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[5] We note that two-dimensional systems are expected to have long-range order once an anisotropic term of sufficient size is present, in addition to the Heisenberg term, in the Hamiltonian. Such terms are almost inevitably present in real two-dimensional systems for there will exist spin dipolar forces which do not cancel out (because of the two-dimensional character of the lattice). These terms will generally be large enough to have this effect.

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Intercell Corrections for Ionic Motion in Displacement Ferroelectrics

M. E. Lines
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

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A set of microscopic parameters determined for $LiTaO_3$ in an earlier paper by comparing dielectric properties with the results of a statistical calculation are analyzed in terms of a point-charge-plus-electronic-polarizability model for the system. The results indicate the existence of very strong intercell correlations for ionic motion to temperatures considerably in excess of the Curie point T_C. These correlations are weak functions of temperatures to the extent that they do not produce deviations from effective-field (e.g., Curie-Weiss) behavior near T_C. Neglect of correlation effects leads to many inconsistencies and indicates that the use of random-phase Lorentz fields in statistical theories for displacement ferroelectrics is qualitatively unsound. Spontaneous polarization for $LiTaO_3$ is found to be 45% ionic, 55% electronic; the tantalum-oxygen bond is very markedly covalent, with estimated ionic charges of +0.8 and −0.6 electronic units, respectively.

I. INTRODUCTION

In an earlier series of papers,[1] a statistical theory for displacement ferroelectrics was developed and applied in some detail for the salt lithium tantalate $LiTaO_3$. The statistical approximation adopted to describe equilibrium bulk dielectric properties was to replace all primitive cells except one by their ensemble averages, thereby including long-range (intercell) interactions only in a Hartree or effective-field approximation. In this way it was possible to write an effective system Hamiltonian in terms of the normal vibrational modes of a single cell. For some displacement ferroelectrics, only a single transverse optic mode of lattice vibration is grossly temperature dependent (the "soft" mode); $LiTaO_3$ and $LiNbO_3$ are good examples.[2] For these systems, the effective Hamiltonian contains sufficiently few parameters for them to be comfortably overdetermined by comparison of bulk ferroelectric properties with the results of the statistical theory.

In principle, by choosing a model for the microscopic system, the Hamiltonian parameters (which are microscopic quantities) could be determined from first principles. In practice, for most of the parameters involved, such a calculation at the present time is not very meaningful, and in the lithium tantalate work,[1] we adopted the "spin-Hamiltonian" philosophy from magnetism, treating the parameters simply as numbers to be determined by comparing theory with experiment. The problem was overdetermined to a considerable degree, and the self-consistency of the results was surprisingly good, even with completely temperature-independent parameters. Initially, this was taken to imply that the random-phase approximation (RPA) for intercell interactions was adequate in this context and that, consequently, correlation effects were not a major factor.

However, certain Hamiltonian parameters are fairly easily interpreted in terms of more fundamental microscopic properties of the lattice and constituent ions and, when an effort was made[1] to translate the "best-fit" parameter values into more familiar microscopic concepts, some baffling results were obtained: Lorentz fields more than an order of magnitude smaller than expectation and a Lorentz-field electronic contribution to polarization of opposite sign to the ionic term. In the present paper, we shall show that these, and other inconsistencies which follow, disappear completely when an allowance is made for intercell correlations between the ionic motions of neighboring primitive cells of the lattice.

The way in which the numerous pieces of the interpretational jigsaw fall neatly into place with-out exception, once the importance of correlations is realized, gives confidence that the explanation is basically the correct one. The correlations involved are very significant, seemingly to temperatures considerably in excess of the ferroelectric Curie temperature T_C and throughout this range (excluding, presumably, the immediate vicinity of the Curie point, where a critical divergence of correlation length must take place for a second-order phase transition[3]) appear to be at most a very slow varying function of temperature. It is for this reason alone that the random-phase formalism of Ref. 1, with its Curie-Weiss laws and typical Landau[4] critical parameters, still applies in its entirety when correlations of the present form are included. The form of the effective Hamiltonian and the statistical analysis of the earlier papers remains valid (which is presumably why the self-consistency of the method was found to be good for $LiTaO_3$); only the interpretation of the Hamiltonian parameters in terms of fundamental microscopics is modified. Fortunately, for ferroelectrics the true critical region near T_C, for which the present type of theory would break down, seems to be of such minute extension[3] that experimentally, to date, deviation from Landau (effective-field) behavior has rarely been observed near ferroelectric phase transitions. A lesson of the present work is that it is dangerous to construe this as evidence for the absence of correlation effects.

In Sec. II we show how ionic correlations can be included in an analysis leading to an effective Hamiltonian for a displacement ferroelectric, and how one is led back to exactly the same algebraic form for the "displacement" Hamiltonian used in Ref. 1. Section III reexamines the $LiTaO_3$ findings in the light of the new approach, redefining the earlier problems and difficulties and demonstrating their natural explanation when correlation effects are recognized. Finally, we are led to a fairly accurate method for obtaining effective ionic charges in ferroelectrics. Using the analyses of relevant data for $LiTaO_3$ (present paper) and $LiNbO_3$,[5] we find effective charges for tantalum and oxygen in $LiTaO_3$ and for niobium and oxygen in $LiNbO_3$, which are in close agreement with those obtained by Peterson and Bridenbaugh[6] from an analysis of nuclear quadrupole resonance experiments. We conclude that for both salts the spontaneous polarization is about 45% ionic and 55% electronic.

