

## Collective Dynamics of Off-Center Ions in $K_{1-x}Li_xTaO_3$ : A Model of Relaxor Behavior

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The relaxor behavior is characteristic of the class of disordered ferroelectrics. These systems possess a high dielectric constant with a broad relaxation peak and a low frequency dispersion. Because of their complexity, there exist various explanations for their dielectric and polarization behavior, but no unifying model. In the present paper we show that the simpler system,  $K_{1-x}Li_xTaO_3$ , is also a relaxor and a generic one at that. We describe its dynamical behavior with a general microscopic model and show that the relaxor behavior is intrinsically due to the dipolar interaction between randomly distributed off-center ions mediated by a highly polarizable lattice.

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In the large family of ferroelectrics, a new group has been identified. They are mixed and disordered ferroelectrics called "relaxors" such as  $PbMg_{1/3}Nb_{2/3}O_3$  (PMN) or  $PbSc_{1/2}Ta_{1/2}O_3$  (PST). Relaxor ferroelectrics possess very unusual properties which have been the subject of several recent investigations [1–5]. Their most intriguing property is a very large dielectric constant with a broad relaxation peak and a low frequency dispersion. In the early studies on relaxors [6], this peak was viewed as the mark of a ferroelectric phase transition, which, because of the frequency dispersion, was said to be diffuse. In a recent birefringence study [1] of PMN, the apparently diffuse character of the phase transition has been attributed to the presence of quenched random fields while, in another study [3], the broad dielectric relaxation peak has been interpreted as a sign of glassy behavior and spin glass models have been invoked. In the case of PST, a recent study [7] has revealed, in addition to the relaxor behavior, a sharp drop in the dielectric constant which has been interpreted as a spontaneous transformation from relaxor to ferroelectric. This diversity of interpretations is due to the fact that, so far, there does not exist a general microscopic model capable of describing the generic behavior of all relaxors. Moreover, of the proposed phenomenological models [8–10], none can simultaneously predict the very large dielectric constant which is a sign of, at least, incipient long-range order, and of the low frequency dispersion, characteristic of disordered systems. One of the obstacles in understanding the behavior of relaxors has been their complex structure, with the imbalance in valence of the two central atoms and the existence of chemically ordered and electrically charged regions [11]. It is therefore desirable to find a simpler system which nevertheless also displays the relaxor behavior and on which a microscopic model can be tested. Here, we propose  $K_{1-x}Li_xTaO_3$  as a new prototype for relaxors, describe its dynamics using a microscopic model which should be also applicable to other relaxors, and point out the specificity of different relaxors.

$K_{1-x}Li_xTaO_3$  (KLT) belongs to the same perovskite family as PMN and PST, yet it has the great advantage that

K and Li are simple ions and both carry the same charge. The most important characteristic of KLT is the  $\langle 100 \rangle$  off-center location of  $Li^+$  which therefore carries an electric dipole moment [12]. In the typical relaxor PMN,  $Pb^{2+}$  has also recently been found off-centered in the  $\langle 110 \rangle$  direction and  $Nb^{5+}$  in the  $\langle 111 \rangle$  and  $\langle 110 \rangle$  directions [13,14]. Here, we first show that the essential features of relaxor behavior, i.e., a large dielectric constant, a broad relaxation peak with a low frequency dispersion, and a slim hysteresis loop in the polarization, are all observed in KLT where they can also coexist with a structural transition.

In order to demonstrate the relaxor character of KLT, it is appropriate to compare its dielectric behavior with that of PMN and PST, both well-recognized relaxors. This is done in Fig. 1 where the frequency dispersion of the dielectric peak is clearly apparent for all three systems. For Li concentrations greater than the critical concentration of 2.2% Li, KLT behaves as disordered but stoichiometric PST. In this case, the dielectric constant exhibits a sudden drop at a frequency-independent temperature. Raman [15] and neutron scattering [16] studies of KLT have also clearly shown the existence of a structural transition at the same temperature. By contrast, as was shown in the dielectric study of KLT reported in Ref. [17], the drop in the dielectric constant is not observed below the critical concentration just as it is absent in PMN or in PST with Pb vacancies. In PMN, neither the dielectric constant nor Raman scattering, or even x-ray diffraction, have revealed a transition for zero electric field [18]. Therefore, below the critical concentration, KLT behaves more like PMN or like PST with Pb vacancies.

