Statistical Theory for Displacement Ferroelectrics. III. Comparison with Experiment for Lithium Tantalate

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The theory developed in parts I and II of the present series of papers is used to interpret the dielectric properties of $LiTaO_3$. The problem is comfortably overdetermined, allowing both for a determination of the parameters involved in the theory and for a consistency check of the theory itself. The agreement between theory and experiment is quite good using completely temperature-independent parameters, but becomes excellent if a temperature dependence of the Lorentz field parameter is allowed. When the values obtained for the parameters of the effective Hamiltonian are related to a detailed description of the system in terms of a microscopic model, it becomes apparent that a representation in terms of a set of effective point charges at the various nuclear sites is inadequate. It is suggested that a representation of each ion by two effective charges, a core charge and a shell charge, may be more appropriate.

1. INTRODUCTION

IN parts I and II[1,2] of the present series of papers, an effective-field theory has been developed to describe the lattice dynamics of ferroelectric systems. The theory, as so far developed, uses classical statistics and takes its simplest form for systems in which the ferroelectric phenomena are, to a good approximation, describable in terms of a single-"soft"-optic mode of lattice vibration. For such a system, quantitative theoretical calculations have been carried out in parts I and II with an emphasis on displacement ferroelectrics and second-order phase transitions, although, as stressed in the earlier papers, the theoretical method is readily extended to include order-disorder ferroelectrics and first-order transitions.

In the present paper we apply the theory in detail to the displacement ferroelectric lithium tantalate $LiTaO_3$. The choice of $LiTaO_3$ as our first "test case" was made for a number of separate reasons. First, measurements of the temperature dependence of Raman scattering in $LiTaO_3$ for temperatures below the Curie point show[3] that only one vibrational mode is grossly temperature-dependent and that this has the correct symmetry (infrared active for the electric vector parallel to the direction of spontaneous polarization) to control the ferroelectric behavior of the system. Second, the soft mode at low temperatures $(T \ll T_c)$ has an energy which is some three times smaller than the energy kT_c associated with the Curie temperature T_c. This means that quantum effects associated with dielectric phenomena are certainly small until the temperature T falls below $T_c/3$, so that most of the temperature range of interest, and the phase transition in particular, is adequately described by classical statistics. Third, and perhaps most significantly, a wealth of experimental data on both linear and nonlinear dielectric properties of

$LiTaO_3$ has been accumulated over the past year or so, since single crystals of the compound are of interest for a range of devices in the nonlinear optics field.

The principle behind the theoretical method is to construct an effective Hamiltonian for ionic motion in a ferroelectric system from rather general considerations, believing that the general form of this Hamiltonian will be essentially the same for a wide range of ferroelectrics. The statistical mechanical part of the theoretical problem can then be disposed of, describing the various temperature-dependent dielectric properties in terms of the parameters contained in the Hamiltonian. For some particularly simple ferroelectrics (namely, those with essentially only one soft mode) the problem is comfortably overdetermined, there being considerably more separate pieces of experimental information than there are independent parameters in the effective Hamiltonian. Such is the case for $LiTaO_3$, and it is the purpose of this paper to evaluate the set of parameters which hopefully are sufficient to describe the ferroelectric phenomena associated with this salt. More importantly, however, we shall examine closely the internal self-consistency of the theory looking out, in particular, for a possible temperature dependence of any of the parameters.

The effective-Hamiltonian theory differs fundamentally from a free-energy approach as developed by Devonshire,[4] the latter being a thermodynamic approach with macroscopic variables and parameters. The parameters to be determined in the present paper are microscopic and are therefore related directly to the fundamental interactions within the electron-ion system. The detailed form of the latter cannot be set down until a particular model is chosen to represent the system, and decisions made concerning the origin of the most significant energy contributions. It is not the purpose of the present paper to discuss such models in detail since, at the present stage of development, a detailed description of this kind would necessarily be

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[1] M. E. Lines, first preceeding paper, Phys. Rev. **177**, 797 (1969), hereafter referred to as part I.

[2] M. E. Lines, second preceeding paper, Phys. Rev. **177**, 812 (1969), hereafter referred to as part II.

[3] I. P. Kaminow and W. D. Johnston, Jr., Phys. Rev. **168**, 1045 (1968).

[4] F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon Press, Inc., New York, 1962).

extremely tentative. Nevertheless, even a cursory assessment of the role played by the parameters of the effective Hamiltonian in a microscopic-model theory enables us to use the results obtained below to emphasize at least a few of the less obvious features that a satisfactory model must incorporate.

Following the development of the theory in parts I and II, we attempt to describe the ferroelectric properties of $LiTaO_3$ using the effective or "displacement" Hamiltonian

$$v\mathcal{3C}_{eff} = \tfrac{1}{2}(\pi^2 + \omega_0^2 \xi^2) + A\xi^4 + B\xi^6 - \eta S\xi(E + \gamma\langle P_{ion}\rangle). \quad (1.1)$$

In this Hamiltonian, π and ξ are respectively, the conjugate momentum and displacement coordinates of the soft mode (which will, for a one-soft-mode ferroelectric, alone describe the gross features of the ferroelectric phenomena), v is the volume of a primitive cell in the crystal lattice, and $\langle P_{ion}\rangle = (S/v)\langle\xi\rangle$ is the ensemble (thermally) averaged ionic polarization per unit volume. The external (Maxwell) electric field E is assumed to be applied in the direction of spontaneous polarization, for only in this instance will the one-soft-mode approximation be appropriate.[1] Since the volume v is directly measurable, the Hamiltonian (1.1) contains five unknowns which are to be determined by comparing theory with experiment, namely, ω_0, A, B, ηS, and γS. There is, however, a hidden sixth parameter, because the Hamiltonian (1.1) describes only the ionic motion (or, more accurately, the motion of the ions excluding the ionic distortions arising from the long-range forces or effective fields; see Sec. 3) of the lattice. Most experimental measurements, however, concern the total polarization $\langle P\rangle$ or one of its derivatives where, in part I, we relate $\langle P\rangle$ to $\langle P_{ion}\rangle$ through the equation $\langle P\rangle = \eta'\langle P_{ion}\rangle$, defining a parameter η' which, in our frequency range of interest (at, or below, typical optical-phonon frequencies) is assumed to be independent of frequency. This gives us the extra parameter $\eta'S$.

For the moment these parameters are merely temperature-independent quantities to be determined (and in fact, comfortably overdetermined) by direct comparison of theory with experiment. The assumption concerning temperature independence hopefully relegates thermal expansion and strain effects to a comparatively minor role as far as the gross temperature-dependent features of the bulk ferroelectric properties are concerned. This restriction can also be reassessed later in the paper in the light of the detailed findings for $LiTaO_3$.

2. ANALYSIS OF EXPERIMENTAL DATA

All the theoretical developments and numerical computations required for the interpretation and assessment of the experimental data to be analyzed below have been presented in parts I and II of the present series of papers. We may refer directly to the relevant sections, figures, equations, etc. We shall find that the interpretation of the experimental results for $LiTaO_3$ require a

negative A coefficient in (1.1). In this case, as stressed in Sec. 5b of part I, it is very convenient to work in terms of the dimensionless parameters $\alpha' = (Bk^2T^2)^{1/3}/\omega_0^2$, $\beta' = (Bk^2T^2)^{1/3}/(\eta\gamma S^2/v)$, and $\delta = (B^2kT)^{1/3}/(-A)$, where k is Boltzmann's constant, and, in particular, in terms of the temperature-independent ratios $\beta'/\alpha' = \omega_0^2/(\eta\gamma S^2/v)$ and $(\beta')^{1/2}/\delta = -A/(B\eta\gamma S^2/v)^{1/2}$. Directly below, we derive eight relationships between these two ratios for $LiTaO_3$. This is a measure of the overdetermination of the problem and provides us with a convenient form for assessing self-consistency. Using these results, we shall select optimum values for β'/α' and $(\beta')^{1/2}/\delta$ and then proceed to an evaluation of the six parameters discussed in the introduction.

