), but its origin is still unclear.

ESR measurements reveal several types of spectra on the same samples. Part of the observed lines are represented in Fig. 2. The analysis of the whole observed spectrum and the comparison with those observed earlier[13,14] had shown that the most intensive lines belong to the paramagnetic ion $Fe^{3+}$ substituted for the $K^+$ with interstitial oxygen in the nearest neighborhood ($Fe^{3+}$-$O_I$). ESR linewidth ($\Delta B$) of this center increases with increasing temperature (see Fig. 3). Our analysis had shown that the observed $\Delta B$ data can be fitted by the expression with two exponents:

$$\Delta B[mT] = 30\exp(-E_{sp}/T) + 57000\exp(-E_r/T), \tag{3.1}$$

were $E_{sp} = 850$ K and $E_r = 3800$ K.

In our opinion the first term in Eq. (3.1) is connected with spin-phonon contribution, namely Orbach process with optical phonon of energy $E_{sp} = 850$ K. It is seen from Eq. (3.1) that this mechanism plays the main role at temperatures lower than 300 K. On the other hand, at high temperatures the second term in Eq. (3.1) becomes the main contributor to the linewidth. Its preexponential factor $1/\tau_0 = 57000$ mT $\approx 10^{13}$ $s^{-1}$ has typical value for ESR line motional broad-

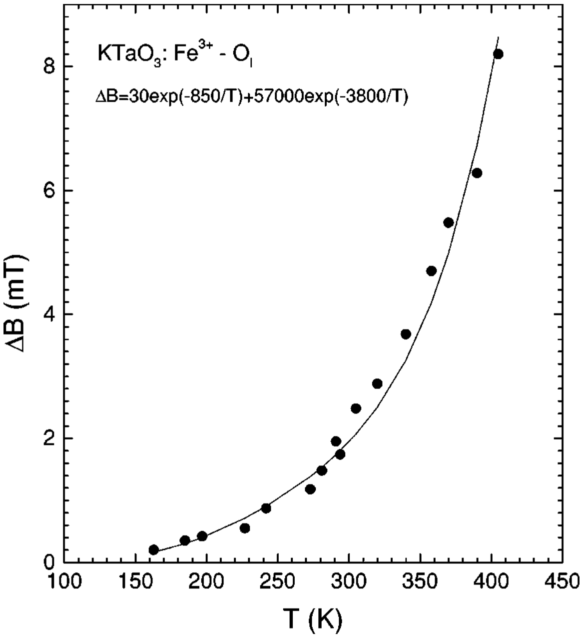

FIG. 3. Temperature dependence of ESR linewidth for $Fe^{3+}$-$O_I$ center at $\mathbf{B} \| [100]$ (solid line, theory; circles, experiment).

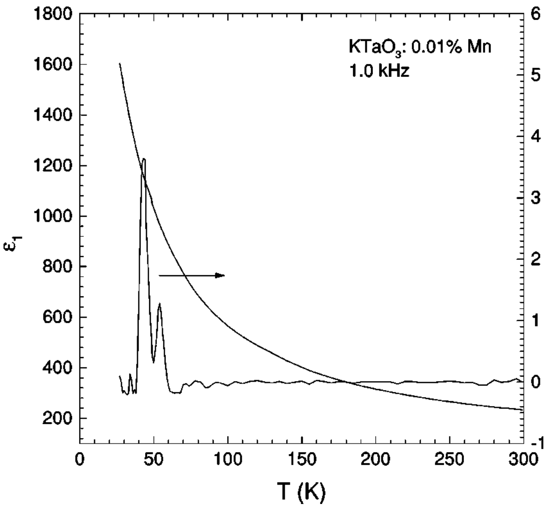

FIG. 4. Real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the dielectric susceptibility taken at 1 kHz vs temperature for KTaO$_3$:0.01 at. % Mn.

ening due to paramagnetic complex reorientations between six equivalent positions along $\langle 001\rangle$ directions. Activation energy of this motion $E_r=3800$ K (or 0.33 eV) is close to $E_r=0.34$ eV obtained from dielectric losses at $T\simeq 185$ K. Therefore, the origin of dielectric losses at $T\simeq 185$ K ($\nu=1.0$ kHz) is reorientational motion of dipole complex Fe$^{3+}$-O$_I$ rather than that of Fe$^{3+}$-$V_O$, as it was assumed earlier in Ref. 10. Moreover, neither symmetry nor linewidth of Fe$^{3+}$-$V_O$ ESR spectrum do not change with temperature up to $T\approx 900$ K, as we had shown earlier,[13] so that there is no essential reorientations of this complex at $T\lesssim 900$ K. To confirm the decisive role of Fe$^{3+}$-O$_I$ dipole complexes in the considered peak of dielectric losses, we performed ESR and dielectric measurements on several samples with different concentrations of these iron centers. The observed correlation between intensities of Fe$^{3+}$-O$_I$ ESR spectrum and dielectric losses at $T\simeq 185$ K gives evidence that these losses really due to Fe$^{3+}$-O$_I$ dipole complex reorientations. Note that there is not direct correlation between the Fe ion content and the intensity of the dielectric losses because the Fe$^{3+}$-O$_I$ are a pair centers, their concentration also depends on the interstitial oxygen content.

