Phase transition into the "polar glass" state in $(K_{1-x}:Li_x)TaO_3$

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The ordering of the electric dipole moments of noncentral Li^+ impurities in the virtual ferroelectric $KTaO_3$ was experimentally investigated. Studies were made of the temperature and electric-field dependences of the static dielectric constant and of the EPR of Mn^{2+} and Gd^{3+} in the system $(K_{1-x}:Li_x)TaO_3$ in a wide range of concentrations ($x = 0$–0.0348) and temperatures ($T = 4.2$–300 K). The results are attributed to a phase transition into a pseudospin polar glass state for the noncentral impurities and to the existence of an electret state.

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1. INTRODUCTION

A system of electric dipole impurities in a crystal is of considerable interest because of the possible transitions to an ordered state.[1,2] Similar phase transitions arise as a result of the interaction of the dipole moments with one another and with the lattice. It was shown in Ref. 2 that the dipole-dipole interaction of impurities can lead to transitions into the polar pseudospin-glass phase. Ferroelectrics whose phonon spectrum contains soft transverse optical modes are the most favorable objects for the appearance of such effects—the formation of polar pseudospin glass.[3] It was shown in Ref. 3, in an investigation of indirect dipole-dipole interaction via soft optical phonons, that in ferroelectrics with dipole impurities the temperature T_c^* of the transition into the phase of the polar pseudospin glass should increase, and estimates of T_c^* were made for the system of noncentral Li impurities in the virtual ferroelectric $KTaO_3$. This effect was observed[4] in a study of the dielectric relaxation and of the thermoelectret-polarization effects in $(K_{1-x}:Li_x)TaO_3$. To prove the existence of the polar glass phase it was necessary to investigate such a system also by other methods that permit identification of the phase transition into the state of polar glass. Also needed is a comparison of the theory with experiment. This would make it possible to determine the internal parameters of the system in this case. Such investigations are the subject of the present paper.

We have studied the static dielectric constant of the system $(K_{1-x}:Li_x)TaO_3$, as well as the EPR of Mn^{2+} and Gd^{3+} in a wide range of Li^+ concentrations ($x = 0$–0.038) and temperatures ($T = 4.2$–300 K). The results allow us to conclude that a polar pseudospin glass phase and an electret state exist in the case considered.

2. EXPERIMENTAL RESULTS

The EPR spectra were measured with an RÉ-1301 microwave spectrometer. The dielectric constant was measured with an R-589 ac bridge. The temperature was varied by pumping on helium or nitrogen vapor. The temperature was measured with a copper-constantan thermocouple. The $KTaO_3$ crystals were grown by the Czochralski method. The paramagnetic impurity and the second component (Li) were introduced in the melt. The Li concentration was monitored by flame photometry.

Figure 1 shows the temperature dependence of the dielectric constant of $(K_{1-x}:Li_x)TaO_3$ with different lithium concentrations. Formation of a susceptibility peak due to the introduction of the lithium can be seen. The strong $\varepsilon(T)$ dependence at $x = 0.038$ can be attributed to the presence of two peaks of ε, at $T_{p1} = 60$ K and $T_{p2} = 120$ K (T_p is the temperature of the ε peak). With increasing Li concentration, the susceptibility maximum shifts towards higher temperatures. This is clearly seen in Fig. 2, which slows in addition the point with $x = 0.049$ (only the susceptibility-maximum temperature was measured for this concentration).

The EPR also undergoes substantial changes at temperatures in the region of the susceptibility peak. The electric-field effect in the EPR of Mn^{2+} is greatly

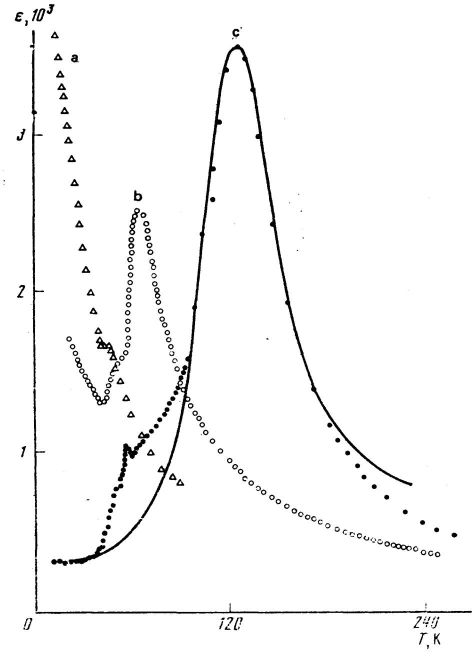

FIG. 1. Temperature dependence of the dielectric susceptibility at 15 kHz for $x = 0.0005$ (a), $x = 0.007$ (b), and $x = 0.038$ (c). Solid line—theory, points—experiment.