A. Spontaneous Polarization as a Function of Temperature

A number of measurements of the spontaneous polarization of $LiTaO_3$ have recently been reported. Two separate measurements of room-temperature polarization, one obtained by a static pyroelectric technique[5] and the other by switching the polarization using liquid electrodes and high pulsed fields,[6] agree on a value of 50 $\mu C/cm^2$ to an accuracy of a few percent. The most complete measurements of the temperature dependence of spontaneous polarization have been made by Glass[7] using the dynamic technique of Chynoweth.[8] He reports a measurement of reduced polarization P/P_0 (where P_0 is the saturation value of spontaneous polarization at low temperatures as a function of reduced temperature T/T_c for temperatures between 300°K and the Curie point, which is close to 890°K.

The experimental curve is shown in Fig. 1, where it is compared with a set of theoretical curves taken from Fig. 8 of part I, which are drawn for the particular case $\beta'/\alpha' = 1$. For this case, a best-fit theoretical curve has $(\beta')^{1/2}/\delta \approx 1.75$. The fit is quite good but the theoretical curve falls off a little too slowly with temperature at low temperatures. A similar set of theoretical curves can be drawn for arbitrary β'/α' values, the agreement between theory and experiment being about equally good for all cases. Thus, the fitting procedure defines a relationship between the two ratio parameters and this is sketched in Fig. 2.

B. Specific Heat

Also measured by Glass[7] was the specific-heat curve for $LiTaO_3$ in the vicinity of the Curie temperature. A marked anomaly could be distinguished at T_c with a form indicating a second-order phase transition (no

[5] H. Iwasaki, N. Ushida, and T. Yamada, Japan J. Appl. Phys. 6, 1336 (1967).

[6] S. H. Wemple, M. DiDomenico and I. Camlibel, Appl. Phys. Letters 12, 209 (1968).

[7] A. M. Glass, Phys. Rev. 172, 564 (1968).

[8] A. G. Chynoweth, J. Appl. Phys. 27, 78 (1956).
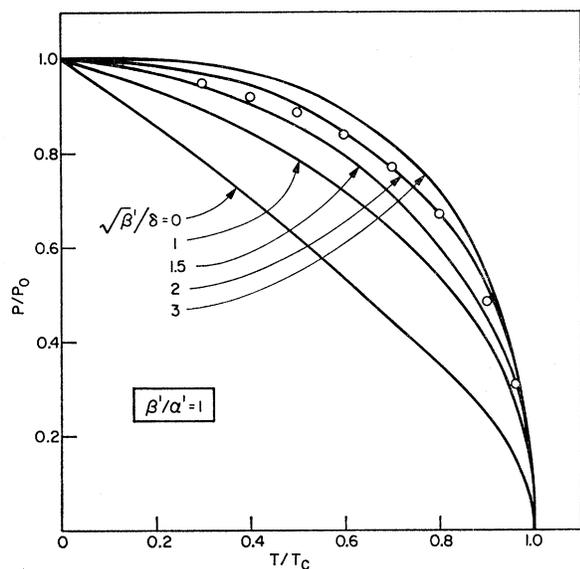
Fig. 1. The curves of reduced spontaneous polarization versus reduced temperature for the particular case $\beta'/\alpha'=1$ are reproduced from Fig. 8 of part I. They are compared with the experimental findings (open circles) for LiTaO$_3$.

Fig. 2. A number of curves, each derived from experimental data for LiTaO$_3$, are compared on a α'/β', $(\beta')^{1/2}/\delta$ plot. Curve (i) is derived from the shape of the spontaneous polarization curve, (ii) from the specific-heat discontinuity at the Curie temperature, (iii) from the soft-mode frequency at low temperatures, and (iv) from the value of spontaneous polarization at low temperatures. Shaded area (v) contains points consistent with the findings for soft-mode frequency near the Curie temperature combined with the limits (dashed curves) that the transition must be of displacement type and of second order. The filled circle and arrows indicate the degree of self-consistency of the data.

latent heat). As stressed by Glass, a fit of theory with experiment for the dielectric anomaly is complicated by a lack of knowledge concerning the "background" specific heat, which is due to all the other phonons in the lattice and far outweighs the "dielectric" contribution from the soft mode. Nevertheless, the magnitude of the specific-heat discontinuity at T_c is quite definite and is presumably explicable in terms of the dielectric contribution alone. Glass[7] measures the specific-heat jump to be 1.6 cal/mole deg which, in terms of the microscopic units used in the theoretical discussion of part II, is 1.6 (k/v), where k is the Boltzmann constant and v is the volume of a primitive cell (which, for the LiTaO$_3$ structures is[9] 106×10^{-24} cm^3 and contains two formula weights). Using the specific-heat theory of part II, e.g., Figs. 2 and 3 of that paper, this condition again defines a relationship between the parameters β'/α' and $(\beta')^{1/2}/\delta$ which is also shown in Fig. 2.

We note from the measurements of Glass that quantum effects are already quite apparent in the background specific heat for temperatures $\sim T_c$. They suggest a mean frequency for background phonons of ~ 400 cm^{-1}. As stressed in part II, this is not inconsistent with the use of a classical theory for the dielectric anomaly, since the soft-mode frequency has an energy which is always very much smaller than kT_c. Quantum effects for the soft mode will certainly not be apparent for temperatures much above 300°K.

It is apparent that the experimental and theoretical curve shapes for the specific-heat anomaly are qualitatively similar and, by choosing a rather arbitrary

[9] S. C. Abrahams, W. C. Hamilton, and A. Sequeira, J. Phys. Chem. Solids **28**, 1693 (1967).

background contribution, some test of curve shape can be attempted (see, for example Glass[7] who uses a Devonshire thermodynamic approach). Nothing very quantitative results from such a comparison because of the uncertainty concerning background contributions. Nevertheless, it is perhaps of interest to show the "best-fit" curves and this we do as follows. Jumping ahead, we take values of β'/α' and $(\beta')^{1/2}/\delta$ which will be found later to be close to the optimum values for LiTaO$_3$, viz., 2.3 and 1.9, respectively. Using these values we compute the classical specific-heat curve for the soft mode using the theory of part II. The result is shown in Fig. 3. This curve is now used for comparison with the experimental results (Fig. 4). The fit is quite good but not perfect. Some similarities and some differences are evident when a comparison is made with the Devonshire approach of Glass (Fig. 4 of Ref. 7). First, in both cases the specific-heat jump at T_c is experimentally some 15% smaller than theory, and the theoretical curve shapes are comparable. However, the statistical dielectric contribution to specific heat contains a sizable high-temperature tail
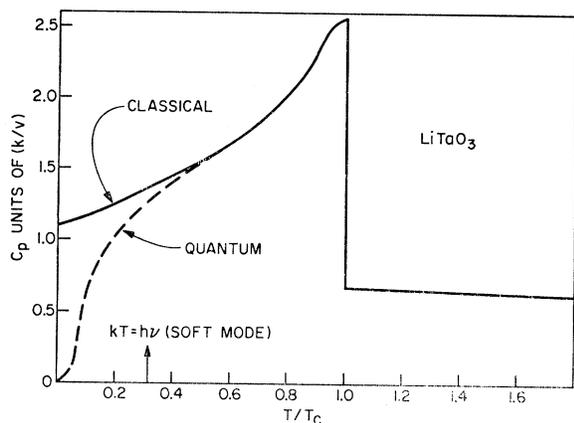
FIG. 3. The contribution of the soft mode to specific heat is calculated classically for LiTaO$_3$ using the optimum values of α'/β' and $(\beta')^{1/2}/\delta$ deduced from Fig. 2 and discussed in the text. The quantum-mechanical "freezing out" of the soft-mode specific heat affects the calculation for LiTaO$_3$ only when $T/T_c \ll 1$ and is indicated (dashed curve) in the figure.