The relaxation peak at 150 K cannot be associated with any known Fe$^{3+}$ paramagnetic centers in KTaO$_3$ since we did not observe any ESR spectrum with intensity correlated with the relaxation peak height. Apparently, these dielectric losses origin is nonparamagnetic Fe$^{2+}$ complexes as it was assumed in Ref. 10.

## B. KTaO$_3$: Mn

### *1. Experiment*

*a. Dielectric and ESR spectra*. The observed dielectric losses near $T\approx 55$ K in KTaO$_3$ crystals doped by Mn are represented in Fig. 4, their characteristics being close to those observed earlier.[10] The magnitude of losses is small enough ($\tan\delta=\varepsilon_2/\varepsilon_1\approx 10-20\cdot 10^{-4}$) at small concentration of Mn ($n\sim 10^{-3}-10^{-2}$ at. %). However, at $n\approx 0.2-0.5$ at. % $\tan\delta\approx 0.25$ and pronounced peak in real part of dielectric permittivity similar to that in KTaO$_3$:Li arises (Fig. 5). The relaxation rate obtained from the observed frequency dependence of the dielectric losses peak position was described by Arrhenius law with parameters $E_r=0.11$ eV and $\tau_0^{-1}=5\cdot 10^{13}$ s$^{-1}$.

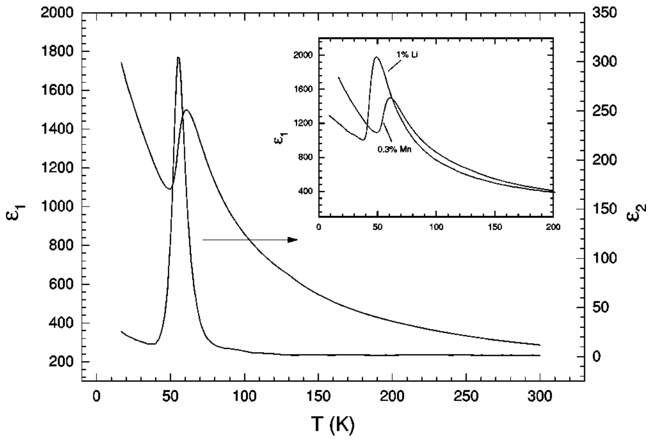

FIG. 5. Real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the dielectric susceptibility taken at 1 kHz versus temperature for KTaO$_3$:0.3 at. % Mn. Inset: $\varepsilon_1$ as a function of $T$ for KTaO$_3$:0.3% Mn and 1% Li.

In the same samples we observed ESR spectra of Mn$^{2+}$. The intensities of spectral lines correlate with the intensity of low-frequency dielectric losses near $T\approx 55$ K. The angular dependence of the resonance fields was described by a spin Hamiltonian of the following form:

$$\hat{H}=\beta\hat{\mathbf{S}}\cdot\mathbf{g}\cdot\mathbf{B}+\frac{1}{3}b_2^0O_2^0+\frac{1}{60}(b_4^0O_4^0+b_4^4O_4^4)+\hat{\mathbf{S}}\cdot\mathbf{A}\cdot\hat{\mathbf{I}}, \tag{3.2}$$

where $g_{xx}=g_{yy}=2.000$, $g_{zz}=1.998$, $b_2^0=0.148$ cm$^{-1}$, $b_4^0=-1.2\cdot 10^{-4}$ cm$^{-1}$, $b_4^4=2\cdot 10^{-4}$ cm$^{-1}$, $A_{xx}=A_{yy}=-82.7\cdot 10^{-4}$ cm$^{-1}$, $A_{zz}=-85.9\cdot 10^{-4}$ cm$^{-1}$, their values being the same as those obtained earlier by Hannon.[15] The spectra of three magnetically nonequivalent centers of Mn$^{2+}$ with axes along $\langle 001\rangle$ directions were observed.