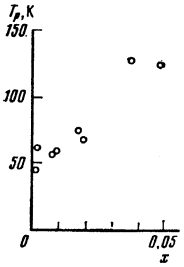

FIG. 2. Concentration dependence of the susceptibility-peak temperature (1 kHz).

weakened. Thus, the shift of the EPR line of Mn^{2+} (the transition $-5/2 \rightarrow -3/2$) at $x = 0.038$ and $T = 77$ K is less than the experimental error.

The reorientation of the "Mn^{2+} + oxygen vacancy" dipoles in an external field E also exhibits anomalous properties in the susceptibility-peak region. At $T < T_p$ the reorientation in the field E takes place only starting with $E > E'$ ($E' = 10$ kV/cm), whereas at $T > T_p$ there is no threshold E field causing reorientation, and the intensities of EPR lines of Mn^{2+} with different directions of the crystal-field axes vary at $E \neq 0$ in accord with the reorientational transitions, in analogy with Ref. 4. As a result of the reorientation of the dipole moments in the field E, the system becomes polarized, and the polarization P is preserved when the field E is turned off. It becomes possible then to change the direction of the polarization in the external electric field. To observe the change of the polarization direction, contacts were secured with conducting adhesive to four planes of the samples in such a way that the electric field could be applied in succession in two perpendicular directions. Figure 3 shows the change of the intensities of the EPR lines of Mn^{2+} $(-5/2 \rightarrow -3/2)$ vs the electric field $E_\perp$ after first applying $E_\parallel = 10$ kV/cm in a perpendicular direction. Reversal of the sign of $I - I_0$ (I_0 is the line intensity at $P = 0$) corresponds to a change in the direction of the polarization. It is seen that the polarization-reversal effect has a "memory," for in this case reorientation takes place even at $E_\perp < 10$ kV/cm. The rate τ^{-1} of the orientational relaxation of the "Mn^{2+} + vacancy" dipole moment at $T = 77$ K, obtained by investigating the EPR with rapid switching of the field, amounts to $\tau^{-1} > 10^3$ sec^{-1}. In this case, such a polarization effect should be due to the dipole moments of the noncentral Li ions.

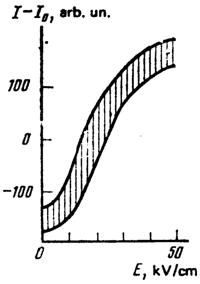

FIG. 3. Change of the Mn^{2+} EPR line intensities in $(K_{1-x}:Li_x)TaO_3$ at $x = 0.038$ and $T = 77$ K vs. the field E after prior application of a field in the perpendicular direction. The shaded region corresponds to the scatter of the values of $I - I_0$.

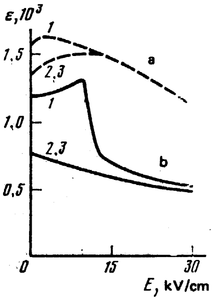

FIG. 4. Electric-field dependences of the dielectric susceptibility of single-crystal $(K_{1-x}:Li_x)$ in the [100] TaO_3 direction at $T = 77$ K: a) $T_c^* < x = 0.007$, b) $T_c^* > T$, $x = 0.38$ (plotted with E increasing; the numbers on the curves are those of the plots).

Such a state of the polarized noncentral ions in the crystal corresponds to the electret state. The electric field that leads to the electret state of the sample can be observed also in investigations of the dependence of the dielectric constant on the electric field. Figure 4 show this dependence at $T > T_p$ ($x = 0.007$) and $T < T_p$ ($x = 0.038$). Both measurements were made at 77 K. Curves 1 were obtained at the first application of the constant electric field, and curves 2 and 3 after repeated applications. The strong decrease of the dielectric constant corresponds to the critical field E'. A similar behavior is observed both for the case when the impurity is only Li^+, and for Li^+ and Mn^{2+} thus confirming the connection of the electret state with the system of noncentral Li^+ ions. The change of the dielectric constant upon reversal of the direction of the electric field at $T \sim T_p$ ($T = 77$ K; $x = 0.017$) is similar to the change obtained in Ref. 5 at microwave frequencies with $T = 4.2$ K and $x = 0$.

