Off-center lithium ions in KTaO$_3$

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We present a polarizable point-charge model for the KTaO$_3$ lattice that permits the calculation of the off-center displacement d of Li ions that substitute for K. We find $d = 1.35$ Å in good agreement with a value $d = 1.26$ Å derived from NMR measurements. The permanent dipole created by the off-center Li ion is found to be screened by the dipoles induced in the lattice: The "screening volume" is strongly anisotropic, reminiscent of the correlation volume for polarization fluctuations. The dielectric susceptibility of the Li-dipole system is considerably enhanced by local-field effects.

I. INTRODUCTION

Potassium tantalate is a cubic perovskite that shows incipient ferroelectricity: Its dielectric behavior closely resembles that of a ferroelectric with a Curie temperature at or below 0 K. Substituting Li or Na for K, or Nb for Ta, results in mixed crystals that show marked polar behavior in the temperature region around 50 K (for low levels of substitution, typically less than 10%). While for KTaO$_3$:Nb (Ref. 1) the generally accepted view is that the system becomes truly ferroelectric, the situation in KTaO$_3$:Na (Ref. 2) and KTaO$_3$:Li (Ref. 3) seems to be more complicated. In this paper we develop a polarizable point-charge model for the latter system to describe some of its properties at low dopant levels.

Experimentally, it has been found[3] that the substitutional Li ions go off center in $\langle 100 \rangle$ directions with respect to the K site, thus creating a local electric dipole. As Matthew[4] has pointed out, the energy balance between electrostatic point-charge interaction, core repulsion, and polarization energies may favor such an arrangement for small-size substitutional ions such as Li. Probably the simplest and most extensively studied example of such a system is KCl:Li.[5,6]

An important difference between the KCl and the KTaO$_3$ host lattices is the high dielectric constant of the latter. To reflect this property in our model we will follow Slater's description of BaTiO$_3$,[7] assigning an additional point dipolar polarizability to the Ta ions to reflect the effect of the soft mode on the *static* dielectric properties of KTaO$_3$. Although none of the ionic polarizabilities so introduced is considerably higher than that of Cl$^-$ in KCl, the lack of cubic symmetry around the oxygen ions leads to a much higher dielectric constant. As a consequence, the gain in polarization energy by off-center displacement of Li will be more important in KTaO$_3$:Li than in KCl:Li. The off-center well is deeper, so that thermally-activated hopping between equivalent orientations is expected, rather than tunneling as in KCl:Li.

The organization of the rest of this paper is as follows. In Sec. II we describe the model used in our calculations of the off-center position of Li and Na in KTaO$_3$, together with the values of the atomic constants used. In Sec. III we give the numerical results for these displacements, and compare them to experimental results from ^{7}Li and ^{23}Na NMR. Section IV discusses the calculated values for the dipole moments induced in the KTaO$_3$ lattice by the off-center ions, and their relation to the experimentally found remanent polarization in field-cooled samples. Section V contains a qualitative discussion of Li-Li interaction, and an expression for the "enhancement factor" found in the dielectric susceptibility of a dilute Li system in KTaO$_3$. A brief summary of the results is in Sec. VI.

II. DESCRIPTION OF THE MODEL

The electric properties of the ions on the KTaO$_3$ lattice are represented as those of point-polarizable point charges. All ions are assumed to be fixed at their ideal positions, except for a single Li ion replacing for K at the origin. It is allowed to move along a $\langle 100 \rangle$ direction, thereby changing both the Coulomb energy E_C of the system of point charges and the polarization energy E_p (the energy of the system of induced dipoles). The gain in electrostatic energy that occurs when the Li ion goes off center, is finally balanced by the repulsion from core overlap with the nearest-neighbor oxygens. The repulsive energy is described by the Born-Mayer potential:

$$E_R = b \exp(-r/\rho) . \qquad (1)$$

Since the O^{2-} ion has the same core as the F$^-$ ion, we will use parameters obtained by fitting alkali-halide data:[8]

$$b_{\text{Li-O}} = 80.57 ,$$

$$b_{\text{Na-O}} = 244.5 ,$$

$$\rho = 0.3333 ,$$

with $b_{\text{Li-O}}$ and $b_{\text{Na-O}}$ in units of eV, and ρ in units of Å. To calculate the Coulomb energy of the system of point charges E_C, we attributed to them the charges of the corresponding ions: $+e$ for K, $-2e$ for O, and $+5e$ for Ta. The lattice parameter used throughout was 3.9884 Å.

Whereas the calculation of E_C and E_R is relatively straightforward, the determination of E_p is somewhat more delicate. It is (in the polarizable point-dipole ap-

proximation) given by

$$E_p = -\frac{1}{2}\sum_i \alpha_i \vec{E}_i^2 , \tag{2}$$

where the index i runs over all the ions in the lattice, α is the polarizability, and $\vec{E}_i$ the local electric field acting at site i. Let us first discuss our choice for the α_i. Virtually all of the (incipient) ferroelectric perovskites are oxides, which suggests that the properties of the oxygen ion are of decisive importance. The special role attributed to the oxygen ions in lattice-dynamical calculations on $KTaO_3$ (Ref. 9) shows up at a more phenomenological level as an anisotropic polarizability: The oxygen is more strongly polarizable along a Ta—O—Ta direction than in the plane perpendicular to the latter. The values for $\alpha_{O,||}$ and $\alpha_{O,\perp}$ that result from the parameter values in the model of Migoni et al.[9] are given in Eq. (9) below. The potassium ions perform no special function for the polar behavior, and we have taken a commonly accepted literature value[10] for α_K, also given below.

