Interaction of dipole defects in ferroelectrics

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The density ($0.4 \leq x \leq 3$ at.%), temperature ($77 \leq T \leq 220$ K) and angular dependences of the EPR line width of the Fe^{3+}–V_0 axial center line width were investigated in the virtual ferroelectric K$_{1-x}$Li$_x$TaO$_3$. A contribution to the width of the electric dipole–dipole interaction of the paramagnetic center with the noncentral Li$^+$ ions was observed. It is shown that the observed nonlinear dependence of the line width on the Li$^+$ density and the deviation of the line shape from a Lorentzian are due to the long-range contribution made to the dipole–dipole interaction in ferroelectrics because of the presence of correlated polarization regions.

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INTRODUCTION

Considerable progress was made recently in the understanding of the role of defects in crystals with structural phase transitions.[1] A large number of experimental data could be explained by assuming the existence of defects that interact linearly with the order parameter. However, since the identification of such defects entails considerable difficulty, there are only isolated investigations in which the anomalies of some other property of the crystal can be unambiguously connected with the action of the impurity.

In ferroelectrics, impurities that interact linearly with the order parameter (with the lattice polarization) should have a dipole moment. Owing to the high polarizability of ferroelectrics and to the presence in them of correlated polarization regions, the interaction of the impurity dipoles should be substantially different here than in ordinary crystals, and should become more and more long-range as the phase-transition temperature is approached. It is precisely the presence of long-range fields induced by the defects which causes the different anomalies in the properties of real ferroelectrics (see, e.g., Ref. 2). At the same time, no direct investigations of the features of the interaction of dipole defects in such strongly polarizable substances have been made so far.

We propose in this paper a method of investigating these singularities by studying the broadening of an EPR line by dipole defects. In particular, the features of the dipole-dipole interaction should manifest themselves in a deviation of the electric-dipole broadening of the EPR line from a linear dependence on the density of the defects, and in a characteristic temperature dependence of this broadening. This becomes understandable if account is taken of the fact that with increasing parameter nr_c^3 (n is the density of the defects and r_c is the temperature-dependent polarization correlation radius) an ever increasing number of defects interact effectively with each paramagnetic center. As a result, at $nr_c^3 \gg 1$ the line profile in the case of static defects, according to the central limit theorem, should be Gaussian, with a width proportional to $(n/r_c{}^3(T))^{1/2}$.

The object of the investigation in the present study was the crystal K$_{1-x}$Li$_x$TaO$_3$ with paramagnetic impurity Fe^{3+}. It is known[3] that the Li$^+$ ions, replacing isomorphously the K$^+$ ions in the lattice of the virtual ferroelectric KTaO$_3$, occupy noncentral positions near the vacant potassium site, and form dipoles. The Fe^{3+} ions, replacing the Ta^{5+} ions in the KTaO$_3$ lattice, produce an axial Fe^{3+}–$V_{\rm O}$ center with an oxygen vacancy in the nearest environment.[4] Owing to the lack of a symmetry center, Fe^{3+}–$V_{\rm O}$ has an electrospin dipole moment and can therefore serve as a probe for the investigation of electric fields produced by Li$^+$ dipoles.

The purpose of the experiments described below was to study the mechanism of broadening of the EPR line of Fe^{3+}–$V_{\rm O}$ by Li$^+$ dipole defects, inasmuch as in accord with the foregoing one can expect to observe in it singularities connected with the increase of the long-range action in ferroelectric crystals.

EXPERIMENT. IDENTIFICATION OF BROADENING MECHANISMS

1. The K$_{1-x}$Li$_x$TaO$_3$ single crystals were grown by the Czochralski method, and were then oriented to make the surface a (100) cubic plane. The lithium impurity was introduced in the charge in the form of Li$_2$CO$_3$, while the density of the Li$^+$ in the single crystal was measured by the plasma-photometry analysis method and ranged from 0.4 to 3 at.%.

Measurements of the EPR spectra of iron in K$_{1-x}$Li$_x$TaO$_3$ were performed with an RE-1306 microwave spectrometer in the temperature range 77–220 K. We investigated the EPR spectrum of the Fe^{3+}–$V_{\rm O}$ axial center. The EPR spectrum of this center in KTaO$_3$ has been thoroughly investigated[4,5] and can be described by the spin-Hamiltonian

$$\mathcal{H} = g\beta H(\hat{S}_z\cos\theta + \hat{S}_x\sin\theta) + D\hat{S}_z^2, \qquad (1)$$

where $g = 2.00$ and $D = 1.44$ cm^{-1}.