(due primarily, though not entirely, to a temperature-independent contribution of $\frac{1}{2}(k/v)$ from the momentum coordinate of the soft mode) and it decreases much more slowly with decreasing temperature in the ferro-electric region. These differences have just been absorbed into the unknown background specific heat and do not affect significantly the fit with experiment. Also indicated in Fig. 3 is a semiquantitative estimate of the quantum-mechanical quenching of specific heat at low temperatures, calculated on the assumption that the soft mode is quasiharmonic at low temperatures.

C. Dielectric Constant

The dielectric constant at or about room temperature has been investigated for LiTaO$_3$ by Barker[10] by
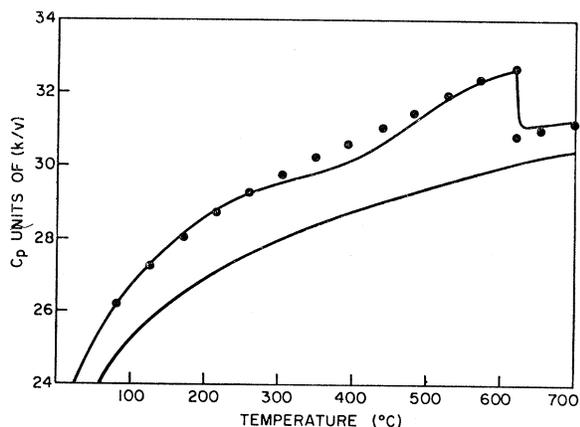
FIG. 4. The upper curve shows the experimental specific-heat curve for LiTaO$_3$. The best fit of theory (Fig. 3) with experiment is obtained by choosing a smooth "background" specific heat as indicated by the lower curve. The resulting total specific heat is then given theoretically by the filled circles.

[10] A. S. Barker, Jr., and J. A. Ditzenberger (to be published).

studying infrared reflection spectra. Assuming a dielectric function at frequency ω to be given by

$$\epsilon = \epsilon_\infty + \sum_j \frac{S_j \Omega_j^2}{\Omega_j^2 - \omega^2 + i\omega\gamma_j}, \qquad (2.1)$$

where S_j, Ω_j, γ_j, are the strength, frequency, and linewidth, respectively, of the jth infrared-active mode (and ϵ_∞ is the frequency-independent contribution to the dielectric constant arising from the vacuum and high-frequency electronic process), Barker[10] finds the best oscillator fit to give a value 30 for the strength of the soft mode in LiTaO$_3$ at room temperature. This then is a measure of the contribution of the soft mode to the dielectric constant at room temperature.

As the temperature approaches T_c, the contribution of the soft mode to dielectric constant becomes very large and the entire magnitude of the dielectric constant becomes, to a good approximation, that of the soft mode alone. Glass[7] has measured ϵ for LiTaO$_3$ near the Curie point at 1 kHz in both the polar and nonpolar phases. In each phase he finds a Curie-Weiss law for temperatures close enough to T_c as follows:

$$\epsilon_{\text{para}} = \frac{1.6 \times 10^5}{T - T_c}, \quad \epsilon_{\text{ferro}} = \frac{0.72 \times 10^5}{T_c - T}. \qquad (2.2)$$

Theoretically, from part I, we have (noting that $\epsilon = 4\pi\eta'\chi_{\text{ion}}$)

$$\epsilon_{\text{para}} = \frac{4\pi\eta'}{\gamma} \frac{T_c}{T - T_c} \frac{1}{\Phi_p}, \quad \epsilon_{\text{ferro}} = \frac{4\pi\eta'}{\gamma} \frac{T_c}{T - T_c} \frac{1}{\Phi_f}, \qquad (2.3)$$

where $\Phi_p = -\frac{1}{2}\Phi_f = \frac{2}{3} - \mu'$, and μ' has been computed in Fig. 12 of part I. Applying and adiabatic correction to ϵ_{ferro} (see Glass[7]), since the theory calculates isothermal values, modifies the numerical coefficient in (2.2) only marginally, to 0.76. Using (2.2) and (2.3) we deduce

$$\eta'/\gamma = 14(\tfrac{2}{3} - \mu'), \qquad (2.4)$$

where we have used the fact that $T_c = 890°$K. The value of $\frac{2}{3} - \mu'$ is already quite well determined from the spontaneous polarization and specific-heat curves of Fig. 2 since it is a rather slowly varying function of the parameters in this region of β'/α', $(\beta')^{1/2}/\delta$ space. Using Fig. 2 of this paper, and Figs. 6 and 12 of part I, we find

$$\tfrac{2}{3} - \mu' = 0.95 \pm 0.10, \qquad (2.5)$$

from which it follows that $\eta'/\gamma \sim 13 \pm 1$ for LiTaO$_3$.

D. Soft-Mode Frequency

The temperature dependence of the soft-mode frequency in the ferroelectric phase of LiTaO$_3$ has been measured both by a study of the infrared reflection spectra[10] and of the Raman spectra.[3] At very low temperatures, the soft mode has a frequency which

approaches 218 cm^{-1} as $T \rightarrow 0°$K. At room temperature the frequency has decreased to 200 cm^{-1}, and from $\sim 300°$K right up to the Curie point (890°K) it follows fairly closely the law $\omega(T) = 245[(T_c - T)/T_c]^{1/2}$ cm^{-1}.

At room temperature, we can combine Barker's value of 30 for the soft-mode strength [Eq. (2.1)] with the theoretical estimate [Eq. (7.7) of part I] for the contribution of the soft mode to ionic susceptibility. Neglecting linewidth, we can express the strength of the soft mode as

$$S = \frac{4\pi\eta\eta'S^2}{v\omega^2(T)}, \qquad (2.6)$$

where we have written the soft-mode frequency as $\omega(T)$ to conform with the notation of part II. A question arises here as to whether we are justified in using the same effective Hamiltonian parameters to interpret the low-frequency susceptibility results of Glass[7] and the high-frequency results of the infrared reflectivity and Raman experiments since, presumably, the former measures properties of the free system (frequencies below the piezoelectric resonances) and the latter properties of the clamped system. The answer is probably yes since, although the pertinent experiment does not appear to have been carried out for LiTaO$_3$, the low-frequency dielectric constant (for external field parallel to spontaneous polarization) in isomorphic LiNbO$_3$ is almost entirely connected with phonons and therefore very insensitive to frequency right up to frequencies of the order of, but still below, those of the phonon modes.[10,11]

Using (2.6) for $T = 300°$K, we find

$$\omega^2(300)/\omega_0^2 = (4\pi/30)(\eta'/\gamma)(\alpha'/\beta'), \qquad (2.7)$$

where we have used the fact that $\eta\gamma S^2/v\omega_0^2 = \alpha'/\beta'$ by definition. Since $\omega(0)/\omega(300) = 218/200$, it follows that

$$\omega^2(0)/\omega_0^2 = 0.50(\eta'/\gamma)(\alpha'/\beta'). \qquad (2.8)$$

Putting $\eta'/\gamma = 13$ as calculated above, (2.8) gives $\omega(0)/\omega_0$ as a function of α'/β'. But, $\omega^2(0)/\omega_0^2$ has already been calculated quite generally as a function of β'/α' and $(\beta')^{1/2}/\delta$ in Fig. 6 of part II. Combining the latter with (2.8) provides us with another relationship between these dimensionless parameters which is plotted, with the others, in Fig. 2.