Substantial changes take place also in the EPR spectra of Gd^{3+} at temperatures in the region of the maxi-

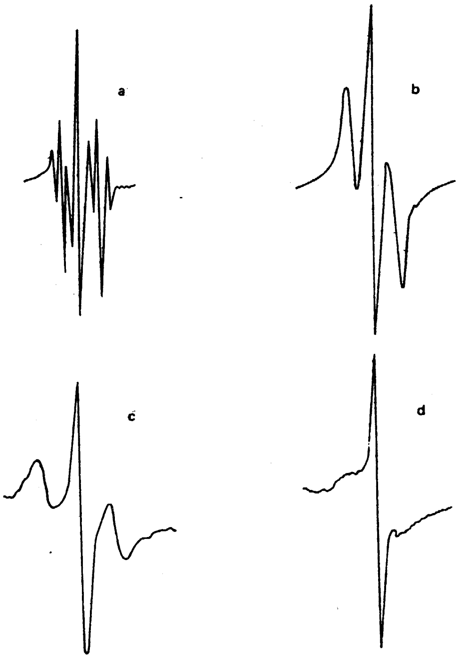

FIG. 5. EPR spectra Cd^{3+} at $x = 0$ and $T = 77$ K (a) $x = 0.038$ and $T \gg T_c^*$ (b), $T \lesssim T_c^*$ (c) and $T \ll T_c^*$ (d).

mum ε (Fig. 5). The line intensities of the transitions $M \to M-1$ with $M \neq 1/2$ decrease when T decreases in the region $T < T^2$. This intensity decrease is probably due to line broadening.

3. DISCUSSION OF RESULTS IN THE MODEL OF ORDERING IN A SYSTEM OF NONCENTRAL IMPURITY IMPURITY IONS

The temperature T_p of the experimentally observed peak increases with increasing x, depending on $\varepsilon(T)$, with no peak of $\varepsilon(T)$ at $x=0$. This allows us to regard the observed $\varepsilon(T)$ peak as being of impurity origin.

In $(K_{1-x}:\mathrm{Li}_x)\mathrm{TaO}_3$ the impurity lithium ion replaces a potassium ion and occupies a noncentral position[6] displaced from a site in one of the six [001] directions. Such a system of noncentral ions in an ion crystal constitutes a system of interacting electric dipoles. It is therefore natural to attribute the observed anomaly of $\varepsilon(T)$ to the ordering of the interacting noncentral impurity ions.

If soft transverse optical modes are present in the phonon system of the crystal, as in the considered case of KTaO_3, the dipole-dipole interaction of the nonecentral ions increases strongly and raises the ordering temperature.[3] In this case the law of decrease of the interaction energy with distance r differs from $H_{dd} \sim r^{-3}$ at $r \leq r_c$, and when allowance is made for $r < r_c$ we have, averaged over the directions, $H_{dd} \neq 0$. This points to the possibility of ferroelectric ordering of noncentral ions spaced less than r_c apart.

At small concentrations n and sufficient $(T-T_c)$, when the condition $r_c^3 n \ll 1$ is satisfied, the greater part of the central ions have no neighbors at distances $r < r_c$. For such fields $H_{dd} \sim r^{-3}$ and is an increasing function as $T \to T_c$.[3] Then the average over the directions is $\langle H_{dd} \rangle = 0$, so that the noncentral ions cannot have a ferroelectric order. In this case, however, a transition to the polar pseudospin glass phase becomes possible.[2]

To analyze the transition into the polar glass phase in strongly polarizing crystals, we use the results of Vugmeister and Glinchuk.[7] They derived an expression for the temperature T_g of the transition to the polar-glass phase at $nr_c^3 \ll 1$ in the molecular-field approximation, in the form

$$T_g = \frac{1}{27k_B}\gamma^2 e^2 x_0{}^2 \left(\frac{4\pi n}{3r_c{}^3}\right)^{1/2} [\varepsilon(T_g) - \varepsilon_\infty], \tag{1}$$

e is the elementary charge, x_0 is the displacement from the site of the noncentral ion, and γ is the Lorentz-field attenuation factor.

We compare now the observed T_p of the $\varepsilon(T)$ peak at low concentrations with T_g. By comparing (1) with experiment we can determine the value of x_0 for Li^+ in KTaO_3. Putting in our case $\gamma \approx 0.09$, which corresponds to the value calculated from Slater's theory,[8] and $r_c \approx 6.8$ Å at $T_g \approx 40$ K for $x = 5\times 10^{-4}$, and taking into account the experimentally determined $\varepsilon(40\ \mathrm{K}) \approx 1.6 \times 10^3$, we find from (1) that $x_0 = 1$ Å. To find the correlation radius r_c, we used Barret's experimental data.[9] We note that the value of r_c obtained here corresponds to the correlation radius obtained from the experimental values of $\omega_t^{(i)}$, ε, and ε_∞ using the Lyddane-Sachs-Teller relation. The proposed phase transition into the polar-glass state leads thus to agreement between theory and experiment at a reasonable value of the dipole moment of the noncentral impurity.