The magnetic field H lies in the zx (010) plane and makes an angle θ with the direction [001] of the z axis of the center. In pure potassium tantalate in the 3-cm band, one EPR line is observed, corresponding to a transition between the states of the lower Kramers doublet. Application of an external electric field E splits the line.1) The angular dependence of this splitting $\Delta H_p = \mathbf{p}\cdot\mathbf{E}$ (p is the electrospin dipole moment of

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the paramagnetic center) correlates[5] with the angular dependence of the rate of change of the resonant field $dH_p/d\theta$, which, as follows from (1), takes for the lower Kramers doublet the form

$$\frac{dH_p}{d\theta}=-\frac{4h\nu}{g\beta}\frac{\sin 2\theta}{(\cos^2\theta+9\sin^2\theta)^{3/2}}. \tag{2}$$

2. Introduction of Li^+ ions in $KTaO_3$ leads to a change in the EPR spectrum. Figure 1 shows the EPR spectra of $Fe^{3+}-V_O$ in $K_{1-x}Li_xTaO_3$ at $T=77$ K for different densities of the Li^+ ions. A reduction of the spectrum shows that the $KTaO_3:Li^+$ spectrum contains, in addition to the central line corresponding to the $Fe^{3+}-V_O$ line in pure $KTaO_3$, also symmetrically located satellite lines (the dashed curves in Fig. 1), whose intensity increases with increasing density of the lithium ions, and whose position remains practically unchanged. Notice should also be taken of the correlation of the angular dependence of the satellite position with the quantity $dH_p/d\theta$. These experimental results suggest that the presence of satellite lines is due apparently to the paramagnetic $Fe^{3+}-V_O$ centers with Li^+ ions in the first coordination sphere.

We note that satellite lines whose position correlates with $dH_p/d\theta$ could generally speaking be the result of the presence of macroscopic regions with nonzero polarization P, as assumed in Ref. 6. In that case, however, the shift of the satellites should increase with increasing lithium density, at constant intensity of the satellite lines, which is at variance with the experiment.

3. From a comparison of the width of the central line in $KTaO_3:Li^+$ with the width of the corresponding EPR line in pure potassium tantalate it follows that introduction of the Li^+ ions in the single crystal leads to a noticeable broadening of the EPR line of the axial center[2)] $Fe^{3+}-V_O$, and the line shape is also changed. Figure 2 shows the angular dependences of the line widths in pure potassium tantalate and in crystals with lithium. The solid lines are plotted in accordance with (2). The figure shows the correlation between the broadening of the central line and the quantity $dH_p/d\theta$ and consequently, as indicated above, with the shift of the EPR line in the external electric field. This correlation usually takes place in the case of line broadening by the electric field of defect[7] and may be connected in the case considered with electric dipole-dipole interaction between the electrospin dipole moment of the paramagnetic center and the dipole moments of the noncentral ions.

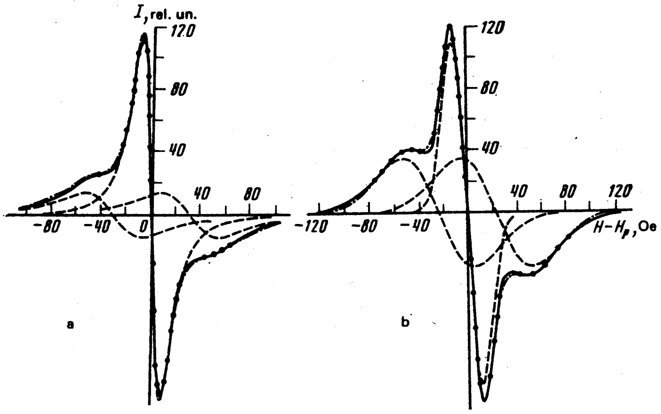

FIG. 1. EPR spectra of $Fe^{3+}-V_O$ in $K_{1-x}Li_xTaO_3$ at $\theta=14°$: a) $x=0.4$ at.%; b) $x=1.2$ at.%; solid curves—experiment, dashed—line components, dash-dot—summary lines.

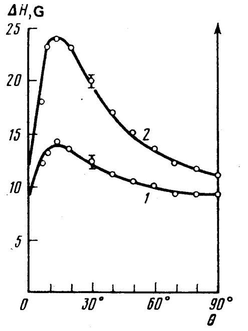

FIG. 2. Angular dependences of the line widths at $T=77$ K in $KTaO_3$ (1) and in $K_{1-x}Li_xTaO_3$, $x=1.9$ at.% (2). The solid curves were calculated from the formula $\Delta H_p=\Delta H_m(0)+A_m dH_p/d\theta$, where $\Delta H_2(0)=11$ G, $A_2=3.7\cdot10^{-3}$ rad, $\Delta H_1(0)=9$ G, and $A_1=1.8\cdot10^{-3}$ rad.