For somewhat higher temperatures, both theory and experiment suggest a law $\omega(T) \propto (T_c - T)^{1/2}$. Consider first the small-anharmonicity approximation for soft-mode frequency near the Curie point which, although rather crude for the present case, has a very simple form and can be used to demonstrate our procedure for this limit. It is, for the ferroelectric phase,

$$\omega^2(T)/\omega_0^2 = = 2(\tfrac{2}{3} - \mu')(T_c - T)/T_c. \qquad (2.9)$$

Experimentally, this form holds right down to room

temperature. If this is to be so theoretically also, we must have

$$\omega^2(300)/\omega_0^2 = \tfrac{4}{3}(\tfrac{2}{3} - \mu'). \qquad (2.10)$$

Using (2.7) we find

$$\beta'/\alpha' = (\pi/10)(\eta'/\gamma)[(\tfrac{2}{3}) - \mu']^{-1}, \qquad (2.11)$$

which, by use of (2.4), reduces to $\beta'/\alpha' = 4.4$, demonstrating that LiTaO$_3$ is not a small-anharmonicity system ($\beta'/\alpha' \approx 1$), and indicating that the negative sign of the quartic anharmonicity plays a vital part in the appearance of ferroelectricity in this salt, i.e., in the presence of a positive quartic anharmonicity, this value of β'/α' would not sustain a ferroelectric order at any temperature.

To proceed more quantitatively for the case when anharmonicity is not small we use the theory developed in part II. Computing numerically we find a value $\beta'/\alpha' = 2.5 \pm 0.5$ where the error brackets indicate errors possibly incurred through the use of the approximation outlined in the last paragraph of part II coupled with the approximate evaluation of numerical integrals.

Coupling this result with the quite definite limits on β'/α' and $(\beta')^{1/2}/\delta$ resulting from the conditions that the phase transition is of second order and the nonpolar phase centrosymmetric, restricts these parameters to a small region $\beta'/\alpha' = 2.5 \pm 0.5$, $(\beta')^{1/2}/\delta = 2.0 \pm 0.4$, which is indicated in Fig. 2. As discussed in part II, the system has a centrosymmetric nonpolar state (displacement phase transition) if $\beta'/\alpha' > \tfrac{1}{2}(\beta'^{1/2}/\delta)^2$, and the transition is of second order if $\beta'/\alpha' < 1 + \tfrac{2}{5}(\beta'^{1/2}/\delta)^2$. The limiting curves are shown (dashed) in Fig. 2. One further restriction discussed in part II could also be applied in the present case. Experimentally the soft-mode frequency would seem to go to zero as $T \rightarrow T_c$. Classically, this occurs only when $\beta'/\alpha' > \tfrac{2}{3}(\beta'^{1/2}/\delta)^2$. However, because of the possible relaxation of this condition when quantum tunnelling is allowed for, we have not attached much weight to it even though it is not in conflict with the other findings.

E. Crystal-Structure Data

Single-crystal x-ray and neutron-diffraction studies of LiTaO$_3$ have been carried out by Abrahams et al.[9,12] The structure below the Curie point is well established, having crystal space group $R3c(C_{3v}^6)$ and the primitive cell contains two formula units. Above the Curie temperature the structure is almost certainly $R\bar{3}c(D_{3d}^6)$ which is centrosymmetric. The basic structure in the nonpolar phase consists of planes of oxygen ions as sketched in Fig. 5, with Ta ions in inversion center positions midway between adjacent planes and with the Li ions coplanar with the oxygen triangles. In going to the ferroelectric phase, the ions move with respect to their center of mass and, at room temperature,

[11] K. Nassau, H. J. Levinstein, and G. M. Loiacono, J. Phys. Chem. Solids **27**, 989 (1966).

[12] S. C. Abrahams and J. L. Bernstein, J. Phys. Chem. Solids **28**, 1685 (1967).
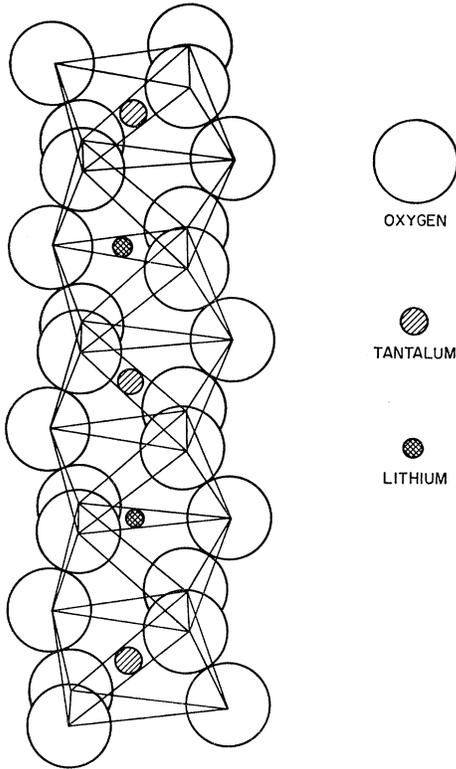
FIG. 5. The $LiTaO_3$ crystal structure in the nonpolar phase indicating a sequence of distorted (oxygen ion) octahedra along the polar axis. The Li ions are coplanar with oxygen triangles and the Ta ions are in inversion center positions midway between adjacent oxygen triangles. In the polar phase, the Li and Ta ions shift along the c axis with respect to the oxygen framework.

the magnitude of the respective shifts along the direction of the polar axis have been measured by Abrahams *et al.* to be $q(Li) = 0.43$ Å, $q(O) = -0.17$ Å, and $q(Ta) = 0.029$ Å.

Now, from part I (Sec. 3), the variable ξ is defined in terms of the q's for the single-soft-mode approximation by

$$q_b = u_b \xi, \quad \sum_b M_b u_b^2 = 1, \quad (2.12)$$

where b runs over all ions in a primitive cell, and where M signifies mass. Using (2.12) in conjunction with the measured shifts for $LiTaO_3$, we find $\langle \xi \rangle = 2.38$ amu$^{1/2}$ Å at room temperature.

This is of great interest since the spontaneous polarization is immediately expressible in terms of $\langle \xi \rangle$ as $\langle P \rangle = \eta'(S/v)\langle \xi \rangle$. Using (2.6), and putting the soft-mode strength equal to 30 at room temperature, we obtain

$$\langle P \rangle^2 = \frac{30\omega^2(300)\eta'}{4\pi v\eta}\langle \xi \rangle^2. \quad (2.13)$$

Everything is known in this equation except the ratio η'/η. Thus, using the measured values of spontaneous

polarization and soft-mode frequency at room temperature ($50\ \mu C/cm^2$ and $200\ cm^{-1}$, respectively) we obtain $\eta/\eta' = 1.34$.

The possibility of making use of the soft-mode strength in the present context to eliminate the charge-dependent variable S from the basic equation for spontaneous polarization has also been realized by Axe.[13] However, he uses the approximation $\eta = \eta' = 1$, thereby neglecting the electronic contribution to polarization except insofar as the use of the experimental value for soft-mode frequency includes it implicity.