II. MICROSCOPIC THEORY

Since classical statistics were found to be adequate in the context of Ref. 1, the arguments will again be presented in classical terms. The basic procedure is to write down that part of the system Hamiltonian which involves explicitly the coordinates of a particular (or "primary") primitive cell of the lattice (say the ith cell) and to approximate intercell interactions in some statistical sense, so that the resulting effective Hamiltonian involves ith cell coordinates only and can then be used to evaluate relevant ensemble averages in a self-consistent way.

We define an elementary polarization p^j for an arbitrary jth cell. It can, in general, be thought of as the sum of two parts: $p^j_{E=0}$, polarization when the Maxwell field E is absent, and p^j_Δ, additional contribution resulting from the introduction of field E. In particular, we define polarizations $P=Np^i$, $P_{E=0}=Np^i_{E=0}$, and $P_\Delta=Np^i_\Delta$, where N is the number of primitive cells per unit volume and i is the primary cell for which an effective Hamiltonian is to be constructed.

At the outset we make the supposition that electronic polarizabilities are independent of ionic motion in the lattice, i.e., $p^j_\Delta=p^i_\Delta$ for all j. This being so, the contribution to local field E^b_{loc} (at site b of the primary lattice cell) which arises from the influence of Maxwell field alone is thermal-motion independent and is given by

$$E^b_{\text{loc}}-E^b_{\text{loc}}(E=0)=E+\gamma^b_{\text{RPA}}P_\Delta\,, \qquad (2.1)$$

where γ^b_{RPA} is the effective-field or Lorentz[7] parameter for site b. The local field in the absence of E, viz., $E^b_{\text{loc}}(E=0)$, *is* motion dependent, however, and can formally be written as a sum of zero-field dipolar contributions from all $j\neq i$, i.e., as

$$\sum^{j\neq i}\gamma^{bj}p^j_{E=0}\,,$$

where γ^{bj} is the effective-field parameter at site b of the primary cell for the dipolar contribution from cell j. Now $p^j_{E=0}$ is *not* independent of j (or, more accurately, $j-i$) because of thermal motion, and we here encounter the many-body aspects of the problem. To proceed, statistical approximation is necessary.

To reduce the problem to an effective Hamiltonian involving only the coordinates of the primary cell i, from which ensemble averages $\langle\cdots\rangle$ for the system can be calculated using classical statistics, the intercell forces must be related using a physical criterion to properties connected with the motion of the ith cell alone. The simplest approximation is the RPA for which $p^j_{E=0}$ is replaced by $\langle p^i_{E=0}\rangle$ for all $j\neq i$. This approximation relates intercell forces only to the averaged motion of the primary cell. What is neglected here is the effect of intercell correlations, in particular, the dependence of $E^b_{\text{loc}}(E=0)$ on the deviations of the motion of the primary cell from its average, i.e., on $P_{E=0}-\langle P_{E=0}\rangle$. Thus, RPA theory can be improved by allowing $E^b_{\text{loc}}\ (E=0)$ to depend both on the instantaneous and the averaged motion of the primary cell. Including deviations from random phase in lowest order, we write

$$E^b_{\text{loc}}(E=0)=\gamma^b_{\text{RPA}}\langle P\rangle_{E=0}+\gamma^b_{\text{corr}}(P_{E=0}-\langle P\rangle_{E=0}) \tag{2.2a}$$

or, identically,

$$E^b_{\text{loc}}(E=0)=\gamma^b\langle P\rangle_{E=0}+\gamma^b_{\text{corr}}P_{E=0}, \tag{2.2b}$$

$$\text{where}\quad \gamma^b+\gamma^b_{\text{corr}}=\gamma^b_{\text{RPA}}\ . \tag{2.2c}$$

In these equations $\langle P\rangle_{E=0}\equiv\langle P_{E=0}\rangle=N\langle p^i_{E=0}\rangle$, and we have defined a new dimensionless effective-field parameter for correlated motion γ^b_{corr} (and an associated parameter γ^b). The new concept γ^b_{corr} allows us, in particular, to recognize the existence of intercell dipolar forces in the nonpolar phase arising from correlation effects, i.e.,

$$E^b_{\text{loc}}(E=0)=\gamma^b_{\text{corr}}P_{E=0},\quad T>T_C\ .$$

The linear form of the last term in Eq. (2.2b) is dictated not only by being the lowest-order correction to RPA and hence valid for weakly correlated systems (high temperatures), but also by the fact that it becomes exact in the opposite (low-temperature) fully correlated limit for which $p^j_{E=0}=p^i_{E=0}$ for all j and hence, $E^b_{\text{loc}}(E=0)=\gamma^b_{\text{RPA}}P_{E=0}$, i.e., $\gamma^b_{\text{corr}}\rightarrow\gamma^b_{\text{RPA}}$ in this limit.