*b. Electric-field dependences of Mn$^{2+}$ ESR spectra*. We had shown earlier[16] that application of external electric field $E\|[001]$ leads to the redistribution of ESR lines intensities: the intensity of the spectrum with axis parallel to $E$ increases whereas the intensities of the spectra of other Mn$^{2+}$ centers decrease. However, the measurements in Ref. 16 were performed only at $T=77$ K, so that the behavior of manganese dipole complexes in vicinity of dielectric properties anomalies stayed unclear. Our measurements at $T<77$ K reveal new interesting peculiarities. As an example, in Fig. 6 we have represented part of ESR spectra recorded at $T=26$ K and $\theta=78^o$ ($\theta$ is an angle between magnetic field and [001] direction). It is seen that application of electric field results in essential enhancement in the intensity of the spectrum for which the center axis is directed along external electric field. This behavior is clearly seen from the most intensive lines of $-5/2\leftrightarrow -3/2$ transition. Contrary to this, the intensity of ESR lines of the centers with the axes perpendicular to $E$, decreases. At $E=10$ kV/cm latter lines disappear com-

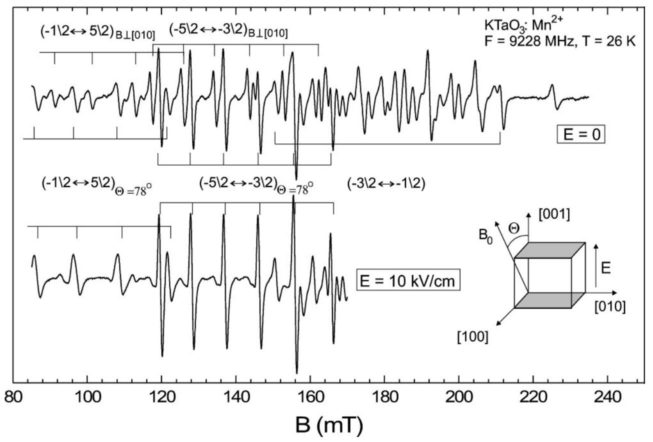

FIG. 6. Electric-field dependence of $Mn^{2+}$ ESR spectrum in $KTaO_3$:0.01% Mn at $T=26$ K and $\theta=78°$. Inset: sketch of the geometry of the experimental setup.

pletely. Therefore, the dipole complexes of $Mn^{2+}$ in $KTaO_3$ are reoriented by external electric field and try to align along $\vec{E}$.

Let us introduce the quantity

$$\eta=\frac{I_1+I_2}{4I_3+I_1+I_2} \tag{3.3}$$

as the measure of the dipoles orientation along the electric field, where $I_1 \sim N_1$, $I_2 \sim N_2$, $I_3 \sim N_3$ are the normalized spectra intensities of the centers with orientation along, opposite and across to $\vec{E}$ direction, respectively. The dependence of ESR resonance intensity on the center orientation in external magnetic field was taken into account. $N_1$, $N_2$, and $N_3$ are corresponding to the number of appropriate centers. Note that since for $-5/2 \leftrightarrow -3/2$ transition the external electric field does not lift the degeneracy of ESR spectra of $Mn^{2+}$ with $\pm\alpha(\alpha=x,y,z)$ axes orientations, we can measure only total ESR intensity of two centers with opposite axes directions. This fact was taken into account in Eq. (3.3). So, the value of $\eta$ changes from 1/3 at zero external field (where $I_1=I_2=I_3$) up to 1 in the case of full dipole alignment along electric field (in which case $I_1 \rightarrow 1, I_2=I_3=0$). The Eq. (3.3) then can be rewritten as

$$\eta=\frac{N_1+N_2}{4N_3+N_1+N_2}. \tag{3.4}$$

In the considered case $N_1$, $N_2$, and $N_3$ correspond to populations of the levels with energies $\pm d \cdot E_{loc}$ and zero, respectively, where $d$ is dipole moment and

$$E_{loc}=E+\frac{1}{3\varepsilon_0}\gamma P \tag{3.5}$$

stands for a local electric field[17,18] ($\gamma$ and $P$ are, respectively, Lorentz factor and polarization). In equilibrium state the populations of the levels obey to Boltzmann law: $N_1/N_3=\exp(dE_{loc}/kT)$ and $N_2/N_3=\exp(-dE_{loc}/kT)$. In this case we obtain from Eq. (3.4):