Expression (1) turns out to be valid, however, only for the lowest investigated Li^+ concentrations. At high concentrations, $nr_c^3 \sim 1$, and the character of the ordering of the noncentral ions changes. In this case, as before, an appreciable part of the noncentral impurities has no neighboring noncentral impurities at $r < r_c$, and can be regarded as "isolated" in this sense. For these noncentral ions, averaging over the directions yields $\langle H_{dd} \rangle = 0$, so that a transition into the polar-glass phase can be considered. However, the approximation with zero correlations becomes incorrect in the statistical theory. The results could be qualitatively described in this concentration region by using a phase transition into the state of polar glass in the one-dimensional Ising model, with allowance for the interaction between the chains[10] (see Fig. 1c). The energy parameter is then a random quantity with a Gaussian distribution. The dielectric susceptibility is given in this case by

$$\chi = \beta\mu^2 \{(1-\tilde{p}^2)^{-1} [e^{2\beta J_0}(1-\tilde{p}^2) + \tilde{p}^2]^{-1/2} - 2\beta J_0 \eta\}^{-1}. \tag{2}$$

Here $\tilde{p}$ is the ratio of the polarizability of the impurity system to the maximum possible (in the case of complete ordering), μ is the effective dipole moment, J_0 is the most probable value of the energy parameter, and η is the parameter of the ratio of the interaction energies within the chain and between the chains. We note that μ differs from the true dipole moment of the noncentral ion in (1) by an amount connected with the difference between the field E_{loc} acting on the dipole moment and the external field E. The equilibrium polarizability in the presence of an external field E. The equilibrium polarizability in the presence of an external field E was determined by solving the equation

$$\frac{\tilde{p}}{(1-\tilde{p}^2)^{1/2}} e^{-\beta J_0} \operatorname{ch}(\beta\mu E) - \left[\frac{1-\tilde{p}^2+\tilde{p}^2 e^{-2\beta J_0}}{1-\tilde{p}^2}\right]^{1/2} \operatorname{sh}(\beta\mu E) = \operatorname{sh}(2\eta\beta J_0 \tilde{p}). \tag{3}$$

At $nr_c^3 \approx 1$ a fraction of the noncentral ions have neighbors at $r < r_c$. For such cluster, the character of the indirect dipole-dipole interaction via the field of the transverse optical phonons changes.[3] Thus, at $r \ll r_c$, according to Ref. 3, the potential of the interaction of the dipole moments P_i and P_j via the soft transverse optical mode is represented in the form

$$H_{dd} \approx -\frac{\varepsilon_\infty[\omega_l{}^2 - \omega_0{}^2]}{18vr} (\mathbf{P}_i \mathbf{P}_j + P_{ir} P_{jr}), \tag{4}$$

P_{ir} is the projection of the i-th dipole moment on the direction of the vector $\mathbf{r}_i - \mathbf{r}_j$. Formula (4) corresponds to a dispersion law for the transverse optical phonon in the form $\omega_k = (\omega_0^2 + vk^2)^{1/2}$. It follows from (4) that in such noncentral-ion clusters the energy is a minimum when the dipole moments of the noncentral ions are parallel, so that ferroelectric ordering becomes possible in such clusters. Such a ferroelectric phase transition coexists with the transition into the phase of polar pseudospin glass for "isolated" noncentral ions, and should manifest itself as an additional peak in the $\varepsilon(T)$ plot. Indeed, at relatively high Li^+ concentrations, when $nr_c^3 \sim 1$, for example at $x=0.038$, the form of $\varepsilon(T)$ is more complicated, possibly because of the presence of an additional peak of $\varepsilon(T)$ at $T_{p1} = 60$ K.

The discussed ferroelectric ordering in clusters does not lead to the appearance of a macroscopic polarizability **P**, since the directions of the polarizabilities of the individual clusters are randomly distributed in space. A macroscopic polarizability appears only at $nr_c^3 \gg 1$, when the dimensions of the ordered clusters are of the order of or larger than the distances between the clusters, and the individual clusters merge. The experimentally observed abrupt decrease of the main $\varepsilon(T)$ peak with increasing field can be interpreted as destruction of the polar-glass phase when E_{loc} becomes of the order of the internal electric field.

In conclusion, we discuss the possible cause of the broadening of the Gd^{3+} EPR lines in $KTaO_3$ with decreasing temperature. This broadening is probably due to the fields of the dipole moments of the noncentral lithium ions. The broadening increases noticeably on going to the polar-glass phase. It can be assumed that the electric fields of the defects at the paramagnetic centers become stronger, and therefore one observes at $T \sim T_p$ a broadening of the EPR lines corresponding to spin projections with $M \neq \frac{1}{2}$.

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