The Lorentz parameters γ^b and γ^b_{corr} will be generally temperature dependent. The concept proves very useful for displacement ferroelectrics, however, since we shall find that this temperature variation is so small that it can be neglected for calculations in the vicinity of phase-transition temperature T_C and leads to the concept of noncritical correlation phenomena associated with ferroelectric phase transitions. Finally, for total local field at site b of the primary cell

$$E^b_{\text{loc}}=E+\gamma^b_{\text{RPA}}P_\Delta+\gamma^b\langle P\rangle_{E=0}+\gamma^b_{\text{corr}}P_{E=0}\,. \tag{2.3}$$

The Lorentz parameters γ^b and γ^b_{corr}, as γ^b_{RPA}, will be second-rank tensors. We shall, however, maintain a simplistic scalar formalism; the generalization to tensor notation is quite formal and readily accomplished if desired.

Using Eq. (2.3) and writing electronic polarizabilities α_b, we find a total polarization for the particular primitive cell of interest, expressed in units of polarization per unit volume, as

$$P=(1/v)\textstyle\sum_b\left[\alpha_b(E+\gamma^b_{\text{RPA}}P_\Delta+\gamma^b\langle P\rangle_{E=0}+\gamma^b_{\text{corr}}P_{E=0})+e_bq_b\right], \tag{2.4}$$

where v is the volume of a primitive lattice cell, and ions at sites b possess point (effective) charge e_b and are displaced a distance q_b from centrosymmetry. The sum $\sum_b$ is over all sites in the primitive cell. A question of semantics enters at this point concerning the $\gamma^b_{\text{corr}}P_{E=0}$ term of Eq. (2.4), i.e., whether it should be included as part of the ionic or electronic polarizations. Its physical origin is obviously electronic, but it enters the theory fully correlated to ionic motion and therefore can be formally included as an additional contribution to ionic charge. We have chosen to restrict the term "ionic polarization" to the physically ionic [last term of Eq. (2.4)] characteristic of the system, including all other terms as an electronic contribution to polarization. However, we shall reserve the term "dynamic charge contribution to polarization" for the combined action of the last two terms in Eq. (2.4). Thus, in the absence of an "applied" field E, and in a nonpolar phase, the effective charges associated with ionic vibrations are thought of as "dynamic charges"; they differ, often very significantly, from the true ionic charges because of the effects of short-range correlations contained in the $\gamma^b_{\text{corr}}P_{E=0}$ terms above.

At frequencies of applied field very much higher than optic phonon frequencies, all ionic motion will be relaxed completely and the equation for polarization reduces to

$$P_\Delta=(1/v)\textstyle\sum_b\alpha_b(E+\gamma^b_{\text{RPA}}P_\Delta), \tag{2.5}$$

from which we find that

$$P_\Delta=\eta'_{\text{RPA}}\,\alpha E, \tag{2.6}$$

$$\text{where}\quad \alpha=(1/v)\textstyle\sum_b\alpha_b \tag{2.7}$$

$$\text{and}\quad \eta'_{\text{RPA}}=[1-(1/v)\textstyle\sum_b\alpha_b\gamma^b_{\text{RPA}}]^{-1}\ . \tag{2.8}$$

Equation (2.6) is just a generalization of the Clausius-Mossotti equation for electronic susceptibility.

Relationships are also readily deduced relating the total thermodynamic polarization $\langle P\rangle$ to the ionic polarization $\langle P_{\text{ion}}\rangle$ and to the dynamic-charge contribution to polarization $\langle P_{\text{d-ch}}\rangle$. We may write the ensemble average of Eq. (2.4) in the form

$$\langle P\rangle=P_\Delta+(1/v)\textstyle\sum_b(\alpha_b\gamma^b\langle P\rangle_{E=0})+\langle P_{\text{d-ch}}\rangle, \tag{2.9}$$

from which, using the fact that

$$\langle P\rangle_{E=0}=\langle P\rangle-P_\Delta, \tag{2.10}$$

$$\text{we obtain}\quad \langle P\rangle=\eta'_{\text{d-ch}}\langle P_{\text{d-ch}}\rangle+\eta'_{\text{RPA}}\,\alpha E, \tag{2.11}$$

$$\text{where}\quad \eta'_{\text{d-ch}}=[1-(1/v)\textstyle\sum_b\alpha_b\gamma^b]^{-1}\ . \tag{2.12}$$

Also, from Eq. (2.11), it follows that

$$\langle P\rangle_{E=0}=\eta'_{\text{d-ch}}\langle P_{\text{d-ch}}\rangle\ . \tag{2.13}$$

By definition, we may write

$$\langle P_{\text{d-ch}}\rangle=\langle P_{\text{ion}}\rangle+(1/v)\textstyle\sum_b\alpha_b\gamma^b_{\text{corr}}\langle P\rangle_{E=0}\,, \tag{2.14}$$

from which, using Eq. (2.13), we find that

$$\eta'_{\text{d-ch}}\langle P_{\text{d-ch}}\rangle = \eta'_{\text{RPA}}\langle P_{\text{ion}}\rangle , \tag{2.15}$$

where we have also made use of Eqs. (2.2c) and (2.12). It follows that

$$\langle P\rangle = \eta'_{\text{RPA}}(\langle P_{\text{ion}}\rangle + \alpha E) . \tag{2.16}$$