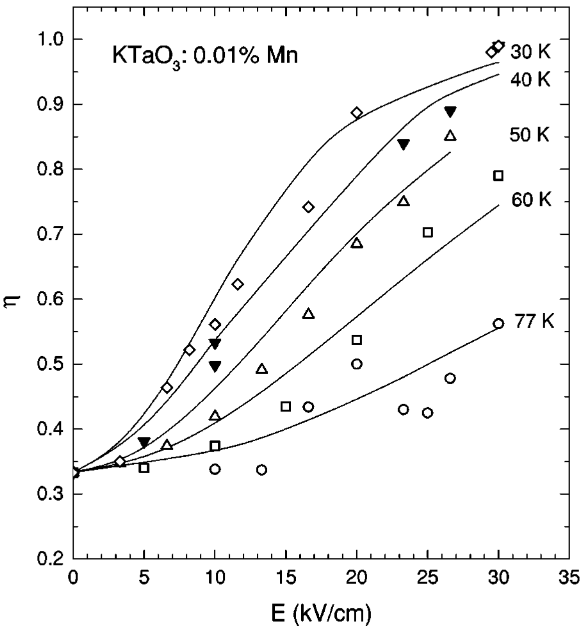

FIG. 7. Electric-field dependence of $Mn^{2+}$ centers alignment along external electric field for various temperatures in $KTaO_3$:0.01% Mn. Solid lines correspond to data calculated with Eq. (3.6).

$$\eta=\frac{\cosh(dE_{loc}/kT)}{2+\cosh(dE_{loc}/kT)}. \tag{3.6}$$

In accordance with Eq. (3.6) the value of $\eta$ has to be dependent on $E$ and $T$. These dependences were actually observed and they are depicted in Fig. 7 and Fig. 8 for two Mn concentrations. It is seen that the degree of the centers alignment along $E$ increases as temperature decreases but it is different for two Mn species. We will discuss these differences below.

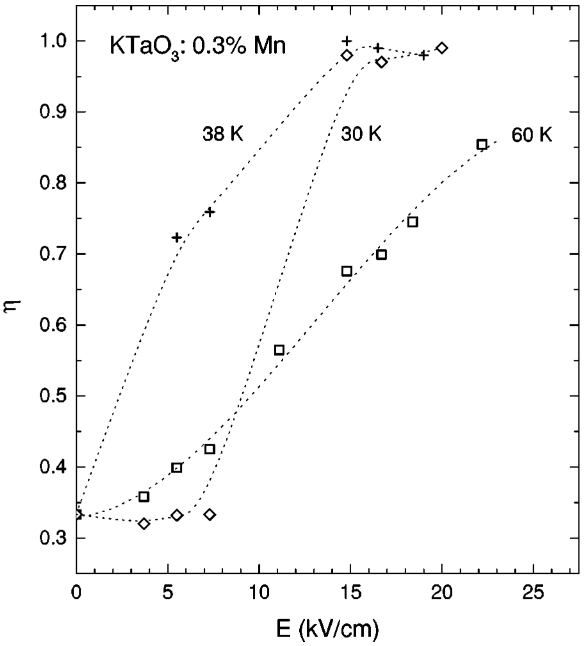

FIG. 8. Electric-field dependence of $Mn^{2+}$ centers alignment along external electric field for various temperatures in $KTaO_3$:0.3% Mn. Dotted lines are guide for eye.

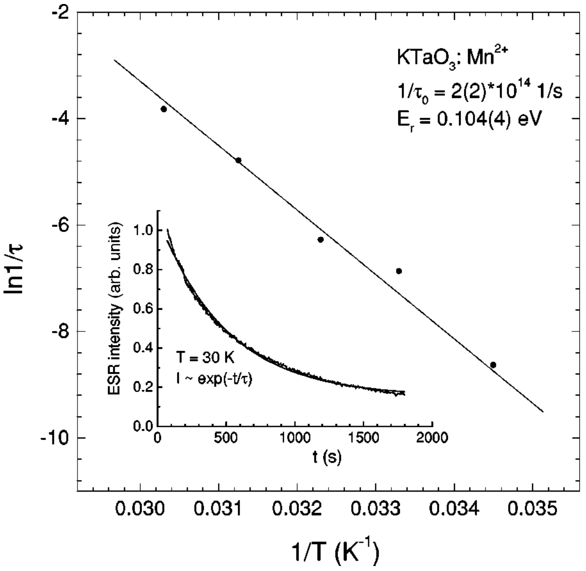

FIG. 9. Dielectric relaxation time $\tau$ as a function of $1/T$ for a $KTaO_3$:0.01% Mn crystal deduced from the ESR data. Inset: the time dependence of ESR intensity after polarizing electric field swiching off.

At $T<27$ K the dipoles orientation remains the same for a long time after field was switched off. Note, that for $T>27$ K the orientation of dipoles can be thermally destroyed during finite time from several minutes to several hours, which is sufficient for this process observation. As an example, we have represented the time dependence of intensity of ESR lines of the center 1 in the inset to Fig. 9. One can see there the exponential time decay of the intensity after polarizing electric field switching off.