From the above comparison one can clearly see that KLT does indeed belong to the family of relaxors and, in fact, can be studied as a generic system of this family since it exhibits both a strong frequency dispersion and a structural transition or not, depending upon the Li concentration. We now show that the relaxor features of KLT as well as its transition can be described by a microscopic model [19] that takes into account exactly the pairwise interaction between neighboring off-center Li ions (forming a cluster) and uses a random local

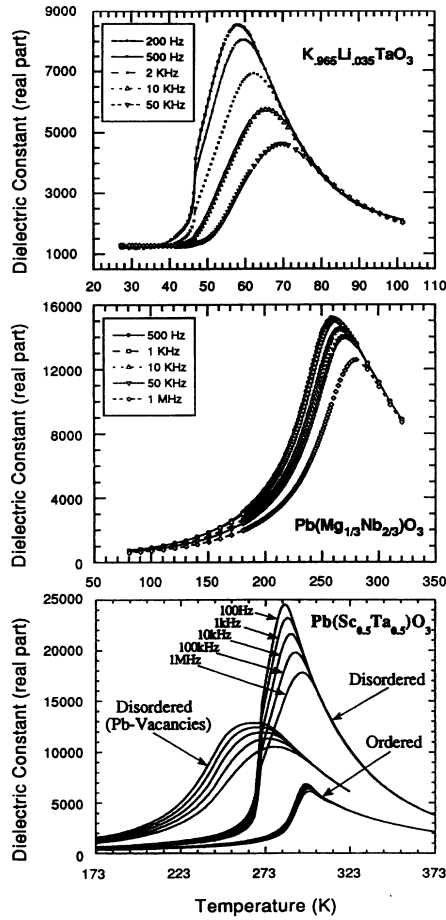


FIG. 1. Dielectric constant of KLT, PMN, and PST showing the typical frequency dispersion observed in relaxors. The PMN and KLT data are from the present work and are comparable to data found in Refs. [4] and [17], respectively. The PST data are from Ref. [7].

field approach developed earlier by one of us [20] to describe the interaction between these and more distant off-center ions. Such an approach is a generalization of the well-known Bethe-Peierls cluster theory for systems with configurational disorder.

Due to the high polarizability of the lattice, each off-center ion carries an effective dipole moment,  $d^*$ , which interacts with all the other dipoles. The Hamiltonian of the dipolar system is then written [20]

$$H = -\frac{1}{2} \sum_{ij} K_{ij} l_i l_j - \sum_i l_i (E_i^s + e) \equiv - \sum_i l_i (E_i + e), \quad (1)$$

where  $\mathbf{l}_i = \mathbf{d}^*/|d^*|$  is a unit vector along the direction of the dipole moment located at  $r_i$ ,  $e$  is the external electric field, and  $E_i^s$  is an extra random field that must be included in order to describe properly the experimental results, the origin of which is discussed later in the paper. Assuming, for simplicity, Ising-like dipoles ( $l_i = l_{iz} = \pm 1$ ), the coupling constant,  $K_{ij} = K(r_{ij})$ , is calculated to be [20]

$$K(\mathbf{r}) = \frac{d^{*2}}{\epsilon_0} \left\{ \frac{2}{3} \frac{1}{rr_c^2} e^{-r/r_c} + (3 \cos^2 \theta - 1) \times \left( \frac{1}{r^3} - e^{-r/r_c} \left[ \frac{1}{r^3} + \frac{1}{r^2 r_c} + \frac{1}{3 r r_c^2} \right] \right) \right\} \quad (2)$$