F. Spontaneous Polarization as $T \to 0$

In part I, we found that a rather simple relationship existed between the spontaneous polarization at low temperatures and the Curie temperature T_c. We may write it

$$kT_c = \rho' v(\gamma/\eta')(\eta/\eta')\langle P_0 \rangle^2, \quad (2.14)$$

where ρ' as a function of the dimensionless variables has been computed in Fig. 10 of part I, Using the values $\eta/\eta' = 1.34$ and $\eta'/\gamma \approx 13$ established above, this reduces to direct evaluation of ρ'. Experimentally, we know the room-temperature value of spontaneous polarization is[5,6] $50\ \mu C/cm^2$ and that the Curie temperature is[7] $890°K$. Using the temperature dependence of polarization data of Glass,[7] we estimate a limiting value of spontaneous polarization as temperature $T \to 0$ to be $53\ \mu C/cm^3$. With these numbers, Eq. (2.14) reduces to $\rho' \approx 0.45$ which, from Fig. 10 of part I provides us with another relationship between β'/α' and $(\beta')^{1/2}/\delta$ for $LiTaO_3$. However, Eq. (2.14) also has solutions outside the $\eta'/\gamma \approx 13$ region and, for completeness, we have solved Eqs. (2.4) and (2.14) simultaneously to obtain the more general form of this final condition relating the dimensionless parameters; it is shown, with the others, in Fig. 2.

We are now in a position to assess the self-consistency of the data as interpreted by the effective-field theory. All the relevant information is in Fig. 2, where we find that it is possible to select a pair of values

$$\beta'/\alpha' = 2.5 \pm 0.5, \quad (\beta')^{1/2}/\delta = 2.0 \pm 0.25, \quad (2.15)$$

which, with the error brackets indicated, are able to account for all the data obtained thus far, i.e., five separate pieces of information concerning equalities and three concerning inequalities.

Using the values (2.15), it is now a straightforward process to estimate the values of the effective-Hamiltonian parameters for $LiTaO_3$. The equation $\langle P \rangle = (\eta'S/v)\langle \xi \rangle$, considered earlier in connection with Eq. (2.13), yields directly $\eta'S = 520\ cm^{3/2}\ sec^{-1}$, the errors involved here being dominantly those incurred experimentally and may be typically $\sim \pm 10\%$. From

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[13] J. D. Axe, Solid State Commun. **5**, 413 (1967).

this we calculate the frequency

$$(\eta\gamma S^2/v)^{1/2} = (\eta'S)(\eta/\eta')^{1/2}(\gamma/\eta')^{1/2}(1/v)^{1/2}$$
$$\approx 88 \text{ cm}^{-1}, \quad (2.16)$$

which in turn leads to $\omega_0 = (\beta'/\alpha')^{1/2}(\eta\gamma S^2/v)^{1/2} \approx 140$ cm^{-1}. The probable errors involved are perhaps $\pm 15\%$ for the former and $\pm 20\%$ for the latter.

The ratio of the anharmonicity coefficients, or more precisely $-A/(B)^{1/2}$, is also determined with fairly good accuracy as follows:

$$-A/(B)^{1/2} = (\beta'^{1/2}/\delta)(\eta\gamma S^2/v)^{1/2}$$
$$\approx 176 \text{ cm}^{-1}(\pm 25\%). \quad (2.17)$$

The absolute values of the anharmonicities, however, are determined by our present data with rather less precision. From Fig. 6 of part I we may determine the parameter β_c' which controls the Curie temperature through the Eq. (5.32) of part I which is

$$kT_c = (1/B)^{1/2}(\eta\gamma S^2/v)^{3/2}(\beta_c')^{3/2}. \quad (2.18)$$

In fact, Fig. 6 of part I is only plotted up to values of β'/α' slightly in excess of the value 2. We extend this plot to larger values of this parameter in Fig. 6 of the present paper. It follows, using the values (2.15), that $\beta_c' = 0.5 \pm 0.1$ for LiTaO$_3$ and hence, from (2.18), we find

$$(1/B)^{1/2}(\eta\gamma S^2/v)^{3/2} \approx 2500k, \quad (\pm 30\%), \quad (2.19)$$

where k is the Boltzmann constant. From (2.17) and (2.19) we obtain

$$A \approx -90k \text{ amu}^{-2} \text{ Å}^{-4}, \quad B \approx 6k(\text{amu})^{-3}(\text{Å})^{-6} \quad (2.20)$$

with an accuracy only of order plus or minus a factor 3.

This completes the determination of the parameters which govern the ferroelectric properties (in the effective-field approximation) for lithium tantalate. We list them, together with the crude assessment of their accuracy in Table I. We have already made some comment on the self-consistency of the approximation, but it is more instructive to put this into a form where we can compare directly the predictions of theory with experiment. Starting from a definite choice for the temperature-independent parameters in the effective Hamiltonian, we have calculated 13 separate linear dielectric properties for LiTaO$_3$ in Table II. Eleven of these have been measured to date. It is also possible to calculate the ionic contributions of the lattice to the nonlinear properties for this salt. However, since experimental results have not yet become available for the separate electronic and ionic contributions to nonlinear properties, we shall not discuss the theoretical calculations for the latter at the present time.

The comparison of theory with experiment for the linear properties is shown in Table II. Only two of the theoretical estimates are in error by more than 20%, these being the soft-mode frequency at low temperatures (28% error) and the strength of the soft mode (45%
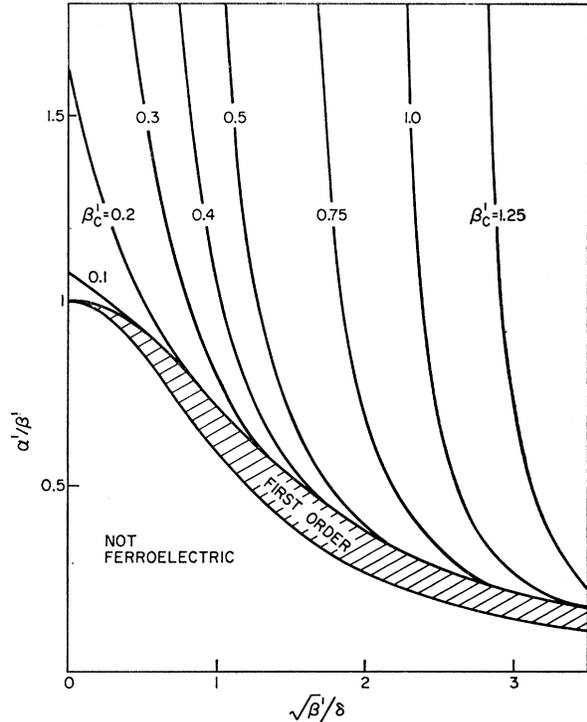
FIG. 6. The parameter β_c' which controls the Curie temperature through Eq. (2.18) is plotted as a function of α'/β' and $(\beta')^{1/2}/\delta$ for a ferroelectric system exhibiting a second-order phase transition.

error). These errors can be reduced (by varying the effective-Hamiltonian parameters) only at the expense of markedly increasing the errors in a number of other properties. Thus, Table II represents about the best that can be done with the present theory using completely temperature-independent parameters. This degree of agreement between theory and experiment is already quite gratifying, but it can be improved very markedly by allowing for the temperature dependence of just one parameter, the Lorentz parameter γ. This, in turn, may be indicative of the importance of correlation effects neglected in the effective field approximation or possibly of a markedly position-dependent Lorentz

TABLE I. Effective-Hamiltonian parameters for LiTaO$_3$:
$$\mathcal{H}_{eff} = (1/v)\{\tfrac{1}{2}(\pi^2 + \omega_0^2\xi^2) + A\xi^4 + B\xi^6 - \eta S\xi[E + (\gamma/\eta')\langle P \rangle]\},$$
$$\langle P \rangle = (\eta'S/v)\langle \xi \rangle.$$