To assign a polarizability to the tantalum ions we observe, following Slater[7] and other authors, that the optical dielectric constant ϵ_∞ for $KTaO_3$ has the value $(2.27)^2 = 5.15$, which is no larger than one would expect from the purely electronic polarizabilities α of its constituents.[10] This leads one to attribute the large value (and the temperature dependence) of the static dielectric constant ϵ_0 (Ref. 11) to an ionic (or displacement) polarization α'. From geometric arguments[7] this additional ionic polarization is attributed to the Ta ion; in our model we will describe α'_{Ta} also as a point polarizability of a dipole located at the ideal Ta position. Since we have already fixed our choice for the oxygen and the potassium polarizabilities, we must choose α_{Ta} and α'_{Ta} such that the total system of point dipoles has the optical and static dielectric constants of $KTaO_3$. This can be done by following Slater's calculation[7] for the Lorentz correction that we will briefly recall for convenience (in simpler cubic systems such as KCl the relation is given directly by the Clausius-Mosotti equation, but this is not the case for the more complicated perovskite structure).

Consider for simplicity a spherical specimen: The local field $\vec{E}_i$ at a certain site i is composed of the uniform applied field $\vec{E}_0$, the depolarization field $(4\pi/3)\vec{P}$, and the dipolar fields $\vec{E}_{ij}$ at site i due to all other dipoles μ_j in the system. Assuming the applied field to be along the z axis, the direction of the depolarization field and of the induced dipoles will also be the z axis, and

$$E_{ij} = \frac{3\cos^2\theta_{ij}-1}{r_{ij}^3}\mu_j . \tag{3}$$

The $KTaO_3$ lattice consists of five interlaced simple cubic lattices, denoted as K, Ta, O_I, O_{IIa}, and O_{IIb}. The O_I lattice is defined by Ta—O_I—Ta being along z (and therefore the polarizability of O_I is high) whereas O_{IIa} and O_{IIb}, with their Ta—O—Ta directions along x and y, are less polarizable. We have for the induced dipoles μ_i:

$$\frac{\mu_i}{\alpha_i} = E_i = E_0 + \frac{4\pi}{3}P + \sum_j E_{ij} . \tag{4}$$

Since the polarization on each of the five lattices will be uniform, we can consider in turn the cases where site i is the center of each of the five cubic lattices. The sum over j can be broken into five sums over each of the lattices:

$$\frac{\mu_i}{\alpha_i} = E_0 + \frac{4\pi}{3}\sum_{k=1}^5 P_k + \frac{1}{v}\sum_{k=1}^5 \mu_k C_{ik} , \tag{5}$$

where the P_k are the polarization of the individual lattices, and

$$C_{ik} = v\sum_{j\in k}\frac{3\cos^2\theta_{ij}-1}{r_{ij}^3} ,$$

where $j \in k$ is meant as a summation over all sites j belonging to lattice k. The unit-cell volume (identical for all five lattices) is denoted by v. We may write $\mu_j = vP_j$, and defining the partial susceptibilities X_j as

$$P_j = X_j E_0 , \tag{6}$$

we have finally a system of five equations

$$\sum_k \left[\frac{v}{\alpha_k}\delta_{ik} - \frac{4\pi}{3} - C_{ik}\right]X_k = 1 \tag{7}$$

that connects the polarizabilities α_k to the dielectric constant through

$$\epsilon - 1 = 4\pi\sum_k X_k . \tag{8}$$

Actually, the O_{IIa} and O_{IIb} lattices are equivalent, and the number of independent equations is four. The coefficients C_{ik} can be taken from Ref. 7 and are given in Table I. The set of polarizabilities so adopted is, in cgs units,

$$\alpha_K = 1.14\times 10^{-24} ,$$

$$\alpha_{Ta} = 0.70\times 10^{-24} ,$$

$$\alpha_{Ta} + \alpha'_{Ta} = 1.10\times 10^{-24} , \tag{9}$$

$$\alpha_{O,I} = \alpha_{O,||} = 2.44\times 10^{-24} ,$$

$$\alpha_{O,IIa} = \alpha_{O,IIb} = \alpha_{O,\perp} = 0.93\times 10^{-24}$$

(all in units of cm^3) where the indices $||$ and $\perp$ on the oxygen polarizabilities refer, respectively, to the Ta—O—Ta direction and directions perpendicular to it. Solving the system of five equations, Eq. (7), for the X_I and converting to the total dielectric constant ϵ, we obtain $\epsilon_0 = 204$ for the above choice of polarizabilities. We note that the optical dielectric constant ($\epsilon_\infty = 5.15$) results from the choice $\alpha_{Ta} = 0.7\times 10^{-24}$ cm^3, whereas spontaneous polarization occurs for $\alpha_{Ta} + \alpha'_{Ta} \approx 1.109\times 10^{-24}$ cm^3.