We now consider the contribution to the system Hamiltonian resulting from dipolar forces. We shall be concerned with the equation of motion for the ionic coordinates of a particular (e.g., the *i*th) primitive lattice cell. We may therefore disregard all contributions not involving *i*th lattice-cell coordinates. In general, we have a dipolar contribution of the form

$$V' = -(1/v)\textstyle\sum_b [e_b q_b E^b_{\text{loc}} + \frac{1}{2}\alpha_b (E^b_{\text{loc}})^2] . \tag{2.17}$$

If we include only intercell dipolar forces in E^b_{loc}, taking all intra-*i*th-cell dipolar interactions into the isolated *i*th cell system Hamiltonian (see Ref. 1), then E^b_{loc} does not contain any *i*th cell coordinates and Eq. (2.17) reduces to

$$\begin{aligned} V'(i) = -(1/v)\textstyle\sum_b e_b q_b(i)\,[E + \gamma^b_{\text{RPA}}P_\Delta + \gamma^b\eta'_{\text{RPA}}\langle P_{\text{ion}}\rangle \\ + \gamma^b_{\text{corr}} N p^j(\text{corr})_{E=0}] , \end{aligned} \tag{2.18}$$

where $p^j\,(\text{corr})_{E=0}$ denotes the fully correlated polarization of an arbitrary cell $j\neq i$. Quite generally, a potential function containing terms $q(i)\,q(j)$, which is restricted by correlations to $q(i)=q(j)$, yields the same equations of motion as the potential function which is the same except that $q(i)\,q(j)$ has been replaced by $\frac{1}{2}[q(i)]^2$. Thus, dropping subscripts i and j, we can write for the particular primitive cell of interest

$$\begin{aligned} V' = -(1/v)\textstyle\sum_b e_b q_b (E + \gamma^b_{\text{RPA}}P_\Delta + \gamma^b\eta'_{\text{RPA}}\langle P_{\text{ion}}\rangle \\ + \frac{1}{2}\gamma^b_{\text{corr}}P_{E=0}) . \end{aligned} \tag{2.19}$$

To ensure that γ^b_{RPA} in Eqs. (2.1) and (2.2) refer to the same Lorentz parameters, it is convenient to include the intracell dipolar contribution to E^b_{loc} in Eq. (2.18). This merely has the effect of changing the meaning of γ^b_{corr} in Eq. (2.19) to include intracell as well as intercell effects. The coefficient $\frac{1}{2}$ in the intracell case is required in order to avoid counting the interactions twice in the sum over cell sites b. Thus, all Lorentz parameters are now defined in conventional fashion, i.e., including contributions from all ions except the one in question.

The basic approximation of the statistical theory of Ref. 1 is that, in the absence of dipolar interactions, optical modes of lattice vibration are sufficiently weakly varying functions of wave vector that it makes sense to neglect this variation and describe the motion in terms of normal modes of vibration of a single primitive cell. The formalism is simplest for those ferroelectrics which exhibit a gross temperature variation of only a single (soft) mode. For such systems we retain only that part of the system Hamiltonian describing this single (transverse optic) mode. The resulting Hamiltonian may be expressed in terms of the conjugate momentum and displacement coordinates π and ξ of this mode in the form[1]

$$v\mathcal{H} = \tfrac{1}{2}\pi^2 + \tfrac{1}{2}\Omega_0^2\xi^2 + A\xi^4 + B\xi^6 , \tag{2.20}$$

$$\text{where}\quad p_b = M_b u_b \pi, \quad q_b = u_b\xi , \tag{2.21}$$

$$\textstyle\sum_b M_b u_b^2 = 1 , \tag{2.22}$$

and where M_b, p_b, q_b are, respectively, the mass, momentum, and displacement of the bth ion, and $u_b M_b^{1/2}$ the bth component of normalized eigenvector.

The dipolar contribution V' of Eq. (2.19) can now be expressed in terms of the normal-mode coordinates and added to Eq. (2.20) to give the final "displacement" Hamiltonian. Transforming Eq. (2.19) we obtain

$$\begin{aligned} vV'(\xi) = -\eta S\xi\,[E + (\gamma S/v)\langle\xi\rangle] \\ - \tfrac{1}{2}(\eta\gamma_{\text{corr}}S^2/v)\,\xi^2 , \end{aligned} \tag{2.23}$$

$$\text{where}\quad S = \textstyle\sum_b e_b u_b , \tag{2.24}$$

$$\eta S = \textstyle\sum_b [1 + \eta'_{\text{RPA}}\gamma^b_{\text{RPA}}\alpha]e_b u_b , \tag{2.25}$$

$$\eta\gamma S = \textstyle\sum_b \eta'_{\text{RPA}}\gamma^b e_b u_b , \tag{2.26}$$

$$\eta\gamma_{\text{corr}} S = \textstyle\sum_b \eta'_{\text{RPA}}\gamma^b_{\text{corr}} e_b u_b . \tag{2.27}$$

We note, in particular, that S is an ionic-charge parameter, in terms of which the ionic contribution to polarization $\langle P_{\text{ion}}\rangle = (S/v)\langle\xi\rangle$. We have also extended the finding $\langle P\rangle_{E=0} = \eta'_{\text{RPA}}\langle P_{\text{ion}}\rangle$ of Eq. (2.16) for use as $P_{E=0} = \eta'_{\text{RPA}}P_{\text{ion}}$, thereby assuming a constant ratio of ionic to electronic polarization during fully correlated ionic motion. Adding Eq. (2.23) to Eq. (2.20) we obtain a final displacement Hamiltonian for our single-soft-mode ferroelectric in the form

$$v\mathcal{H} = \tfrac{1}{2}(\pi^2 + \omega_0^2\xi^2) + A\xi^4 + B\xi^6 - \eta S\xi[E + (\gamma S/v)\langle\xi\rangle] , \tag{2.28}$$

$$\text{where}\quad \omega_0^2 = \Omega_0^2 - (\eta\gamma_{\text{corr}}S^2/v) . \tag{2.29}$$