Directly measurable
$v = 106 \times 10^{-24}$ cm^3
Deduced from statistical calculations
$\omega_0 = 140$ cm$^{-1}(\pm 20\%)$
$-A/\sqrt{B} = 176$ cm$^{-1}(\pm 25\%)$
$A = -90k$ amu^{-2} Å^{-4} ($\pm$factor 3)
$B = 6k(\text{amu})^{-3}(\text{Å})^{-6}$ ($\pm$factor 3)
$\eta'S = 520$ cm$^{3/2}$ sec^{-1} ($\pm 10\%$)
$\eta/\eta' = 1.3$ ($\pm 10\%$)
$\eta'/\gamma = 13$ ($\pm 10\%$)

TABLE II. The best fit of theory with experiment obtainable using completely temperature-independent parameters; obtained with $\omega_0 = 128$ cm^{-1}, $A = -71k$(amu)$^{-2}$(Å)$^{-4}$, $B = 4.5k$(amu)$^{-3}$(Å)$^{-6}$, $\eta'S = 500$ cm$^{3/2}$ sec^{-1}, $\eta/\eta' = 1.3$, $\eta'/\gamma = 12$.

Property	Theory	Expt	Difference
1. Curie Temperature T_c (°K)	894	890	+0%
2. Paraelectric susceptibility near T_c	$1.50 \times 10^5/(T - T_c)$	$1.6 \times 10^5/(T - T_c)$	−6%
3. Ferroelectric susceptibility near T_c	$0.75 \times 10^5/(T_c - T)$	$0.72 \times 10^5/(T_c - T)$	+4%
4. Shape of polarization curve	1.00[a]	1.04[a]	−4%
5. Soft-mode frequency near T_c in the nonpolar phase (cm^{-1})	$115[(T - T_c)/T_c]^{1/2}$	not known	...
6. and in the polar phase (cm^{-1})	$230[(T_c - T)/T_c]^{1/2}$	$245[(T_c - T)/T_c]^{1/2}$	−6%
7. Specific-heat jump at T_c (cal/mole deg)	1.9	1.6	+19%
8. Polarization near T_c (μC/cm^2)	$86.3[(T_c - T)/T_c]^{1/2}$	$85[(T_c - T)/T_c]^{1/2}$	+2%
9. Energy of order	$0.63kT_c/v$	not known	...
10. Magnitude $\langle \xi \rangle$ of distortion from nonpolar phase, at room temperature (amu$^{1/2}$ Å)	2.79	2.38	+17%
11. Spontaneous polarization as $T \to 0$ μC/cm^2	60	53	+13%
12. Soft-mode frequency as $T \to 0$ (cm^{-1})	279	218	+28%
13. Soft-mode strength at room temperature	16.5	30	−45%

[a] Measured as the value of the radius vector for the case $P/P_0 = T/T_c$.

factor γb. For the moment, we shall merely introduce this temperature dependence as an extra parameter to be determined, like to others, by a comparison of theory with experiment. The problem is still comfortably over-determined. In Table III, we show the results of the modified theory in which the Lorentz parameter is allowed to vary smoothly from $\gamma \to \gamma/3$ as the temperature goes from $T_c \to 0$. Thus, only the low temperature properties from Table II have been modified. The result is to reduce the error between theory and experiment to less than 10% in every case except one. The one exception is now the specific-heat discontinuity at T_c with an error of 19% an estimate which is not changed by the introduction of a temperature dependence to γ. This discrepancy is not serious since the experimental accuracy of this result would seem only a little better than ±20% (Glass[7]).

We have managed to obtain a fairly quantitative description of the ferroelectric properties of LiTaO$_3$ in terms of an effective Hamiltonian. To this extent the immediate goal, as set out in part I, has been achieved for this particular system. However, as stressed in part I, the statistical problem is only part of the story. Its solution, in the effective-field approximation, has proved tractable without the necessity of recourse to a detailed

TABLE III. Like Table II but with one modification. The parameter γ is allowed to be temperature-dependent to the extent $\gamma \to \frac{1}{3}\gamma$ as $T_c \to T \to 0$. Thus, only the low-temperature results 10–13 are modified from Table II, on substituting $\gamma/3$ for γ.

Property	Theory	Expt	Difference
10. Magnitude $\langle \xi \rangle$ of distortion from nonpolar phase, at room temperature (amu$^{1/2}$ Å)	2.37	2.38	−0%
11. Spontaneous polarization as $T \to 0$ (μc/Cm^2)	51	53	−4%
12. Soft-mode frequency as $T \to 0$ (cm^{-1})	205	218	−6%
13. Soft-mode strength at room temperature	30.6	30	+2%

model for the system. This is the strength of the method. It also stresses, however, that there is still a lot to be done before a complete understanding of the origin of all the important microscopic contributions to energy can be obtained. Nevertheless, even at this stage, it is instructive to ponder the results obtained for the parameters of the effective Hamiltonian. They do shed light on a few of the difficulties which will be encountered when an attempt is made to construct a realistic model for a ferroelectric system of the present type.

3. EFFECTIVE CHARGES IN LiTaO$_3$

In constructing the effective (or "displacement") Hamiltonian in part I we did, in fact, make use of a rudimentary model, using the concepts of effective point charges and electronic polarizabilities to construct microscopic equations connecting these quantities to parameters of the displacement Hamiltonian. We have not used these equations thus far and, since we feel that the form of the displacement Hamiltonian is probably more general than the model used in part I to establish it, we do so now only to point out the great care that is necessary in assessing results on such a simple model.

In Sec. 3 of part I, we described the ferroelectric system in terms of effective point charges e_b (each experiencing an internal field $E_{loc}{}^b$) and electronic polarizabilities α_b. From part I, using the one-soft-mode approximation and dropping all tensor notation (all displacements along the polar axis), we have

$$S = \sum_b e_b u_b, \tag{3.1}$$

$$\eta S = \sum_b (1 + \eta' \alpha \gamma_b) e_b u_b, \tag{3.2}$$

$$\eta \gamma S = \sum_b \eta' \gamma_b e_b u_b, \tag{3.3}$$

where

$$\alpha = \frac{1}{v} \sum_b \alpha_b, \tag{3.4}$$

$$\eta' = \left(1 - \frac{1}{v} \sum_b \alpha_b \gamma_b\right)^{-1}, \tag{3.5}$$

$$E_{\text{loc}}{}^b = E + \gamma_b \langle P \rangle. \tag{3.6}$$

In all the above, the summation b runs over all effective charge sites in the primitive cell of the lattice.