### 2. Analysis of experimental data

*a. $Mn^{2+}$ dipole moment*. The Eq. (3.6) was applied to the analysis of single $Mn^{2+}$ dipoles alignment along external electric field direction. Such analysis has been performed for the samples with low manganese concentrations, in which there are no correlations between aforementioned dipoles. The experimental data were fitted with Eq. (3.6). The polarization $P$ in Eq. (3.5) has been calculated with respect to the first nonlinear term in free-energy power series[19]:

$$E=\left(\frac{\partial\Phi}{\partial P}\right)_T=\chi^{-1}(T)P+\xi P^3, \tag{3.7}$$

where $\chi(T)$ is linear dielectric susceptibility. In practice this quantity is measured by application of small amplitude a.c. electric field, when nonlinear term $\xi P^3$ can be neglected. The value of Lorentz factor $\gamma$ in Eq. (3.5) was taken to be similar to $Li^+$ on $K^+$ site ($\gamma=-0.1$) because $Mn^{2+}$ also substitutes $K^{+1}$.[20] The coefficient of nonlinearity was chosen to be $\xi=0.5\cdot 10^{10}$ mks units.[19] The fitting of observed data with Eq. (3.6) with respect to Eq. (3.7) yields $d=1.4(2)e$Å. This quantity corresponds to $Mn^{2+}$ ion dipole moment, which is temperature independent within the accuracy of our measurements.

As it has been noted earlier, $\eta(E,T)$ has another form for larger concentration of manganese (see Fig. 8). In particular, at $T\lesssim T_m$ ($T_m$ corresponds to maximum of dielectric permittivity $\varepsilon$) some critical electric field $E_c(T)$ appears, reorientation of the dipoles being possible only at $E>E_c$. To our mind, this is due to dipole-dipole correlations, which increase near dielectric permittivity maximum. Such correlations can result in the appearance of clusters with dipole glass dynamics, which clearly does not obey the Arrhenius law, peculiar to isolated dipole dynamics only. The similarity of $\varepsilon(T)$ behavior for $KTaO_3$ with 1% Li and with 0.3% Mn confirms latter statement (see Fig. 5). It is clear that any collective (like dipole-dipole correlations) and nonequilibrium effects (like glassy dynamics in clusters) do not taken into account by simple Eq. (3.6). Also, in dipole glasses, which are known to be nonergodic systems, the results of measurements have to depend on the regimes of field application on cooling or heating, So, for complete elucidation of nonequilibrium cluster dynamics, the more complex ESR and dielectric measurements should be performed. They will be performed in the near future and reported elsewhere. Here, however, the main attention will be concentrated on the properties of the isolated dipoles, i.e., on the samples with small concentration of Mn.

*b. Reorientation rate of $Mn^{2+}$ dipoles*. One of the most important characteristics of an impurity dipole is the height of barrier between its equivalent orientations in a host lattice. In the ESR method this quantity can be measured on the basis of spectra change in the regime of motional narrowing (broadening) under the conditions $\Delta\omega\tau<1$ ($\Delta\omega\tau>1$), $\Delta\omega$ is the spectra splitting due to magnetically nonequivalent positions of the dipole, $\tau$ is reorientation time. This procedure was used for $Fe^{3+}$-$O_I$ centers in previous subsection. Note that earlier such measurements were performed by us for $KTaO_3$:$Mn^{2+}$ (Ref. 21) (for $T>77$ K only) as well as in Ref. 22 for the $KTaO_3$ with 3% Nb. Although the analysis of the experimental data seems to be more accurate in Ref. 22 than in Ref. 21, barrier height obtained in Ref. 22 $E_r=(0.065\pm 0.01)$ eV appeared to be two times smaller than that obtained from dielectric measurements. This discrepancy makes it difficult to determine the mechanism of dielectric losses in $KTaO_3$:Mn as well as to clarify the local structure of $Mn^{2+}$ center. In particular, this discrepancy could be the result of confusion between 90° and 180° reorientations in ESR or dielectric measurements, respectively. To clarify these questions we performed the measurements of $Mn^{2+}$ dipoles dynamics at the temperatures close to low-frequency $T_m$. Namely, we performed the direct measurements of the rate of $90^0$—reorientation of $Mn^{2+}$ dipoles on the basis of relaxation time observation in ESR measurements after external electric field switching off. Since there are six equivalent orientations of $Mn^{2+}$ dipoles along $\langle 001\rangle$ directions it could be three different ESR spectra at arbitrary orientation of magnetic field. These spectra intensities have to be proportional to $n_1+n_2$, $n_3+n_4$, and $n_5+n_6$, where $n_i$ is the number of the dipoles with orientations along [001], $[00\bar{1}]$, [010], $[0\bar{1}0]$, [100], and $[\bar{1}00]$ directions.