The Hamiltonian Eq. (2.28) is exactly that used in our earlier work[1] so that all the parameter determination and self-consistency checks carried out previously[1] for LiTaO_3 are still valid. All that has changed are the definitions (2.24)–(2.27) and (2.29) of the Hamiltonian parameters in terms of the more fundamental microscopic parameters.

III. LITHIUM TANTALATE

In Ref. 1, a detailed comparison of statistical theory with experiment for the displacement ferroelectric $LiTaO_3$ showed that an analysis using Hamiltonian (2.28) gave results which were quite self-consistent for a markedly overdetermined problem. However, an attempt to interpret the "best-fit" values for the Hamiltonian parameters in terms of more fundamental microscopics led to some extremely puzzling conclusions. However, this interpretation was made under the assumption that the RPA was essentially valid, e.g., the γ^b values in Eqs. (2.25) and (2.26) were both γ^b_{RPA} and that $\gamma_{\mathrm{corr}}=0$. Let us review the RPA interpretation for $LiTaO_3$ to stress the difficulties.

The really important step in the interpretation of results by RPA theory is the elimination of $\sum_b \gamma^b e_b u_b$ between Eqs. (2.25) and (2.26) to give

$$\eta = 1/(1-\alpha\gamma) \ , \qquad (3.1)$$

a result which is not valid if correlations are present. It will turn out that all the ensuing difficulties can be traced back to Eq. (3.1). Since $\alpha\gamma = (\eta'_{\mathrm{RPA}}\alpha)(\gamma/\eta'_{\mathrm{RPA}}) \approx 0.3 \times \frac{1}{13}$ for $LiTaO_3$,[1] it follows that the η parameter is only a percent or two larger than unity. In conjunction with the results of the overdetermined statistical $LiTaO_3$ problem,[1] viz., $\eta/\eta'_{\mathrm{RPA}} = 1.3$, $\eta'_{\mathrm{RPA}}/\gamma = 13$, $\eta'_{\mathrm{RPA}} S = 520\ \mathrm{cm}^{3/2}\ \mathrm{sec}^{-1}$, this finding then precipitates the results: (i) η'_{RPA} = (total polarization)/(ionic polarization) <1; (ii) Lorentz parameter γ is nearly two orders of magnitude less than the "cubic" value of $\frac{4}{3}\pi$; (iii) effective-charge parameter S is markedly larger than that appropriate for even fully ionic ions. To these embarrassing conclusions we can add still others. From Eq. (2.6) we can relate optical refractive index (or more accurately ϵ_∞ the high-frequency contribution to dielectric constant) to $\eta'_{\mathrm{RPA}}\alpha$ through the equation

$$\epsilon_\infty = 1 + 4\pi\eta'_{\mathrm{RPA}}\alpha \ . \qquad (3.2)$$

Barker and co-workers[8,9] have measured ϵ_∞ from infrared reflectivity experiments for both $LiTaO_3$ and $LiNbO_3$, with the results $\epsilon_\infty(LiTaO_3) = 4.5$ and $\epsilon_\infty(LiNbO_3) = 4.6$ for light polarized with E parallel to the polar axis of the ferroelectrics. Since we anticipate that the electronic polarizability is dominated by the oxygen contribution,[10,11] this very close correspondence for isomorphic structures is not surprising. From Eq. (3.2) we find $\eta'_{\mathrm{RPA}}\alpha = 0.29$ for the niobate and equals 0.28 for the tantalate. Putting $\eta'_{\mathrm{RPA}} = 1.3$ for $LiNbO_3$ (RPA approximation[5]) and $\eta'_{\mathrm{RPA}} = 0.8$ for $LiTaO_3$ we obtain from Eq. (2.7) (primitive cell volume $V = 106\ \text{Å}^3$ for both salts)

$$\begin{aligned} 3\alpha(\mathrm{O}) + \alpha(\mathrm{Ta}) &\sim 19\ \text{Å}^3 \ , \\ 3\alpha(\mathrm{O}) + \alpha(\mathrm{Nb}) &\sim 12\ \text{Å}^3 \ , \end{aligned} \qquad (3.3)$$

where $\alpha(\mathrm{O})$, $\alpha(\mathrm{Ta})$, $\alpha(\mathrm{Nb})$ refer, respectively, to the electronic polarizabilities of oxygen, tantalum, and niobium ions in the two salts. The contribution from lithium ions is, in all probability, negligibly small and has been omitted from Eqs. (3.3). Although no good quantitative estimates are available for $\alpha(\mathrm{Ta})$ and $\alpha(\mathrm{Nb})$, the existing evidence[11,12] suggests that they are small compared with $\alpha(\mathrm{O})$. Thus, Eqs. (3.3) predict $\alpha(\mathrm{O})$ in $LiTaO_3$ of order 6 Å^3 and suggest a very sizable difference between $\alpha(\mathrm{O})$ in $LiTaO_3$ and $LiNbO_3$. In view of the close correspondence of ϵ_∞ values the latter finding is difficult to accept. The former finding $\alpha(\mathrm{O}) \approx 6$ Å^3 for $LiTaO_3$ is, however, completely out of the question. Axe[11] has quantitatively assessed optical polarizabilities from ϵ_∞ data for the perovskites and finds $3\,\alpha(\mathrm{O}) + \alpha(\mathrm{Ta}) = 6.6$ Å^3 in $KTaO_3$, where the tantalate group is essentially just that present in $LiTaO_3$. Also, for a wide range of oxides, values of $\alpha(\mathrm{O})$ seem always to be in the 1- to 3-Å^3 range.[13]