The local fields E_i in Eq. (2) contain important contri-

TABLE I. Dipole sums C_{ij} on the perovskite lattice, as used in Eqs. (7) and (13). In the system of four (rather then five) equations set $\alpha_{O_{IIa}+O_{IIb}} = \alpha_{O_{IIa}} + \alpha_{IIb}$.

	K	Ta	O_I	$O_{IIa+IIb}$
K	0	0	+8.668	−4.334
Ta	0	0	−30.080	+15.040
O_I	+8.668	−30.080	0	−4.334
$O_{IIa+IIb}$	−4.334	+15.040	−4.334	+4.334

butions from the induced-dipole—induced-dipole interactions, whose exact calculation amounts to solving an N-body problem. For simple cubic lattices reportedly efficient procedures using Fourier transforms[12,13] have been devised. Their application to the present problem does not seem straightforward, as we have to deal with five interwoven and interacting lattices. We have therefore adopted a self-consistent calculation in real space, considering only a restricted number of polarizable dipoles around the Li impurity. Initially $\vec{E}_i$, the polarizing field at site i, is taken to be that due to the displaced Li alone, and all resulting induced dipole moments in the volume considered are calculated. In the next cycle the fields of all dipoles so calculated are included in the polarizing fields, and the dipole moments are recalculated. This process is iterated until sufficient convergence is obtained for the polarization energy E_p.

The restriction in the considered volume results in a lower value for the total polarization energy. This error may be estimated from the difference between the values of *net* polarization induced on each of the five lattices in the restricted volume and those for an infinite lattice. The latter can easily be evaluated using a variant of Slater's calculation; we will come back to this question when discussing the results in Sec. IV.

III. THE OFF-CENTER DISPLACEMENT

For a number of assumed values of the off-center displacement d of the Li ion, restricted to be along a $\langle 100 \rangle$ direction, we calculated the Coulombic point-charge energy E_C, the Born-Mayer repulsive energy E_r between the Li and its neighboring oxygens, and the polarization energy E_p. The value of d where a minimum of the total energy occurs then indicates the equilibrium position.

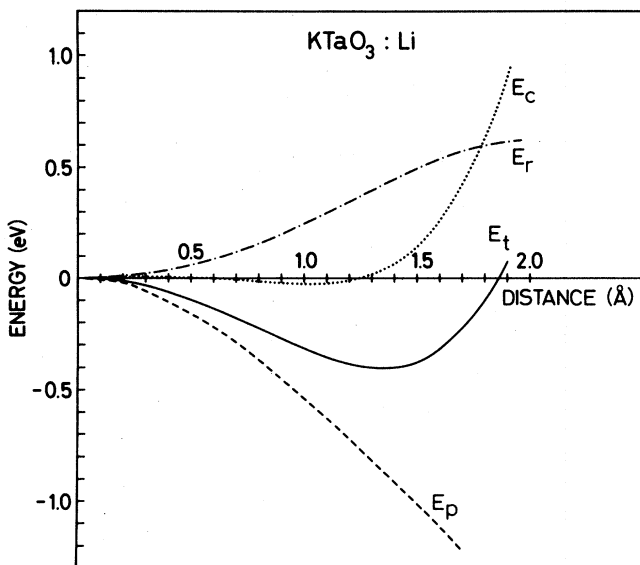The results shown in Fig. 1 have been obtained using

the parameters given in Sec. II. For the calculations of E_C, Evjen's method was used with a cluster comprising 37 659 charges. The values of E_p were obtained by the iterative scheme described in Sec. II, considering the 234 dipoles contained in a cube of $3 \times 3 \times 3$ unit cells around the Li ion. Iteration was stopped after convergence to two significant figures has been obtained.

The resulting value for the off-center displacement d is 1.35 Å, and the depth of the well is 0.4 eV. Experimentally it is known that the depth of the well along $\langle 100 \rangle$ must be more than 86 meV, since the ions reorient through 90° (rather than 180°) jumps over an 86-meV barrier.

The only quantitative experimental data so far concerning the amount of the displacement comes from ^{7}Li NMR measurements.[3] The ^{7}Li nucleus has a quadrupole moment eQ, and if it experiences an electric field gradient V_{zz}, a splitting of the magnetic resonance levels results, which on a frequency scale is given by

$$\nu_Q = |(1-\gamma_\infty)eQV_{zz}| \ . \tag{10}$$

In the case of ^{7}Li, $(1-\gamma_\infty)=0.74$ and $Q=0.042 \times 10^{-24}$ cm^2.

In a cubic environment V_{zz} vanishes, and the quadrupole splitting frequency is zero. For small displacements d along the cubic axes, V_{zz} can be developed in a power series in d/a, where a is the lattice constant. For the KTaO$_3$ lattice and d measured with respect to the K site, we find the first terms to be given by

$$V_{zz} = \frac{e}{a^3} \left[-80.39 \left[\frac{d}{a} \right]^2 + 7936 \left[\frac{d}{a} \right]^4 - \cdots \right] \ . \tag{11}$$

The coefficients have been calculated by summing expres-

FIG. 1. Total energy E_t in KTaO$_3$:Li, consisting of Coulombic point-charge energy E_C, polarization energy E_p, and repulsion energy E_r, as a function of Li displacement d along $\langle 100 \rangle$. A minimum occurs around $d = 1.35$ Å.