The populations dynamics can be described by appropriate master equations. Keeping in mind that we consider the population relaxation after $E$ field switching off, i.e., at $E=0$, the master equations are given by

$$\frac{dn_1}{dt}=W_{\|}n_2+W_{\perp}(n_3+n_4+n_5+n_6)-n_1(W_{\|}+4W_{\perp}), \tag{3.8}$$

$$\frac{dn_2}{dt}=W_{\|}n_1+W_{\perp}(n_3+n_4+n_5+n_6)-n_2(W_{\|}+4W_{\perp}),$$

$$\frac{dn_3}{dt}=W_{\|}n_4+W_{\perp}(n_1+n_2+n_5+n_6)-n_3(W_{\|}+4W_{\perp}),$$

$$\frac{dn_4}{dt}=W_{\|}n_3+W_{\perp}(n_1+n_2+n_5+n_6)-n_4(W_{\|}+4W_{\perp}),$$

where $W_{\|}$ and $W_{\perp}$ are, respectively, the probabilities of 180° and 90° reorientations. The equations for $n_5$ and $n_6$ can be easily obtained from those for $n_3$ and $n_4$ by the interchange of $n_5$ and $4n_3$ as well as $n_6$ and $n_4$. As it was pointed out above, for $-5/2\leftrightarrow-3/2$ transition we cannot distinguish between ESR spectra of $\mathrm{Mn}^{2+}$ with $\pm\alpha(\alpha=x,y,z)$ axes orientations. That is why for the analysis of relaxation process we considered the sum of spectra intensities for centers oriented along and opposite to $\vec{E}$, i.e., $I_1\sim n_1+n_2$ and one of two spectra with the axis perpendicular to $\vec{E}$, i.e., $I_2\sim n_3+n_4$. For these quantities Eqs. (3.8) become very simple:

$$\frac{d(n_i+n_{i+1})}{dt}=-\tau^{-1}\left(n_i+n_{i+1}-\frac{N}{3}\right). \tag{3.9}$$

Here $i=1,3,5$, $N=\Sigma_{i=1}^{6}n_i$ is the total number of the dipoles and $\tau=1/6W_{\perp}$ is the relaxation time. The solution of Eq. (3.9) under the initial conditions $n_1(t=0)=N$ and $n_{i>1}(t=0)=0$ yields

$$n_1+n_2=\frac{N}{3}(1+2e^{-t/\tau}), \tag{3.10}$$

$$n_3+n_4=\frac{N}{3}(1-e^{-t/\tau}).$$

To increase the accuracy of calculations we used the ratio of ESR lines intensities, which is less sensitive to the conditions of measurements. In particular, we used

$$\frac{I_2(t)}{I_1(t)}=k\frac{n_3+n_4}{n_1+n_2}=k\frac{1-e^{-t/\tau}}{1+2e^{-t/\tau}}, \tag{3.11}$$

where $k$ is a scale factor.

This equation made it possible to perform the direct measurements of $\tau(T)$ in the temperature range (27–33) K where ESR spectra intensities had been substantially changed within time interval $4000\ \mathrm{s}\geqslant\tau\geqslant 50\ \mathrm{s}$. Aforementioned variations can be easily fixed by virtue of Eq. (3.11). The results of measurements are represented in Fig. 9. One can see that $\ln(1/\tau)$ is described well by linear dependence on $1/T$, i.e., the relaxation rate obeyed to Arrhenius law

$$\frac{1}{\tau}=\frac{1}{\tau_0}e^{-E_r/kT} \tag{3.12}$$

with $1/\tau_0=2(2)\times10^{14}\ \mathrm{s}^{-1}$, $E_r=0.104(4)$ eV.

The obtained data are in a good agreement with the results of dielectric measurements so, most probably, the results of the earlier paper[22] are incorrect.