At first sight, it is tempting to think of the charge e_b as the static charge (nuclear plus electronic) which resides in some suitably chosen volume surrounding site b, and to think of γ_b as the Lorentz parameter computed for the site b itself. Let us proceed initially with this picture. Now, for LiTaO$_3$, in going from the nonpolar to the polar state, the positive ions (lithium and tantalum) move in the (say) positive direction with respect to the center of mass, the negative ions in the negative direction. Thus, γ_b is positive for all sites. Since polarizabilities are positive for all ions, it follows that η' must be greater than unity [Eq. (3.5)]. Also, from part I, $\langle P_{\text{ion}} \rangle = (1/\eta') \langle P \rangle$, so that the ionic contribution to polarization is less than the total (ionic plus electronic) polarization. This all seems reasonable enough; but consider the following. From the calculations of the previous section $\eta' S \approx 500$ cm$^{3/2}$ sec^{-1} and $\eta/\eta' \approx 1.3$. Therefore, $\eta S \approx 650$ cm$^{3/2}$ sec^{-1} and, from (3.3),

$$\sum_b \gamma_b e_b u_b = (\eta S)(\gamma/\eta') = 54 \text{ cm}^{3/2} \text{ sec}^{-1}, \tag{3.7}$$

where we have put $\eta'/\gamma = 12$ from Table II. Now, combining (3.1) and (3.2), we find

$$650 = (500/\eta') + 54\alpha\eta', \tag{3.8}$$

which is an equation for η' if we can estimate α. The latter can be done by noting the published value[14] for the refractive index at optical frequencies of LiTaO$_3$, which is $n_{\text{optic}} = 2.18$, the difference between ordinary and extraordinary index of refraction being completely negligible in the present context. At optical frequencies, the ionic motion is frozen out and the electronic component of susceptibility χ_{elec} dominates. From Eq. (3.6) of part I we find $\chi_{\text{elec}} = \eta'\alpha$. Using this, together with

$$\epsilon_{\infty} = (n_{\text{optic}})^2 = 1 + 4\pi\chi_{\text{elec}}, \tag{3.9}$$

produces the result $\eta'\alpha \approx 0.30$ which, combined with (3.8) gives $\eta' = 0.79$ and, therefore, $\eta = 1.03$. This finding contradicts the initial assertion that η' must be greater than unity in LiTaO$_3$. Where is the flaw?

Before taking up this question it is helpful to assemble some more conflicting and puzzling evidence. In the "crystal-structure data" subsection of the previous

section, we quote the magnitudes of the ionic shifts (from the nonpolar state) at room temperature as measured for LiTaO$_3$ by x-ray and neutron diffraction. Using (2.12) we calculate the components u_b of the normalized eigenvector of the soft mode as $u(\text{Li}) = 0.18$, $u(\text{Ta}) = 0.012$, $u(0) = -0.071$, in units of amu$^{-1/2}$. Combining this with (3.1) we can learn something about the effective charges. Suppose, as seems reasonable, that lithium goes into LiTaO$_3$ essentially as Li$^+$ with charge $+1$ (units of electronic charge). This being so we have

$$e(\text{Ta}) + 3e(0) = -1, \tag{3.10}$$

in terms of which (3.1) becomes

$$2\{0.18 + 0.012e(\text{Ta}) + 0.071[1 + e(\text{Ta})]\}$$
$$= 500/\eta' \text{ cm}^{3/2} \text{ sec}^{-1} \text{ amu}^{1/2}. \tag{3.11}$$

This reduces to

$$e(\text{Ta}) = (8.1/\eta') - 3.0. \tag{3.12}$$

Thus, this is the value of effective tantalum charge which would appear to be in accord with experimental dielectric measurements and, in particular, with the measured value of spontaneous polarization. If we neglect electronic effects, putting $\eta = \eta' = 1$, we find the ionic values $e(\text{Ta}) \approx +5$, $e(0) \approx -2$. But this is to be compared with the results of a nuclear magnetic resonance study of LiTaO$_3$ by Peterson et al.[15] who also neglect electronic effects and, calculating the electric field gradient at the nucleus in question from an effective point charge environment, find $e(\text{Ta}) = 1.21$, $e(0) = -0.74$.

At least part of the explanation must be that the nuclear magnetic resonance work and the effective charge calculations of the present section measure two essentially different quantities. The former is concerned with the static environment at any particular temperature, the latter with a movement of charge in going from the nonpolar to the polar state.[16] This, however, cannot be the whole story since, in terms of any set of effective ion point charges, the earlier finding that $\eta' < 1$ is still clearly anomalous.

We are led to a possible understanding of the latter by taking note of two other rather surprising results for the effective-Hamiltonian parameters as calculated in Sec. 2. First, the Lorentz parameter γ, which on the naïvest of approximations is the familiar $4\pi/3$, is found to be very small indeed; probably ~ 0.1. Second, a variation in this from γ to $\gamma/3$ as temperature is reduced from T_c to 0 seems very large in view of the calculation of Barker and Loudon[17] for the variation of some Lorentz parameters γ_b in isomorphic LiNbO$_3$ (take care to distinguish the soft-mode Lorentz parameter γ and the Lorentz parameters per site γ_b when the latter vary from site to site).

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[14] P. V. Lenzo, E. H. Turner, E. G. Spencer, and A. A. Ballman, Appl. Phys. Letters **8**, 81 (1966).

[15] G. E. Peterson and P. M. Bridenbaugh, J. Chem. Phys. **48**, 3402 (1968).

[16] This suggestion was made by A. S. Barker, Jr.

[17] A. S. Barker and R. Loudon, Phys. Rev. **158**, 433 (1967).

Consider a tantalum ion in $LiTaO_3$. It has an ion core with charge $+13$ which is quite compact, and an outer shell of anything from 13 to 8 electrons (depending on the degree of covalency) which spreads out over a much larger volume in the lattice. Now, suppose that the degree of covalency in $LiTaO_3$ is sufficiently large to violate the point charge approximation for dipolar interactions. The Lorentz parameter γ_b at the site b will then be position-dependent and vary somewhat over the effective volume of the tantalum ion. Suppose, for the sake of definiteness, that there are 11 outer shell electrons and that the average value of the Lorentz parameter for these more widely distributed electrons is some 10% larger than the value γ_b at the core site. Such a modest variation is perhaps not unreasonable. The Lorentz force on the ion as a whole is now proportional to

$$[13-11(1.1)]\gamma_b = 0.9\gamma_b = \gamma_b(\text{eff})e(\text{Ta}), \quad (3.13)$$

where we have defined an effective Lorentz parameter $\gamma_b(\text{eff})$ and hence an associated effective field $E_{\text{loc}}{}^b(\text{eff}) = E + \gamma_b(\text{eff})\langle P \rangle$ for the whole ion. Since, in the present example, $e(\text{Ta}) = 2$, then $\gamma_b(\text{eff}) = 0.45\gamma_b$. The numbers in this example are not, of course, to be taken too seriously. They do, however, illustrate that if the point charge approximation for dipolar interactions breaks down, then the effective Lorentz parameter for an ion centered at site b may bear little relationship to the actual value of the Lorentz parameter evaluated at or near that site; it may even be of opposite sign. This may help to explain the small value found for the mode parameter γ in $LiTaO_3$. It could also explain a fairly large temperature dependence of this same parameter looking on it as a variation caused by the change of environment in going from the nonpolar to polar state again magnified by the effect depicted in (3.13). A small

variation in γ_b can cause a much larger percentage variation in $\gamma_b(\text{eff})$ and hence in the soft mode γ.

We can now put all these ideas together. Let us consider ions at sites b with charge $+N_b e$ on the ion cores and charge $-n_b e$ in the outer shells (e being the magnitude of the electronic charge). Even in the nonpolar state where $\langle P \rangle = 0$, an ion b probably does not vibrate simply as an undeformed effective charge $(N_b - n_b)e$. When the ion is not in a centrosymmetric environment, it will almost certainly distort under the effects of a combination of electrostatic and covalent forces. In Fig. 7, we depict the motion schematically. Let the ion core move through a distance q_b and the electrons in the outer shell, on the average, through a distance $q_b + \delta q_b$. Then,

$$P = \frac{1}{v}\sum_b N_b e q_b - n_b e(q_b + \delta q_b)$$

$$= \frac{1}{v}\sum_b (N_b - n_b + \delta n_b)e q_b = \frac{1}{v}\sum_b e_b{}^+ q_b, \quad (3.14)$$

where we have defined

$$\delta n_b q_b = -n_b \delta q_b, \quad \text{and} \quad e_b{}^+ = (N_b - n_b + \delta n_b)e. \quad (3.15)$$

The sign of $\delta n_b/(N_b - n_b)$ is such that electrostatic forces tend to make it positive and covalency effects tend to make it negative. If we associate Peterson's[15] charge values with $(N_b - n_b)e$, then it is clear that $\delta n_b/(N_b - n_b)$ is positive for $LiTaO_3$ and that, therefore, electrostatic forces dominate the ionic distortion. If we assume, as a first approximation, that $\delta q_b \propto q_b$ then δn_b is independent of the amplitude of the motion. All the forces operating in this motion are already contained in the parameters ω_0, A, B, of the displacement Hamiltonian (1.1).