in which  $\epsilon_0$  is the high frequency dielectric constant of the doped crystal [21] and  $r_c$  is the noncritical polarization correlation length ( $r_c \sim \sqrt{\epsilon_0}$ ). The first term in  $K(\mathbf{r})$  is an essential feature of the indirect interaction between dipoles, mediated by the highly polarizable lattice. The dipolar order parameter is then written as:

$$L = \langle \overline{l_i} \rangle, \quad (3)$$

where the brackets and the bar, respectively, denote a thermal average and an average over random spatial configurations of off-center ions. The distribution function of local fields  $f(E_i)$ , that enters into the calculation of  $L$ , can be written as a convolution of the distribution function  $f_d(E_i^d)$  of the dipolar fields  $E_i^d = \sum_j K_{ij} l_j$  and the distribution function  $f_s(E_i^s)$  of the extra random fields  $E_i^s$ . We assume here that  $f_s(E_i^s)$  is a Gaussian of width  $\delta$ . In KLT, the width of  $f_s(E_i^s)$  is found to be much greater than the width of  $f_d(E_i^d)$  [22] so that the overall distribution function can be written as

$$f(E_i) = [\sqrt{2\pi}\delta]^{-1} \exp[-(E_i - E_0 L)^2 / 2\delta^2], \quad (4)$$

where  $E_0 = 4\pi n d^* / \epsilon_0$  with  $n$  the concentration (per unit volume) of off-center ions.

In the description of the dynamics, we consider pairs of neighboring dipoles (although not necessarily nearest neighbors) for which we define  $\langle l_{12} \rangle \equiv \langle l_1 + l_2 \rangle / 2$ . The interactions of each dipole in a pair with all other more distant dipoles are described in the framework of the random local field theory outlined above. The dynamics of pairs is described in the framework of a Glauber model, neglecting the small probabilities for the simultaneous reorientation of both dipoles in a pair. Therefore, the reorientation of a pair is assumed to take place in two steps, through an intermediate excited level, as shown in Fig. 2. The reorientation frequency of a pair of neighboring dipoles is thus given by

$$\tau^{-1} = \nu_0 e^{-U_{dd}/T}, \quad (5)$$

where  $\nu_0$  is the reorientation frequency of a single dipole, experimentally shown to follow an Arrhenius law [12]:  $\nu_0 = \tau_0^{-1} e^{-U_d/T}$  and  $U_{dd} = 2K(r_{12})$ . The central dynamical equation is then written as

$$\frac{\partial \langle l_{12}(t) \rangle}{\partial t} = \frac{1}{\tau} [\langle l_{12}(t) \rangle - \langle l_{12} \rangle_{E+e}^{\text{eq}}], \quad (6)$$

where  $\langle l_{12} \rangle_{E+e}^{\text{eq}}$  is the quasiequilibrium orientation of the pair in the field,  $E + e$ . The next step is to average Eq. (6) over the distribution of random internal fields and over the distribution of potential barriers,  $U_{dd}$ . To do this, we rewrite it in integral form and consider only the steady state regime in an oscillating external field,  $e(t) = e_0 \cos \omega t$ :

$$L(t) = \langle \overline{l_{12}(t)} \rangle = - \int_0^t \frac{\partial Q(t')}{\partial t'} L_{12}^{\text{eq}}(t - t') dt'. \quad (7)$$

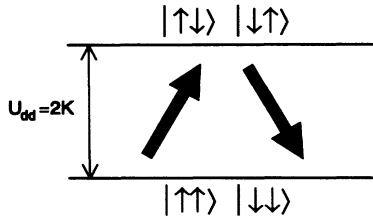


FIG. 2. Energy level diagram of a dipole pair showing the interaction energy,  $U_{dd}$  [see Eq. (5)].