It is possible to attempt an explanation of these various findings in terms of numerous *ad hoc* hypotheses (e.g., total breakdown of the point-charge approximation, large ionic distortion effects from nondipolar sources, etc.) but this is most unsatisfactory at best, particularly in the light of Axe's[11] findings for the perovskites. Moreover, the oxygen polarizability result remains quite unrealistic in any context.

The unsatisfactory aspects disappear completely once one accepts the not very surprising possibility that intercell correlation effects could be significant for ionic motion. To do this we merely relax the RPA restriction on the Lorentz parameters which produced Eq. (3.1) and analyze the $LiTaO_3$ data using Eqs. (2.24)–(2.27). However, before doing this in detail, it is advisable to caution ourselves that a number of approximations have entered even the correlated motion theory. First, the procedure of accounting for electronic susceptibility in terms of a local electric field acting upon an electronic polarizability of the ions is not rigorously justifiable. Dipole contributions resulting from exchange charge effects[14] and from ionic deformation by short-range repulsive interactions with neighbors[14,15] (as conceived in shell-model calculations[16,17]) must be recognized and may be responsible for corrections of order 20% to simple dipolar theory in calculating effective charges. Even within the local field approximation the theory of Sec. II assumes the equality of the RPA Lorentz parameters γ^b_{RPA} for the Maxwell and zero-field contributions to polarization, i.e., for P_Δ and $P_{E=0}$. Since different ionic sublattices do not contribute equal proportions to ionic and electronic polarizations, this will (except for the simpler cubic-type lattices) not be the case and thus involves an additional approximation. The theory can only be refined to allow for this effect if Lorentz parameters are computed for each ion site from all ionic sublattices separately and if detailed knowledge of relevant polarizabilities and soft-mode symmetry is available. The effect, however, is probably not serious for systems with a large electronic contribution to total polarization (we shall estimate electronic contributions to be ~ 55% in $LiTaO_3$ and $LiNbO_3$). These limitations of the theory should be kept in mind when it comes to assessing the quantitativeness of the ensuing calculations.

Using Eq. (3.2), we can estimate η'_{RPA} from the measured high-frequency dielectric constant ϵ_∞ if the relevant polarizabilities are known. We can proceed in two ways, the quantitative consistency of which gives us some confidence in the results. First, we can assume that the polarizability of a tantalate ion $(TaO_3)^-$ is relatively well defined (i.e., comparatively insensitive to environment) and use the value 6.6 Å^3 calculated by Axe[11] for $KTaO_3$ as applicable for $LiTaO_3$. Neglecting the electronic polarizability of lithium (for which the usual estimate is 0.03 Å^3) we proceed to calculate $\eta'_{\mathrm{RPA}} = 2.21$ and α [of Eq. (2.7)] 0.126. We note, from Axe's numbers, that the electronic polarizability of the titanate ion in $BaTiO_3$ and $SrTiO_3$ is constant to within 1% of the value 6.75 Å^3, which lends some support to the idea of an ion group polarizability which is somewhat insensitive to environment. Second, we note that for many cubic structures, including the perovskite lattice, we can write

$$\eta'_{\mathrm{RPA}} = (1 - \tfrac{4}{3}\pi\alpha)^{-1} \tag{3.4}$$

for electronic polarizability, where the anion contributions to electronic polarization are equivalent. (The same equation is not valid for ionic terms in perovskite where one has two inequivalent anion contributions to ionic polarization leading to the famous Slater enhancement effect for Lorentz field[18] in $BaTiO_3$.) It is likely, therefore, that Eq. (3.4) will also be a good approximation for electronic polarizability in the slightly distorted (at room temperature) pseudoperovskite $LiTaO_3$. Using Eqs. (3.4) and (3.2) for $LiTaO_3$ (with $\epsilon_\infty = 4.5$), we calculate values $\eta'_{\mathrm{RPA}} = 2.17$, $\alpha = 0.128$, and a tantalate electronic polarizability of 6.8 Å^3. The agreement is excellent; with some confidence we can write $\eta'_{\mathrm{RPA}} =$ (total polarization)/(ionic polarization) $= 2.19 \pm 0.02$, indicating an electronic contribution to spontaneous polarization of about 55%, and an ionic contribution of about 45%.