As seen from Fig. 2, at angles $\theta=0°$ and $\theta=90°$, where $dH_p/d\theta=0$, there is a certain residual broadening attesting to the presence of a non-electric mechanism that contributes to the total broadening of the EPR lines of $Fe^{3+}-V_O$ by the lithium defects. The cause of this contribution may be that the noncentral Li^+ ions have, besides the electric dipole moment, also an elastic moment that induces an elastic-stress field in the crystal. The elastic broadening mechanism, generally speaking, can also have an angular dependence. To separate the contributions of the electric dipole and elastic broadening mechanisms, we turn to an analysis of the temperature dependences of the line width, which are shown in Fig. 3.

At $\theta=90°$, addition of lithium to the $KTaO_3$ leads to practically no change in the temperature dependence of the line width compared with pure $KTaO_3$, thus indicating a manifestation of a temperature-independent elastic broadening mechanism. At the same time at $\theta=14°$, when the temperature is raised from 77 K, the width of the EPR line of $Fe^{3+}-V_O$ in a crystal with

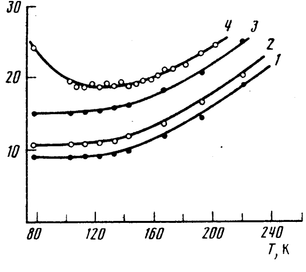

FIG. 3. Temperature dependences of the line widths in $KTaO_3$ (●) and in $K_{1-x}Li_xTaO_3$, $x=1.9$ at.% (○) at angles $\theta=90°$ (curves 1 and 2) and $\theta=14°$ (curves 3 and 4).

lithium decreases, reaching a minimum at $T \approx 120$ K. The observed decrease of the line width is connected with the contribution of the electrodipole broadening to the total line width, which predominates at $\theta = 14°$. The decrease of the electrodipole width in ferroelectrics with increasing temperature is due to the temperature dependence of the electrospin dipole moment of the paramagnetic center in such crystals,[8,9] which duplicates the temperature dependence $\varepsilon(T)$ of the dielectric constant, as well as to a change in the correlation radius.[9] At $T \gtrsim 100$ K, as shown by estimates using the data of Ref. 10, an additional cause of the decrease of the line width can be thermal reorientations of lithium dipoles, which lead to a dynamic narrowing of the line, whereas at lower temperatures the broadening has mainly a static character.

At $T > 120$ K, the line width in the crystal with lithium increases and duplicates at $T \gtrsim 160$ K the temperature dependence of the line width in pure potassium tantalate. This is evidence that the difference between the widths at these temperatures is due to the contribution of the temperature-independent elastic mechanism, so that its contribution to the total broadening at lower temperatures can be determined. Thus, in particular, at $T = 77$ K the contribution of the elastic mechanism to the total line width is ~10%.

The presence of different contributions to the line broadening is evidenced also by the change in the line shape with changing angle θ. Whereas at $\theta = 90°$ the line shape in $KTaO_3 : Li^+$ is close to Lorentzian, as it should in the case of the elastic broadening mechanism,[7] at $\theta = 14°$, where the electrodipole broadening mechanism predominates, the line profile is intermediate between a Lorentzian and a Gaussian, differing more and more from a Lorentzian with increasing n. (In pure potassium tantalate the line shape is close to Lorentzian.)

Figure 4 shows plots of the line width against the density of the noncentral Li^+ ions at $T = 77$ K. The practically linear character of the density dependence at $\theta = 90°$ also agrees with the assumption that the broadening mechanism is elastic, since the intensity of the stress field is inversely proportional to the third power of the distance to the defect. At the same time, the linear approximation of the concentration dependence at $\theta = 14°$ does not provide a sufficiently good description within the limits of the experimental errors indicated in Fig. 4, their increase with increasing Li density notwithstanding. (The increase of the error with increasing n is due to the increased contribution of the satellites to the central-line width.) Nor can the linear approximation be reconciled with the observed non-Lorentzian line profile. Thus, an approximation of the density dependence of the width at $\theta = 14°$ by a relation weaker than linear is preferrable. Such a width dependence and the non-Lorentzian character of the line profile, as will be shown below, can be due to the appearance of dipole-dipole long-range action in strongly polarized $KTaO_3$. It is important to note that any other possible causes of deviation from a linear density dependence of the width should manifest themselves also in the elastic broadening mechanism and be thus excluded from the observed linear density dependence at $\theta = 90°$.