If we now consider the polar state, the situation is changed only by the addition of a local field $E_{\text{loc}}{}^b$ which adds to the polarization an electronic term $\alpha_b E_{\text{loc}}{}^b$ to give

$$P = \frac{1}{v}\sum_b (e_b{}^+ q_b + \alpha_b E_{\text{loc}}{}^b), \quad (3.16)$$

where $E_{\text{loc}}{}^b$ [not $E_{\text{loc}}{}^b(\text{eff})$] is appropriate for the polarizability term. It is clear that $e_b{}^+$ is the important effective charge to consider in conjunction with polarization.

However, another important point arises when we consider the contribution in energy made by the long-range forces (or effective field). This takes the form [compare Eq. (3.3) of part I]

$$V' = \frac{-1}{v}\sum_b [e_b q_b E_{\text{loc}}{}^b(\text{eff}) - n_b e(\delta q_b)E_{\text{loc}}{}^b$$

$$+ \tfrac{1}{2}\alpha_b (E_{\text{loc}}{}^b)^2]. \quad (3.17)$$

If we take α_b to be independent of q_b, we can drop the final term in (3.17) since we are only concerned with

q+δq

q   -(q+δq)

-ne   -ne   -q

+Ne   +Ne

$t = \frac{\pi}{2\omega}$

$t = 0$ OR $\frac{2\pi}{\omega}$ $t = \frac{\pi}{\omega}$

$t = \frac{3\pi}{2\omega}$

FOR OXYGEN IN $LiTaO_3$

$N = 6$
$n \approx 6.7$
$\delta q/q \approx 0.3$

FIG. 7. A schematic representation of the vibrational motion of an oxygen ion in the nonpolar phase, representing the ion by a core of charge $+Ne$ vibrating with amplitude q, and a shell (charge $-ne$) with amplitude $q + \delta q$. The results for $LiTaO_3$ suggest that for this salt, $\delta q/q$ might be of the order of 30%.

the motion of q_b. Doing this we find

$$V' = \frac{-1}{v} \sum_b [e_b{}^+ q_b E + e_b{}^* q_b \gamma_b (\text{eff}) \langle P \rangle], \quad (3.18)$$

where

$$e_b{}^* = (N_b - n_b + w_b \delta n_b) e, \quad (3.19)$$

and

$$w_b = \gamma_b / \gamma_b (\text{eff}). \quad (3.20)$$

Thus, let us suppose that the system cannot be described in terms of a single set of effective charges (one for each ion) and that we must concern ourselves at least with both a core and a shell charge for each ion. It is readily verified that all the previous work on the displacement Hamiltonian is still valid, but now with the definitions

$$S = \sum_b e_b{}^+ u_b, \quad (3.21)$$

$$\eta S = \sum_b (1 + \eta' \alpha \gamma_b') e_b{}^+ u_b, \quad (3.22)$$

$$\eta \gamma S = \sum_b \eta' \gamma_b' e_b{}^+ u_b, \quad (3.23)$$

$$\alpha = \frac{1}{v} \sum_b \alpha_b, \quad (3.24)$$

$$\eta' = \left(1 - \frac{1}{v} \sum_b \alpha_b \gamma_b\right)^{-1}, \quad (3.25)$$

where

$$\gamma_b' = (e_b{}^* / e_b{}^+) \gamma_b (\text{eff}). \quad (3.26)$$

Comparing with Eqs. (3.1) to (3.5) we see that $e_b{}^+$ has replaced e_b, and that γ_b' has replaced γ_b *except* in the definition of η' in (3.25). Since it is only $\gamma_b(\text{eff})$ which is required to be positive for all sites, the finding $\eta' < 1$ is no longer necessarily anomalous. It would result if at some sites (probably the oxygen sites in LiTaO$_3$) γ_b is negative but $\gamma_b(\text{eff})$ positive. Thus, for example, if we write $N = 6$ and $n \approx 7$, this could result if the negative value of γ_b for the oxygen cores has a magnitude greater than 7/6 times that appropriate for the ion shell. We stress, however, that this is being suggested as only one of perhaps many possible explanations in terms of yet more sophisticated models.

Within the new framework we write formally $P_{\text{ion}} = (S/v)\xi$, where $S = \sum_b e_b{}^+ u_b$. It is evident that P_{ion} is now no longer an ionic contribution to polarization in the usual sense but already includes all the electronic contribution resulting from ionic distortion due to short-range forces. Only the contribution from the effective field is missing, and it is just this extra electronic term which is corrected for by the parameter η' when we write $\langle P \rangle = \eta' \langle P_{\text{ion}} \rangle$ for the ferroelectric state.

Finally, we can extract from our numbers just a little information concerning the degree of ionic distortion present in LiTaO$_3$ when the ions are removed from centrosymmetric positions either by the onset of ferroelectricity or merely by vibrational motion in the nonpolar phase.

We have earlier evaluated the components u_b of the normalized eigenvector of the soft mode for LiTaO$_3$. We readily verify that, because of its very large mass, the tantalum ion contributes only a small amount ($\sim 10\%$) to a sum $\sum_b e_b u_b$. Since we expect the tantalum ion to be considerably less polarizable than the oxygens, it probably contributes even less to $\sum_b e_b{}^+ u_b$. Lithium is likely to be present essentially as Li$^+$ and, with a small and compact closed-shell structure, the distortion effects referred to above are likely to be small for it, allowing us to write $e^+(\text{Li}) \approx e(\text{Li}) \approx 1$ electronic unit e. A charge conservation equation of the form (3.10) need not hold for the effective charges $e_b{}^+$ so that we are not justified in using the results (3.10)–(3.12) to write $e^+(\text{Ta}) = 7$, $e(0) = -2.7$ in units of e. Nevertheless, the contribution of the tantalum ion being small, we shall not be greatly in error by allowing about 10% for its contribution to $\sum_b e_b{}^+ u_b$ to estimate

$$0.18e - 0.21 e^+(0) \approx (0.6/\eta') e \approx 0.75 e, \quad (3.27)$$

which is $e^+(0) \approx -2.7e$ and agrees with the earlier estimate. We are not able, however, to say anything about $e^+(\text{Ta})$ and the above value of $7e$ may be completely spurious. If, as seems likely, the nuclear magnetic resonance experiments measure something approximating $(N_b - n_b)e$, then we calculate for the oxygen ions $\delta n \approx -2$. Putting $n \approx 7$, it follows that $\delta q / q = -\delta n / n \approx 0.3$. In words, the outer electron shell of an oxygen ion in LiTaO$_3$ has thermal vibrations in the nonpolar state with amplitude some 30% larger than that of the ion core. A similar effect, but reduced in magnitude by a factor η' (i.e., from about 30% to 25%) results for the thermally averaged positions of the oxygen core and shell when the system cools below its Curie temperature.

ACKNOWLEDGMENTS