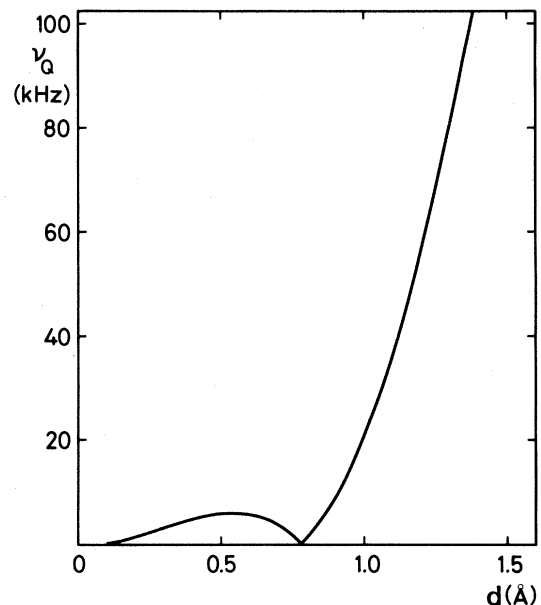
FIG. 2. Quadrupole frequency ν_Q, as given by Eq. (10), at the Li site, as a function of displacement d. Only the point charges on an ideal KTaO$_3$ lattice have been considered as a source of the field gradient, except for a lacking potassium at the origin. The experimental value (see Ref. 3) of $\nu_Q = 70$ kHz corresponds to $d = 1.26$ Å.
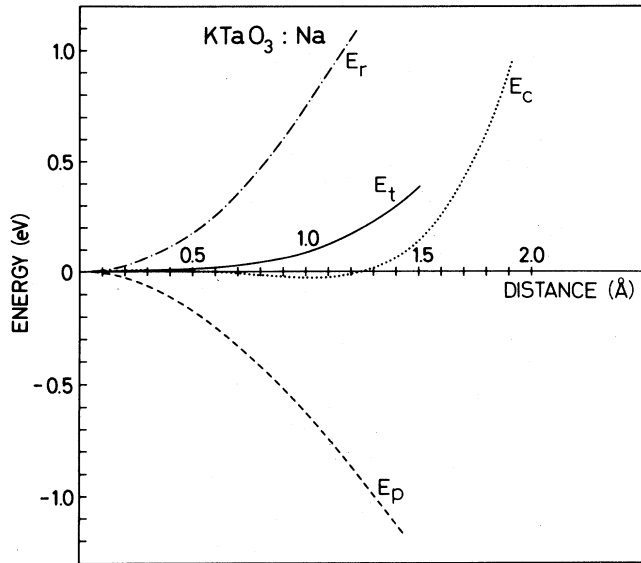
FIG. 3. Total energy E_t in KTaO$_3$:Na. Labeling of the curves as in Fig. 1. Owing to the more important repulsion energy, no Na displacement comparable to that of Li is predicted.

FIG. 4. The five cubic lattices in KTaO$_3$. Without applied electric field and without Li doping the three oxygen lattices are equivalent. If a field is applied along a cubic axis, or if a Li dipole is present, the O$_{IIa}$ and O$_{IIb}$ lattices still are equivalent, but the O$_I$ lattice has different dielectric properties, due to the anisotropic oxygen polarizability [see Eq. (9)].

sions of the type P_{2n}/r^{2n+1}, where P_n is the nth Legendre polynomial, over the five cubic lattices in KTaO$_3$, for a system containing $41\times41\times41$ unit cells. This result is slightly different from Eq. (2) of Ref. 3, where only a summation over nearest neighbors was used.

For $d/a > 0.1$, convergence of the series is slow, and we have therefore calculated directly the field gradient at the displaced Li site due to the 37 659 nearest point charges. The results, in terms of ν_Q, are shown in Fig. 2. (The induced dipoles turn out to give a negligible contribution to V_{zz}; see Sec. IV.) Experimentally,[3] $\nu_Q = 70\pm3$ kHz, from which it may be decided, under the assumption that no important deformation of the lattice occurs, that

$$d = 1.26\pm0.02 ,$$

in units of Å. The agreement between our theoretical calculation of 1.35 Å, and the "semi-experimental" value of 1.26 Å is very satisfactory, given the uncertainties in the parameter values.