Since the ionic contribution to spontaneous polarization $\langle P_{\mathrm{ion}}\rangle$ is directly related to effective ionic charges $e(\mathrm{Li})$, $e(\mathrm{Ta})$, and $e(\mathrm{O})$, we may use the fact that $\langle P_{\mathrm{ion}}\rangle = 0.45\langle P\rangle$ to obtain a relationship between these charges. In general, we have

$$\textstyle\sum_b e_b q_b = \langle P\rangle / \eta'_{\mathrm{RPA}} \,, \tag{3.5}$$

where q_b are the displacements from the nonpolar phase as measured by x-ray and neutron-diffraction techniques.[19] Using the observed room-temperature values $q(\mathrm{Li}) = 0.43$ Å, $q(\mathrm{Ta}) = 0.029$ Å, $q(\mathrm{O}) = -0.17$ Å for displacement[19] and $\langle P\rangle = 50\ \mu\mathrm{C/cm}^3$,[20] we find the equation

$$0.43e(\mathrm{Li}) + 0.029e(\mathrm{Ta}) - 0.51e(\mathrm{O}) = 0.76 \,, \tag{3.6}$$

where we measure effective charge in units of electron charge. Since we have charge conservation, we also know that

$$e(\mathrm{Li}) + e(\mathrm{Ta}) + 3e(\mathrm{O}) = 0 \,. \tag{3.7}$$

The effective charge for Li^+ may safely be taken to be close to +1. Equations (3.6) and (3.7) now determine the effective point charges for tantalum and oxygen as $e(\mathrm{Ta}) = 0.8$ and $e(\mathrm{O}) = -0.6$. An equivalent calculation for $LiNbO_3$ gives[5] $e(\mathrm{Nb}) = 1.4$ and $e(\mathrm{O}) = -0.8$. These numbers are in very good agreement with the estimates of Peterson and Bridenbaugh[7] from a point-charge analysis of nuclear quadrupole resonance data which are $e(\mathrm{Ta}) = 1.2$, $e(\mathrm{O}) = -0.7$ for $LiTaO_3$, and $e(\mathrm{Nb}) = 1.6$, $e(\mathrm{O}) = -0.9$ for $LiNbO_3$. The calculations both indicate that the bonding in the tantalate ion and niobate ion is very far removed from ionic, for which the effective charges would be $e(\mathrm{Ta}) = e(\mathrm{Nb}) = +5$, $e(\mathrm{O}) = -2$. They also indicate a greater degree of covalency for the tantalate, a result in agreement with that expected from electronegativity differences.

It is now trivial to complete the $LiTaO_3$ analysis. Using the parameter ratios determined from the statistical calculation[1] and quoted at the beginning of the present section, it now follows that

$$\eta \approx 2.8, \quad \gamma \approx \tfrac{1}{6}, \quad S \approx 240\ \mathrm{cm}^{3/2}\,\mathrm{sec}^{-1} \,. \tag{3.8}$$

Also, from Eqs. (2.25) and (2.26) we find that

$$\textstyle\sum_b \gamma^b_{\mathrm{RPA}} e_b u_b \approx 6.5S \,, \tag{3.9}$$

$$\textstyle\sum_b \gamma^b e_b u_b \approx 0.22S \,, \tag{3.10}$$

and from Eqs. (2.2c) and (2.27) it follows that

$$\textstyle\sum_b \gamma^b_{\mathrm{corr}} e_b u_b \approx 6.3S \tag{3.11}$$

and $\gamma_{\mathrm{corr}} \approx 4.9$. We can, from Eq. (3.9), define some sort of averaged RPA Lorentz factor with a value 6.5. Although this average is of no particular significance, and is probably not accurate to better than ± 25%, it demonstrates that the Lorentz effects $\langle\gamma^b_{\mathrm{RPA}}\rangle$ are now of the expected order of magnitude, i.e., $\sim \frac{4}{3}\pi$. It is also apparent from Eqs. (3.9)–(3.11) that the motion of the ions which contribute significantly to Lorentz field is almost completely correlated throughout the temperature range $\sim T_C$. As emphasized before, these are not critical correlations in the usual sense since, as evidenced by the Curie-Weiss behavior near T_C, the temperature dependence of these correlations must be very weak over this temperature range.

From the statistical analysis of Ref. 1 we find for the harmonic parameter ω_0 of Hamiltonian (2.28) a value of approximately 140 cm^{-1}. From Eq. (2.29) we can now estimate the separate binding (short-range forces) and correlated dipolar contributions to this parameter. We find values

$$\Omega_0 \approx 480\ \text{cm}^{-1}, \quad (\eta\gamma_{\text{corr}} S^2/v)^{1/2} \approx 460\ \text{cm}^{-1}. \tag{3.12}$$

Thus, the frequency of the soft mode in the absence of dipolar forces is ~ 480 cm^{-1}, which is of the order of, but perhaps a little less than, typical stretching frequencies observed for the tantalum-oxygen covalent bond. The very significant part played by correlation effects is evident from Eq. (3.12), making $\omega_0^2 \ll \Omega_0^2$ and bringing LiTaO$_3$ very close to being an order-disorder ferroelectric.[1] It is interesting to note that recent x-ray and electron-scattering experiments[21,22] seem to support the idea of very significant correlation effects in ferroelectrics. The BaTiO$_3$ controversy[22-24] is particularly relevant, indicating another system where strong lattice correlations seem to bring the system close to an order-disorder situation (which results when ω_0^2 becomes negative, or before that in the presence of negative quartic anharmonicity[1]).