## IV. DISCUSSION

### A. The model of $\mathrm{Mn}^{2+}$ centers

As it was mentioned above, the model of $\mathrm{Mn}^{2+}$ centers in $\mathrm{KTaO}_3$ as well as the nature of their dipole moment is not clear up to now. One can agree with the statements of the works (Refs. 20 and 23) that $\mathrm{Mn}^{2+}$ should be on $\mathrm{K}^{+}$ site rather than on $\mathrm{Ta}^{5+}$ site. However, their assumption that potassium vacancy $V(K)$ near $\mathrm{Mn}^{2+}$ ion is the reason of the center tetragonality, contradicts to our data. Indeed, two facts, namely, the magnitude of the dipole moment $d=1.4\ e$Å and the existence of Lorentz field strongly contradict to the model $\mathrm{Mn}^{2+}$-$V(K)$. For such a center the dipole moment has to be about 3 times larger and the local field has to be equal to external one.[18] On the other hand, in alternative model of the center, $\mathrm{Mn}^{2+}$ ion is shifted from the lattice site on the value $\Delta\simeq 0.9$ Å. As our simple calculation shows, the observed value $d=1.4\ e$Å can be connected with such off-central position of $\mathrm{Mn}^{2+}$. The value $\Delta=0.9$ Å is also in a good agreement with the value $b_2^0=0.147\ \mathrm{cm}^{-1}$ of tetragonal crystalline-field parameter, calculated in superposition model.[20] In such a model, $\mathrm{Mn}^{2+}$ excessive charge compensation can be due to $V(K)$ in the distant spheres, so the $\mathrm{Mn}^{2+}$ impurity is not a pure dipole like $\mathrm{Li}^{+}$ or $\mathrm{Na}^{+}$ substituted for $\mathrm{K}^{+}$. This can result in some peculiarities in the collective behavior of such dipoles, their analysis, however, is beyond the scope of the present paper.

### B. Dielectric losses near $T=40$ K

Here we would like to discuss the nature of dielectric losses in $\mathrm{KTaO}_3$ near $T\approx 40$ K, which was widely discussed in the last years (see, for instance, Refs. 4, 9, 10, 24, and 25).

Peak of dielectric losses at $T\simeq 40$ k was observed in almost all $\mathrm{KTaO}_3$ samples, whose intensity being sample dependent. In particular, the level of crystal purity defines intensity of the peak and it becomes almost unobservable ($\tan\delta<10^{-4}$) in the samples fabricated from the highest purity component or carefully cleaned from the unavoidable impurities. Therefore, there are no doubts that this peak is due to unavoidable impurities, as it has been noted earlier.[10,25] On the other hand, the kinds of these impurities is still not clear because there are many sorts of unavoidable impurities in $\mathrm{KTaO}_3$.[11,12]

The most frequent assumption was that aforementioned peak is due to different dipole centers of iron. For example, it was supposed in Ref. 9 that $\mathrm{Fe}^{3+}$ centers with rhombic symmetry are the sources of the losses. Contrary to that, our recent detailed analysis of these centers ESR spectra temperature dependence[26] had shown, that in the wide temperature range (4.2–500) K these centers are static dipoles rather than reorientable ones. They can not contribute to dielectric losses at $T\simeq 40$ K therefore.

Another, polaronic mechanism of low-temperature losses was proposed in Ref. 4. According to this paper, the polaron-type defects could be oxygen vacancies whose ionization state gradually changes for $T<60$ K. Although this model

TABLE I. Characteristics of low-temperature dielectric relaxation peaks in $KTaO_3$.

| Material | | Peak, $T$ ($K$) | $\tau_0^{-1}$ ($s^{-1}$) | $E_r$ (meV) | References and Remarks |
|---|---|---|---|---|---|
| (a) $KTaO_3$: | ''pure'' | 39.5 (4 kHz) | $6.7\times10^{13}$ | 73.6 | Bidault *et al.* (Ref. 4) |
| | 1.5% Nb | 39 (4 kHz) | | 70.6 | |
| | ''pure'' | 43 (1 kHz) | $3\times10^{12}$ | 72 | Nowick *et al.* (Ref. 10) |
| | 0.01% Cr | | $3.9\times10^{13}$ | 85 | Trepakov *et al.* (Ref. 24) |
| | 1% Fe | | $1.6\times10^{13}$ | 90 | Trepakov *et al.* (Ref. 25) |
| | 0.1% Li | | $3.3\times10^{13}$ | 87 | |
| (b) $KTaO_3$: | ''pure'' | 39 (10 kHz) | $1.5\times10^{13}$ | 69 | This paper |
| | | 48 (10 kHz) | $4.7\times10^{13}$ | 86 | |
| | 1% Fe | 41 (10 kHz) | $2.3\times10^{13}$ | 72 | |
| | | 48.5 (10 kHz) | $2.2\times10^{13}$ | 84 | |
| | 0.1% Fe | 40.3 (10 kHz) | $2\times10^{13}$ | 70 | |
| | | 48 (10 kHz) | $2.7\times10^{13}$ | 83 | |
| | 0.5% Fe | 48 (10 kHz) | $2.4\times10^{13}$ | 83 | contained 0.03 at. % Li |
| (c) $KTaO_3$: | 1.6% Li | | $5\times10^{13}$ | 86 | $^7$Li NMR data<br>Van der Klink *et al.* (Ref. 27) |

seems to be attractive, it contradicts many experimental facts. Also, no microscopic model of polaronic center was proposed in Ref. 4. In our opinion such polaronic dipole centers could be the complexes $Ta^{4+}$-$V(O)$ (Ref. 8) created by electron trapped near oxygen vacancy. However, these complexes were shown to be stable only up to $T\simeq35$ K and free electrons are needed for their appearance. These centers were not observed in nonilluminated crystals.[8]