Let us now turn briefly to the case of KTaO$_3$:Na. In the energy balance between E_C, E_r, and E_p the only essential difference between the cases of Na and Li is in the Born-Mayer parameter b [see Eq. (1)]. The results are given in Fig. 3. The repulsive term is so much more important for Na than for Li, that no displacement on a comparable scale is predicted, and indeed no indications for such a displacement are found in NMR.[2]

IV. THE INDUCED DIPOLE MOMENT

Whereas the calculation of the polarization energy necessitates a knowledge of both the longitudinal (parallel to the Li displacement) and the transversal components of the dipole induced at each lattice site, rendering the problem a difficult one, it is easier to calculate the total induced dipole moment on each of the lattices. By symme-
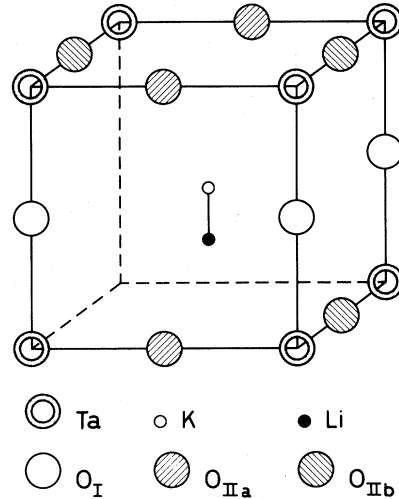
try the net transversal components are zero, and in calculating the longitudinal component E_i of the field at site i we only need to consider the longitudinal components of all other induced dipoles μ_j

$$E_i = \frac{\mu_i}{\alpha_i} = \sum_{j\,(\neq i)} \frac{3\cos^2\theta_{ij}-1}{r_{ij}^3}\mu_j + E_i(ed) ,   (12)$$

where $E_i(ed)$ is the z component of the field at site i due to the (nonideal) dipole ed resulting from the Li displacement along the z axis.

Now we sum over all sites i belonging to each lattice as defined in Fig. 4; denoting the lattices by capital indices we have

$$\frac{\mu_I}{\alpha_I} = \frac{1}{v}\sum_{J\,(\neq I)} C_{IJ}\mu_J + E_I ,   (13)$$

where now the coefficients C_{IJ} do depend on the relative positions of the lattices I and J but not explicitly on the sites i and j. Similarly, of course, $E_I = \sum_i E_i(ed)$ depends only on the position of lattice I with respect to the dipole ed.

The lattice sums C_{IJ} (that are actually the same as those used in Slater's model; see Table I) and E_I were calculated in direct space for a lattice of $41\times41\times41$ unit cells with the Li ion at its center, and the system of Eq. (13) was solved for the μ_I in terms of the Li dipole ed. The results for $d = 1.35$ Å are given in Table II. The total induced moment is

$$\mu/e = -1.44$$

(in units of Å), where the negative sign implies a screening of the Li dipole. We find a total dipole moment associated with the Li of

$$\mu/e + d = -0.09 ,$$

TABLE II. Top: calculated induced dipole moments μ/e on lattices of different sizes. Li displacement is 1.35 Å. Bottom line: calculated polarization energies for the $3\times3\times3$ and $5\times5\times5$ lattices, from which the value for the $41\times41\times41$ lattice has been extrapolated.

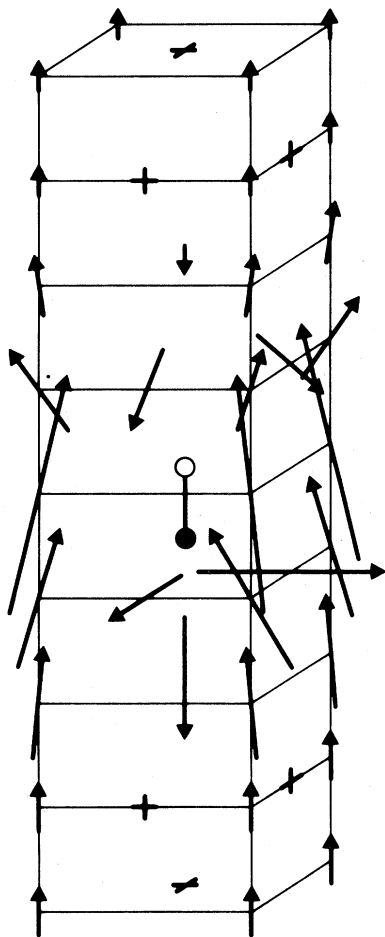|	$3\times3\times3$	$5\times5\times5$	$41\times41\times41$	Units
K	+0.094	+0.12	+0.22	Å
Ta	−0.56	−0.61	−0.69	Å
O$_I$	−0.90	−0.99	−1.14	Å
O$_{II}$	+0.13	+0.14	+0.16	Å
Total	−1.23	−1.34	−1.44	Å
E_p	−0.87	−1.20	−1.29[a]	eV

[a]Extrapolated from Eq. (14).

FIG. 5. Induced dipoles in the KTaO$_3$ lattice. Length and direction of the arrows indicate the induced moments at each site. Crosses indicate that the induced moment is too small to be represented on the scale of the drawing. Represented is a stack of eight half unit cells along the direction of the Li displacement. The two half unit cells in the center have the configuration shown in Fig. 4. The four corner chains are alternating O$_I$−Ta−O$_I$ ions. The chains in the faces are O$_{II}$ ions, and the chain in the center consists of K ions, with the middle one (indicated by an open circle) replaced by a Li ion (the solid circle).

in units of Å. It should be noted that, to the approximation that the dipole ed be considered as ideal, μ will be linearly proportional to ed, and the negative sign of the proportionality constant is due only to the geometry of the KTaO$_3$ lattice and to the choice $\alpha_O > \alpha_{Ta}$, but not to the actual values adopted for the polarizabilities. This can be understood by considering the Li dipole as a permanent point dipole at an exact K site. The directly induced dipoles at nearest-neighbor Ta are zero, since $3\cos^2\theta - 1$ vanishes. The directly induced dipoles at nearest-neighbor O$_I$ are negative, and these induce then a negative dipole on the Ta. The buildup of these O$_I$−Ta−O$_I$ polarized chains leads to screening. (If, for the sake of argument, we were to consider a permanent point dipole at a Ta site, the same line of reasoning predicts an enhancement of the permanent dipole by the surrounding lattice.)