where

$$Q(t) \equiv \overline{e^{-t/\tau}} \approx n \int_{T \ln(t/\tau)}^{\infty} dU_{dd} \int d^3r \delta(U_{dd} - 2K(r)) e^{-4\pi n r^3/3} \quad (8)$$

and

$$L_{12}^{eq}(t - t') = \int_{-\infty}^{+\infty} dE f\{E + e(t - t') - E_0 L(t - t')\} \overline{\langle l_{12} \rangle_E^{eq}} \quad (9)$$

with  $f$  being Gaussian according to Eq. (4). It is important to note that the configurational average in  $Q(t)$  is taken over the relaxation function and not just over the relaxation time. Consequently, the average relaxation function  $Q(t)$  is not exponential and gives rise to the slow dynamics observed. Taking the Fourier transform of Eq. (7) in the limit  $e_0 \rightarrow 0$ , we obtain the susceptibility  $\chi(\omega)$  and the dielectric constant  $\varepsilon(\omega)$ :

$$\chi(\omega) = \frac{\partial L(\omega)}{\partial e_0}, \quad \varepsilon(\omega) = \varepsilon_0 + 4\pi n d^{*2} \chi(\omega). \quad (10)$$

The polarization  $P(\omega, e_0)$  can also be obtained from Eq. (5), since

$$P(\omega, e_0) = n d^* L(\omega, e_0). \quad (11)$$

In the following, the nonlinear response  $L(\omega, e_0)$  has been obtained by numerical integration of the self-consistent Eq. (7).

We note that the model strictly contains only one independent parameter,  $d^*$ . The other parameter, the ratio  $E_0/\delta \equiv z$ , can be calculated from within the model simply using the experimentally determined critical concentration,  $x_{cr} = 2.2\%$  [23]. This calculation yields the same value as that obtained from the fit below. The values for  $\tau_0 = 1.6 \times 10^{-13}$  s and  $U_d = 910$  K have been taken from previous studies [12]. In Fig. 3 we compare the experimental dielectric constant of KLT ( $x = 3.5\%$  Li), measured at three different frequencies, with the calculated dielectric constant obtained from Eqs. (5)–(7) with  $d^* = 8e \text{ \AA}$  and  $z = 1.4$ . The agreement is seen to be very good with regards to the positions and the increase in height of the peaks. The shapes of the three peaks also agree well on the high temperature side. The model predicts a transition at  $T_c = 47$  K, in very good agreement with the observed  $T_c$ .

The model also predicts the existence of hysteresis loops for the polarization in the same temperature range as the dielectric relaxation. Calculated and measured hys-

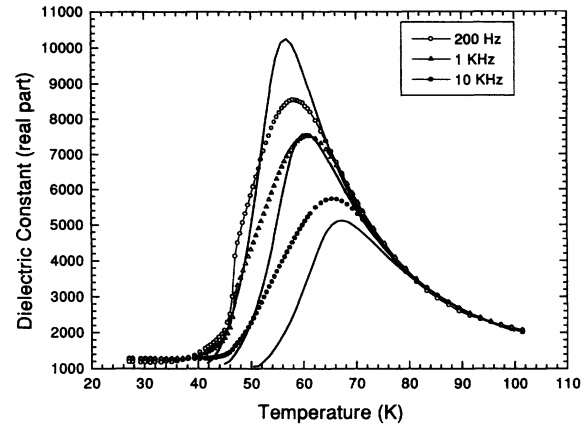


FIG. 3. Experimental (points) and calculated (solid line) dielectric constant of KLT ( $x = 3.5\%$ ) for three different frequencies.

teresis loops for two frequencies are compared in Fig. 4. The calculated loops are obtained from Eq. (11), using the same values of the parameters as those given above for the dielectric constant. Of particular significance is the frequency dependence of these loops at zero field. The polarization observed at zero field is clearly not a spontaneous polarization in the usual sense, but it is only remnant because of the slow relaxation of interacting dipoles. When cycled at a lower frequency, the dipole pairs are given enough time to thermally disorder, and the remnant polarization decreases accordingly, while at the higher frequency more polarization is retained when the field goes through zero. The weaker frequency dependence obtained in the calculated loops is tentatively attributed to the presence of a small fraction of nearest-neighbor Li dipoles, not included in the calculation, with an extremely long relaxation time [17,24]. Similar hysteresis loops are obtained