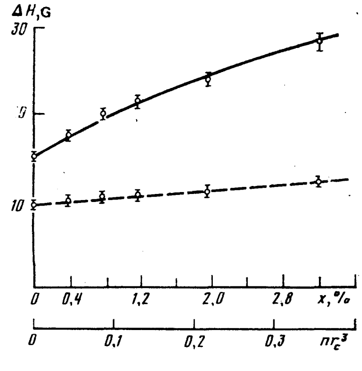

FIG. 4. Concentration dependences of line widths at $T = 77$ K at $\theta = 90°$ (dashed line) and $\theta = 14°$. Solid curve—theory.

DENSITY DEPENDENCE OF THE LINE WIDTH. COMPARISON WITH THEORY

In the case of the ordinary dipole-dipole interaction of a paramagnetic center with noncentral ions, there should be observed a linear dependence of the defect line width on the density of the impurity dipoles, corresponding to the Lorentz shape of the line.[7] The presence in ferroelectrics of a large polarization correlation radius leads to an increase of the long-range character of the dipole interaction and to a weakening of the density dependence of the defect-induced width.[9] The observed deviation from linearity of the density dependence of the width can be described by using the statistical line-shape theory, by recognizing that the resonant-field shift due to the Li^+ dipoles is equal to

$$\Delta H_p = -\mathbf{p} \sum_j \mathbf{E}(r_j),$$

where $\mathbf{E}(\mathbf{r})$ is the electric field of the dipole at the location of the paramagnetic center.

According to Ref. 11, in crystals with weak phonon modes, such as the virtual ferroelectric $KTaO_3$, we have

$$\mathbf{E}(r) = \frac{1}{\varepsilon}\left\{\left(\frac{2}{3}\frac{1}{rr_c^2}e^{-r/r_c} + \frac{4\pi}{3v}\right)d^* + \left[\frac{1}{r^3} - e^{-r/r_c}\left(\frac{1}{r^3} + \frac{1}{r^2 r_c} + \frac{1}{3rr_c^2}\right)\right](3\mathbf{n}(\mathbf{d}^*\mathbf{n}) - \mathbf{d}^*)\right\}, \qquad (3)$$

where $d^* = d\gamma\varepsilon/3$ is the effective electric dipole of the defect, which takes into account the contribution of the Lorentz field in a strongly polarized crystal, d is its intrinsic dipole moment, γ is the Lorentz factor, ε is the dielectric constant of the crystal, and $\mathbf{n} = \mathbf{r}/r$. It is seen from (3) that whereas $\mathbf{E}(\mathbf{r})$ has the usual form $\mathbf{E}(\mathbf{r}) \propto r^{-3}$ at $r \gg r_c$, the interaction of the dipoles follows an entirely different law if the distances between them $r \lesssim r_c$. Since the main contribution to the line width is made by dipoles at medium distances, it is clear from the outset that one should expect singularities in the manifestation of the electrodipole mechanism of the broadening at $nr_c^3 \sim 1$. A numerical calculation of the electrodipole line width was carried out in Ref. 9

for different values of the parameter nr_c^3. It follows from the calculation that the deviation of the density dependence of the width from linearity comes into play already at $nr_c^3 \gtrsim 10^{-2}$.

However, the electrodipole broadening calculated in Ref. 9 cannot be directly compared with the line width observed by us, owing to the presence of several broadening mechanisms and to the complex line shape, which is intermediate between a Lorentzian and a Gaussian. To compare the theory with experiment we have therefore numerically convoluted all the available broadening mechanisms. In accord with experiment, we have assumed that the elastic and density-independent broadening mechanisms lead to a Lorentzian line shape, and the Fourier transform of the electrodipole line shape for the values of nr_c^3 of interest was calculated in accordance with Ref. 9. The total line width obtained in this manner for different values of the Li^+ ion density (or of nr_c^3) with the values of the theory parameters $\gamma d = 0.22$ eÅ and $r_c = 9$ Å is represented by the solid curve in Fig. 4. The electrospin dipole moment $p = 0.1$ G/(kV/cm) was taken from the data of Ref. 5 on the electric-field effect. As seen from the figure, the theoretical curve agrees well with experiment. The obtained value $r_c = 9$ Å is close to the value $r_c = 8$ Å obtained from measurements[12] of the frequency of the soft mode in pure $KTaO_3$. The value $\gamma d = 0.22$ eÅ used in the calculation corresponds to the value $d = 0.86$ eÅ at $\gamma = 0.25$, determined by the NMR method.[13] The value $|\gamma| < 1$ in similar sites is typical for the entire perovskite family.[14]

Thus, the investigations carried out in the present paper offer evidence of the appearance of a long-range character of the interaction of dipole defects in strongly polarizable crystals; this character determines the singularities of the properties of real ferroelectrics.

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1) The line splitting is due to the presence of two inversion-nonequivalent centers.

2) Control measurements have established that the line width is independent of the density of the Fe^{3+} ions.

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