How these polarized chains are distributed around the Li dipole is approximately shown in Fig. 5. This represents 56 induced dipoles out of 880 on a cube of $5\times5\times5$ unit cells that were calculated by the method outlined in Sec. II. The four nearest-neighbor O$_I$−Ti−O$_I$ chains bear 96% of the total polarization on the twenty-four such chains considered in the calculation. The nearest- and next-nearest-neighbor chains of K and of O$_{II}$ ion contain 97% of the K and 96% of the O$_{II}$ polarization. On the $5\times5\times5$ cube, therefore, 96% of the induced moments are contained in a $2\times2\times5$ unit-cell volume.

The shape anisotropy of this volume clearly has the same origin as that of the correlation volume:[14] Correlations along the (incipient) polar axis are stronger than those perpendicular to it. The volume discussed here might more appropriately be called a "screening volume," since the total (permanent-plus-induced) dipole moment it contains is close to zero. In a more quantitative way, the screening effect is shown in Table III. It lists the total dipole moment in each of the 121 chains running parallel to the Li displacement. Their rapid decrease with distance from the center is obvious.

This model thus implies that the large values for the remanent polarization in field-cooled samples of KTaO$_3$:Li (Refs. 3 and 15) cannot be explained in purely electrostatic terms as the alignment by the field of the Li dipoles and their surrounding cloud of induced moments. We therefore speculate that the remanent polarization is the result of a field-induced phase transition of some kind. To support this assertion we show in Fig. 6 the experimental relation between P_0, the field-cooled remanent polarization extrapolated to 0 K, and the temperature T_g at which the zero-field birefringence appears in the same samples, according to data in Ref. 3. This plot does not require a determination of the Li concentration. The linear relation between T_g and P_0 strongly suggests that the latter is not a "single-particle" property, even for low P_0. It is interesting to note that a linear proportionality between the Curie temperature T_c and the saturation polarization at zero temperature is predicted both by simple Weiss mean-field theory and by the theory of quantum ferroelectricity,[16] but that the predicted variation with concentration is different. The failure to observe[3] a T_g for the sample with the lowest P_0 may be related to the fact that around the temperatures where T_g is expected, the

TABLE III. Projection onto the x-y plane of the total dipole moments induced on chains of ions along the z axis. At (0,0) is a Li ion displaced over $d = 1.35$ Å in the z direction. Results are for the $5 \times 5 \times 5$ unit-cell lattice. The lattice parameter is denoted by a. Upper left-hand part shows the alternation of ionic chains (cf. Figs. 4 and 5) and the lower right-hand part is the polarization in the chain, expressed as percent of the total dipole moment induced on *all* of the corresponding chains (cf. Table II). Values are shown for 21 chains. Those for the other 100 chains follow from symmetry: reflections through the diagonal, through the left-hand column, and through the bottom row. It is seen that by far the largest part of the induced dipole moments sites on the chains near the origin.

	0	$\pm\frac{1}{2}a$	$\pm a$	$\pm\frac{3}{2}a$	$\pm 2a$	$\pm\frac{5}{2}a$
$\pm\frac{5}{2}a$	O_{II}	TaO_I	O_{II}	TaO_I	O_{II}	-0.04
$\pm 2a$	K	O_{II}	K	O_{II}	0.05	0.01
$\pm\frac{3}{2}a$	O_{II}	TaO_I	O_{II}	0.18	0.16	-0.08
$\pm a$	K	O_{II}	1.8	0.21	0.17	0.02
$\pm\frac{1}{2}a$	O_{II}	24	-2.1	0.31	-0.01	-0.19
0	68	28	5.3	0.06	0.39	0.13

motion of the Li ions is so extremely slow (see Fig. 11 of Ref. 3) that the transition does not occur in experimental times.

To conclude this section, we consider the effect of a number of approximations made so far. First, we have calculated the contribution to the electric field gradient at the Li site due to the induced dipoles on the $5 \times 5 \times 5$ lattice, and found it negligible. Next we consider what Ta displacement corresponds to the "displacement polarizability" α'_{Ta} for the Ta ions nearest to the Li in Fig. 5.

FIG. 6. Experimental relation between the field-cooled remanent polarization at 0 K, P_0, and the temperature T_g where zero-field birefringence appears in the same samples. Data from Ref. 3. The linear relationship suggests that P_0 is not a "single-particle" property, arising simply from the alignment of Li dipoles by the applied field. The leftmost point represents a sample for which a nonzero P_0 has been found, but no zero-field birefringence above 10 K. This might be related to the effective freezing of the Li dipoles at such low temperatures.

With our choice of the parameters (Sec. II) $\alpha'_{Ta} = 0.4 \times 10^{-24}$ cm^3 and the biggest Ta displacement needed is 0.005 Å. This is a very reasonable value for ferroelectric perovskites.