Additionally, there were some other ideas about the sources of dielectric losses. For instance, the idea about $O^-$ hole centers, which could appear near $Cr^{3+}$ and $Fe^{3+}$ impurities.[25] However, there is no experimental confirmation of this assumption because $O^-$ centers in $KTaO_3$ were observed only in irradiated samples.[11]

We have to draw attention to the fact that parameters of aforementioned losses are different in various papers. In particular, activation energy varies from 70 meV to 90 meV. Since these variations are well beyond measurements accuracy, this may mean, that we are dealing here with several superimposed losses peaks from different dipoles. Predominance of one or another type of the dipoles seems to depend on composition of parent compounds in the process of crystal growth.

To compare, we collected in Table I the parameters of low-temperature losses obtained by different authors, in both nominally pure $KTaO_3$ and slightly doped by impurities. In this table we also included the results of our measurements. Note that in some samples we observed simultaneously two peaks of dielectric losses in the region (38–45) K, as shown in Fig. 10.

The observed maximal magnitude of dielectric losses near tan $\delta$ maximum in the greatest part of the samples was small enough $[\tan\delta\simeq(10-40)\times10^{-4}]$. But in some samples the losses appeared to be $\tan\delta\simeq(200-300)\times10^{-4}$ similar to $KTaO_3$: 0.5% Fe (Table I). The detailed chemical analysis of the latter sample had shown the presence of lithium ions with concentration approximately 0.03 at. %. On the other hand, one can see from the Table I that reorientation parameters of $Li^+$ in $KTaO_3$, obtained by NMR method,[27] are almost similar to those for one out of two relaxational centers observed in many $KTaO_3$ samples. As the matter of fact, this permits us to conclude that many of investigated crystals contain small quantity ($\lesssim0.01$ at. %) of Li ions which can be hardly detected by ordinary analysis. However, even this small concentration of Li dipoles can substantially increase the dielectric losses with following (characteristic for $Li^+$) parameters of Arrhenius law: $E_r=86(2)$ meV and $\tau_0^{-1}=5(2)\times10^{13}$ $s^{-1}$.

The nature of another low-temperature peak of dielectric losses with $E_r=(70–73)$ meV seems to stay unclear. The previous attempt to find it out was discussed in the beginning of this subsection. We have only to add that these losses are not connected with any known up to now paramagnetic centers in $KTaO_3$. Moreover, we observed no ESR spectrum with the reorientation barrier $E_r\simeq72$ meV and with intensity correlated with the dielectric losses magnitude. Therefore, the most probable origin of the latter low-temperature dielectric losses are nonparamagnetic dipole complexes. It is problematic to find out their nature and structure because of

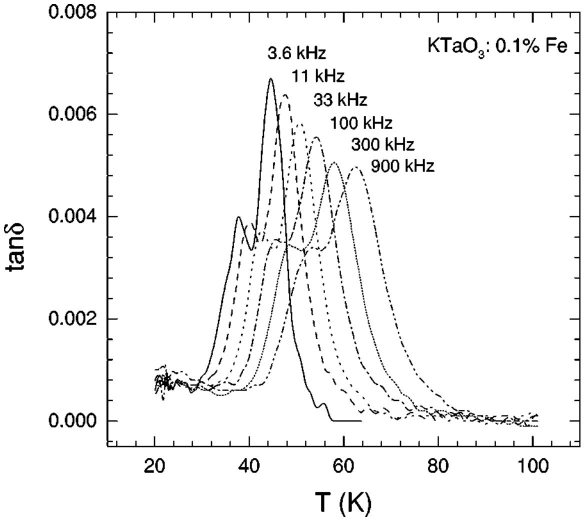

FIG. 10. Temperature dependence of the dielectric loss tan $\delta$ at various frequencies in $KTaO_3$:0.1% Fe.

their negligibly small concentration. The influence of small concentrations of electric dipoles on dielectric response is known to be the peculiar feature of incipient ferroelectric $KTaO_3$. The main reason of such phenomenon is large (4–5 lattice constants) correlation radius of polarization at $T \lesssim 50$ K. In such substances the influence of electric dipoles on dielectric response increases essentially. As a result even a small amount of electric dipoles (e.g., unavoidable impurities in the lattice) would influence essentially the dielectric losses and other low temperature properties of $KTaO_3$.

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