At low temperatures $T \ll T_C$, we are unable to estimate the ionic correlations since they play a very small role in this almost completely ordered range. In the low-temperature statistical theory, the parameters ω_0 and γ enter only in the combination

$$F = \omega_0^2 - (\eta\gamma S^2/v) = \Omega_0^2 - (\eta\gamma_{\text{RPA}} S^2/v), \tag{3.13}$$

where γ_{RPA} is defined by

$$\eta\gamma_{\text{RPA}} S = \textstyle\sum_b \eta'_{\text{RPA}} \gamma^b_{\text{RPA}} e_b u_b\ , \tag{3.14}$$

so that F is independent of correlation effects. In the earlier statistical analysis for LiTaO$_3$ in Ref. 1, we found that the agreement with experiment was improved if the parameter γ was allowed to vary with temperature from $\frac{1}{6}$ near T_C to $\sim\frac{1}{18}$ at low temperatures. The physical reason for this must now be understood from Eq. (3.13) either as a decrease of bonding frequency Ω_0 or an increase in Lorentz parameter γ_{RPA} with increasing temperature. The observed effect is quantitatively explained by a 1% decrease in bonding frequency or by a 2% increase in γ_{RPA} as $0 \to T \to T_C$, indicating a marked temperature independence of these parameters despite the high Curie point ≈ 890 °K.

Finally, it is interesting to consider the dynamic-charge concept introduced earlier in Eqs. (2.12) and (2.13). Since γ is very small we may approximate Eq. (2.12) by

$$\eta'_{\text{d-ch}} = (1 - \alpha\gamma)^{-1} \tag{3.15}$$

to obtain the value $\eta'_{\text{d-ch}} \approx 1.02$ for LiTaO$_3$. Thus, the dynamic-charge contribution to polarization is about 98%, which is only another way of saying that the ionic correlations are very large indeed. In the nonpolar phase just above T_C the correlations have the effect of distorting the electronic clouds of the ions during their vibrational motion. This effect is in the present picture due to dipolar forces via electronic polarizabilities, even though the thermodynamic polarization is zero. In a simple RPA picture (neglecting correlation effects) the ions behave as if they possessed markedly increased point charges, dynamic charges e_b^+, which must be carefully distinguished from the true ionic (or static) charges e_b evaluated for LiTaO$_3$ above. The equation for dynamic charge is

$$\textstyle\sum_b e_b^+ q_b = P_{\text{d-ch}} = P/\eta'_{\text{d-ch}} \tag{3.16}$$

and for LiTaO$_3$ may be written

$$0.43\, e^+(\text{Li}) + 0.029\, e^+(\text{Ta}) - 0.51\, e^+(\text{O}) = 1.62\ , \tag{3.17}$$

where we give dynamic charge in units of electronic charge. For dynamic charge there is no charge conservation law so that Eq. (3.17) comprises our only information in the absence of a detailed knowledge of Lorentz parameters for each site. However, because of the extreme smallness of $\alpha(\text{Li})$ it is safe to assume a value $e^+(\text{Li}) \approx 1$. Since we expect $\alpha(\text{Ta})$ to be smaller than $\alpha(\text{O})$ and because the coefficient of $e^+(\text{Ta})$ in Eq. (3.17) is very small, we shall incur little error if we take $e^+(\text{Ta}) \approx +2$, allowing even with this lack of knowledge concerning the tantalum ion a rather precise estimate for the dynamic oxygen charge. We find the value $e^+(\text{O}) = -2.2$ which is almost four times the static oxygen charge $e(\text{O}) = -0.6$.

IV. CONCLUSIONS

We have analyzed the results of a statistical calculation for LiTaO$_3$. We are forced to the conclusion that very important ion correlations between neighbor primitive cells of the system exist right up to temperatures well in excess of T_C. The correlations are very weak functions of temperature on the temperature scale $\sim T_C$ and, therefore, are not critical correlations in the usual sense. Near T_C, in LiTaO$_3$, about 97 or 98% of the Lorentz field results from fully correlated motion. We find that the neglect of correlations (e.g., the use of simple random-phase local fields proportional to the thermally averaged polarization) leads to many inconsistencies and that these are all removed completely when correlation effects are recognized. With the new interpretation [which now replaces that of Ref. 1, (III 3) although the rest of the earlier work[1] remains valid] we calculate ionic charges $e(\mathrm{Ta}) = 0.8$ and $e(\mathrm{O}) = -0.6$, and a $(\mathrm{TaO_3})^-$ ion polarizability of 6.8 Å^3, which are all in very close agreement with previously published estimates from independent studies.[7,11] We find that the spontaneous polarization is about 55% electronic, 45% ionic, and estimate a soft-mode "bonding frequency" (i.e., frequency is the absence of long-range dipolar forces) of 480 cm^{-1}, which is of the order of, but somewhat less than, a tantalum-oxygen stretching frequency. Finally, very similar strong correlation effects are found for $\mathrm{LiNbO_3}$ to even higher temperatures,[5] suggesting that the phenomenon may not be an isolated one (see Ref. 22). We conclude that the existence of "effective-field-like" Curie-Weiss behavior is not necessarily indicative of the absence of correlation effects, and that the use of random-phase Lorentz field theory for ferroelectric calculations near of above T_C is probably bound to fail for displacement ferroelectrics.

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