The net induced dipole moment is a function of the atomic polarizabilities rather than of the dielectric constant: Taking $\alpha_{Ta} + \alpha'_{Ta} = 1.108 \times 10^{-24}$ cm^3 raises ϵ_0 [see Eq. (8)] to over 160 000, but does not perceptibly alter the results in Table II. Finally, we will try to estimate the error in the polarization energy E_p due to the finite volume considered in its calculation. The net induced moments found on the $41 \times 41 \times 41$, the $5 \times 5 \times 5$, and the $3 \times 3 \times 3$ lattices are given in Table II, together with the polarization energies for the two latter cases. An increase of size increases both the total induced moment and the polarization energy, as is to be expected. To estimate the error in the polarization energy E_p due to the volume truncation, we make the crude assumption that E_p increases with the square of the total moment for the sizes N considered:

$$E_{p,\infty} = E_{p,N} + c\,(\mu_\infty - \mu_N)^2 . \tag{14}$$

Then, from our results for the $3 \times 3 \times 3$ and $5 \times 5 \times 5$ cubes, we have

$$E_{p,\infty} = -1.29 ,$$

in units of eV. From this estimate we expect the actual E_p values around the off-center position to be larger than those used in plotting Fig. 2. Still, if the actual E_p values vary with d in a similar linear way (for $d > 1.0$ Å) as do those for the $3 \times 3 \times 3$ volume used in Fig. 2, the position of the off-center minimum at $d \approx 1.35$ Å will not be affected much. We have calculated the difference $E_{p,\infty} - E_{p,3}$ at $d = 1.20$ Å as well, and find nearly the same values as at $d = 1.35$ Å. It is therefore very likely that the actual minimum is around 0.8 eV deep, and situated at approximately $d = 1.35$ Å. Note however that this reasoning only estimates the effect of the "volume truncation" on the results, and that choices of parameters, especially b and ρ, other than those in Sec. II would certainly give somewhat different values.
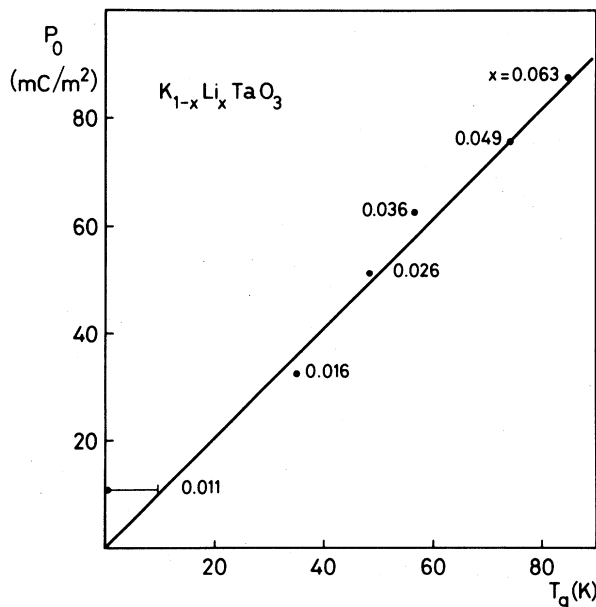
TABLE IV. Local fields at potassium sites in the z-x plane. The z axis runs from bottom to top, the x axis from left to right. Scale such that μ_K/α_K in Eq. (13) has the value 100. Note that the sign change is approximately that of a field due to a point dipole in (0,0). Other data as in Table III.

Sites	$-2a$	$-a$	0	$+a$	$+2a$
$+2a$	$+0.40$	$+1.3$	$+2.1$	$+1.3$	$+0.40$
$+a$	-0.17	$+5.7$	$+52$	$+5.7$	-0.17
0	-0.03	-6.1		-6.1	-0.03
$-a$	-0.16	$+3.6$	$+13.7$	$+3.6$	-0.16
$-2a$	$+0.39$	$+0.7$	$+0.62$	$+0.7$	$+0.39$

V. INTERACTIONS IN DILUTE SYSTEMS

To discuss now the interaction between *two* Li dipoles in such a polarizable lattice, the best way no doubt would be to calculate all local fields in an infinite lattice containing two off-center Li dipoles in various relative positions and orientations and to find the energetically lowest orientation. This clearly is a formidable problem and we have not attempted to attack it. But from Fig. 5 and other results on the 5×5×5 lattice, a number of conjectures may be made. For that purpose we give in Tables IV and V the local fields at the K sites (that are of course proportional to the induced dipoles) in a (100) plane that contains the direction of the Li displacement and in a plane perpendicular to it. To the lowest order of approximation, these local fields would be felt by a second Li dipole put at a potassium site, thus determining its relative orientation. It is seen that the signs of the local field are essentially those of dipole-dipole coupling: positive on the axis of the Li dipole, negative in the plane perpendicular to it, and going once through zero for some intermediate situation. The magnitudes may be different from those for a regular dipole field, especially near the Li site. We will refer to this field as a "modified dipole field." Our conjectures now are the following. (i) If the second Li sits on any of the nearest-neighbor K sites, a parallel alignment will be favored, since this lowers the polarization energy on the strongest polarized O_I-Ta-O_I chains. This probably overcomes the effect of polarization energy elsewhere in the lattice; and the local fields at the K sites themselves are either very small or of such sign as to favor this alignment. (ii) For larger separations the modified dipole-dipole coupling will be important. (iii) For large distances (but perhaps larger on the same axis than on the same plane) the screening of the Li dipoles by their nearest-neighbor oxygen and tantalum ions will considerably

TABLE V. Local fields at potassium sites in the x-y plane. At (0,0) is a lithium displaced over $d = 1.35$ Å in the $+z$ direction. Scale and other data as in Table IV.