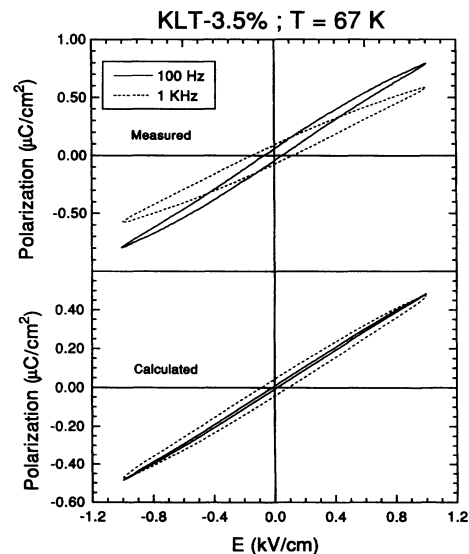


FIG. 4. Measured and calculated hysteresis loops of the polarization in KLT ( $x = 3.5\%$ ) for two different frequencies at  $T = 67$  K.

in PMN, also in the dielectric relaxation range and with a similar frequency dependence, again supporting the common relaxor character of both KLT and PMN.

We now comment on the discrepancy between the measured and calculated relaxation peak, close to the transition. The model, in its present form, predicts a second-order phase transition, while it has been conclusively shown by different experiments [17,25,26] to be first order. This limitation of the model could be possibly eliminated by taking into account the elastic quadrupole moment of the off-center ions. In fact, it has been shown previously [27], in the mean field approximation, that the existence of the quadrupolar moment of the off-center ions induces additional electrostriction, leading to a first-order transition rather than a second-order one. Nevertheless, the good agreement between experiment and theory, for both the positions and the heights of the peaks at different frequencies, supports the present physical model as a basis of relaxor behavior. In this model the relaxor behavior is due to strong pairwise interactions between random off-center ions in a highly polarizable host lattice.

The final question to be answered is: Why do some relaxors eventually undergo a phase transition and others do not? The answer can be found in the value of the ratio  $E_0/\delta$ , i.e., in the strength of the ferroelectric interaction between dipoles relative to that due to extra random fields. As we have already discussed, there exists a critical ratio,  $z(x_{cr}) = (E_0/\delta)_{x_{cr}}$ , below which no transition occurs. As shown in the dielectric constant of Ref. [17], no drop in the dielectric constant of KLT is observed in a crystal with  $x = 1.5\%$  Li. KLT then behaves much like PMN or PST with Pb vacancies. On the other side, for  $x > x_{cr}$  (2.2% Li), KLT exhibits both the relaxor behavior as well as a transition and behaves like stoichiometric disordered PST. While it appears possible to explain the presence or absence of a phase transition in relaxors on the basis of a single ratio  $E_0/\delta$ , the extra random fields determining  $\delta$  may have different physical origins. In KLT, we have suggested that they may be related to the elastic quadrupole moments of the off-center ions and their associated strains. These may also be present in PST and PMN. In addition, an obvious candidate in PST are the Pb vacancies. In PMN, 1 to 1 Mg-Nb ordered regions of average radius, 30 Å, are present and charged [8], also contributing random electrostatic fields.

In conclusion, KLT exhibits the characteristic dynamical behavior of a relaxor. This behavior is well described by a model based on indirect dipolar interactions between randomly distributed off-center ions, mediated by a highly polarizable lattice. However, a quantitative description of the experimental results necessitates the assumption, in addition to the random dipolar fields, of extra random fields which may have different origins in different relaxors. The width  $\delta$  of the distribution of these extra random fields, relative  $E_0$ , determines whether or not a phase transition can take place. The transition in relaxors does not correspond to the maximum of the di-

electric constant and it is not diffuse, but it is clearly identifiable as a distinct frequency independent feature in the various susceptibilities.

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