Sites	0	$\pm a$	$\pm 2a$
$\pm 2a$	-0.03	-0.65	-0.57
$\pm a$	-6.1	-0.50	-0.65
0		-6.1	-0.03

reduce the coupling.

These three regions of Li concentration may give rise to different polar behavior. For low concentrations, lower than somewhere between $(\frac{1}{5})^3$ and $(\frac{1}{3})^3$ (the reciprocals of the volumes that we considered here), we will find a system of noninteracting permanent dipoles, to be discussed in the remainder of this section. At high concentration, let us say above $\frac{1}{6}$, where many nearest-neighbor pairs occur, a ferroelectric behavior, perhaps of percolation character, can be expected. In the intermediate range (if it exists) we might find a system of randomly ordered interacting dipoles, whose low-temperature phase might be a dipole glass.

The dielectric susceptibility of a very dilute system of dipoles can be calculated from Langevin's formula. That essentially is an *energy* consideration: Which orientation of the Li dipole is the lowest in energy in an applied external field? Neglecting for simplicity possible saturation problems on the nearest-neighbors Ta and O, there will be no contribution to energy differences from the moment induced in the lattice by the Li dipole under consideration. The dipole moment to be used in the formula therefore is the bare Li dipole ed. The assumption of noninteracting Li dipoles implies that there is no contribution to the local field E_l from other Li dipoles, and therefore the E_l that enters Langevin's equation is that occurring on the K sites in pure KaTO₃ (to the approximation that the Li dipole is treated as a point dipole at the K site). The resulting susceptibility is [using Eqs. (4) and (6) for E_l]:

$$\chi_{Li}=N_{Li}\frac{(ed)^2}{3kT}\frac{\chi_K}{\alpha_K/v}=x\frac{(ed)^2}{3kT}\frac{\chi_K}{\alpha_K}, \tag{15}$$

which shows that, through the Lorentz corrections, the susceptibility of the Li system is enhanced by the factor $\chi_K v/\alpha_K$.

For a cubic lattice such as KCl the enhancement factor can be derived from the Clausius-Mosottti relation:

$$\chi_K v/\alpha_K=(1-4\pi\alpha_K/3v)^{-1}, \tag{16}$$

which is (taking v as in KTaO₃) equal to 1.08.

From the numerical solution of Eqs. (7) and (8) we find that there is an approximately linear relation between χ_K and ϵ in our model for KTaO₃:

$$\chi_K v/\alpha_K=\epsilon/13.2 . \tag{17}$$

For temperatures around 50 K, the value of $\epsilon/13.2$ for pure KTaO₃ is approximately 100. Otherwise stated, if the susceptibility of the Li system were described by a simple Langevin equation with an "effective dipole" ed', the value of d' would be approximately 13 Å.

VI. SUMMARY

The off-center displacement of Li ions in KTaO₃ can be understood from a balance between Coulomb energy, polarization energy, and nearest-neighbor core repulsion. The parameters of these interactions have all been chosen on the basis of earlier theoretical and experimental work. Our method of calculating the polarization energy is only approximate, but there are reasons to believe that our re-

sult for the value of the displacement, $d = 1.35$ Å, is not much affected by this approximation. If it is assumed that the experimental value[3] of the quadrupolar splitting in ^{7}Li NMR is only slightly or not at all determined by lattice deformations, we find this splitting to correspond to $d = 1.26$ Å. The agreement is very satisfactory.

From the geometry of the $KTaO_3$ lattice, and the resulting dipole-dipole coupling, we find that the dipole created by the off-center Li ion is nearly completely screened by the induced dipole moments in the host lattice. An approximate calculation shows the shape anisotropy of the "screening volume": It is found to be some $2 \times 2 \times 5$ unit cells, but it seems likely that the longer dimension is underestimated by the fact that the total volume considered was only $5 \times 5 \times 5$ unit cells, containing 880 point dipoles.

We have also shown that in a very dilute system of Li dipoles, when no interaction between them occurs, the geometry of the $KTaO_3$ lattice enhances the local field acting on the Li dipole. The apparent value of the Li dipole, taken as a simple Langevin system, is about 10 times its real value, corresponding to an apparent displacement $d' \approx 13$ Å. It has been reported[17] that the d', derived from dielectric experiments, is $d' \approx 19$ Å.

On the other hand, the apparent $d' \approx 10$ Å derived from experiments on remanent polarization in field-cooled samples[15] cannot be understood in the framework of simple electrostatics: Our result, assuming no interaction between the Li dipoles, is that the net (Li displacement plus induced in the lattice) dipole moment is close to zero. A possible explanation would be that the presence of the field triggers a transition in the underlying lattice.

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