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Statistical Theory for Displacement Ferroelectrics

M. E. LINES
Bell Telephone Laboratories, Murray Hill, New Jersey

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A statistical approximation is developed for displacement ferroelectrics which enables dielectric properties to be described directly in terms of a limited number of microscopic parameters. In particular, for systems with only one grossly temperature-dependent optic mode of lattice vibration, the number of parameters is sufficiently few that they can be overdetermined by a direct comparison of theory with dielectric properties alone. These microscopic parameters are very much more closely connected with the fundamental microscopic forces in the system than are the more familiar macroscopic (thermodynamic) parameters. For a single-soft-mode system, many dielectric properties are calculated quantitatively in terms of the microscopic parameters. These properties include polarization, soft-mode frequency, static and dynamic susceptibilities, all as functions of temperature both close to and away from the Curie point. Sections discussing the order of the phase transition and some nonlinear properties of the polar phase are also presented. In parts II and III of the present series of papers the method is extended and used to discuss in detail the dielectric properties of lithium tantalate.

1. INTRODUCTION

THIS paper is the first of a series of three discussing ferroelectric systems and, in particular, displacement ferroelectrics for which a transition to a polar state arises from instabilities against particular modes of vibration.[1–3] They are particularly concerned with the description of bulk dielectric properties, such as polarization, susceptibilities, Curie temperature, nature of the phase transition etc., in terms of microscopic concepts, by use of statistical mechanics.

In interpreting the experimental findings for displacement ferroelectrics, great emphasis has always been placed on macroscopic (thermodynamic) theories expressed in terms of phenomenological free-energy expansions. This contrasts greatly with the situation in magnetic studies, where very little use is made of macroscopic theories, bulk magnetic properties being almost always described directly in terms of a microscopic effective (or spin) Hamiltonian by use of statistical mechanics. The reason for the difference in emphasis is not difficult to find; to the present time, no microscopic "workhorse" theory for displacement ferroelectrics has been presented which is immediately useful (from the experimentalists point of view) in the sense that it contains few enough parameters that they can be determined, or even overdetermined, from dielectric measurements alone.

Thus, the question we are trying to answer here is whether the dielectric properties of displacement ferroelectrics can be described, in a reasonably quantitative fashion, in terms of a few microscopic parameters. If we are concerned with statistical rigor, then the answer is no. This is apparent from the numerous theoretical papers[4–10] which have calculated the formal relationships between microscopic concepts and the thermodynamic parameters of a free-energy expansion. Such relationships, though theoretically illuminating, have limited practical value as far as the experimentalist is concerned, since they relate myriad microscopic parameters to a handful of macroscopic parameters.

In this paper we demonstrate that, by accepting a statistical approximation analogous to that used in the cluster theories of magnetism, it is possible to derive a microscopic effective Hamiltonian which, at least for some displacement ferroelectrics, has few enough parameters to enable their direct evaluation by a comparison of theory with experiment. These parameters are microscopic quantities, and are, therefore, very much more closely connected with the fundamental microscopic forces in the system than are the macroscopic parameters associated with thermodynamic concepts, in terms of which quantitative theories for displacement ferroelectrics are usually cast.

The theory developed in this paper is extended and used in the following papers (parts II and III of the present series) to discuss the dielectric properties of lithium tantalate. We find that it is capable of giving a good quantitative description of the lithium-tantalate system and that the problem is overdetermined to a considerable degree, thus enabling the self-consistency of the method to be assessed. The quantitative values determined for the microscopic parameters of the effective Hamiltonian then prove useful in elucidating some less obvious features of the detailed microscopic behavior of that particular system.

To construct a microscopic theory for ferroelectrics from first principles necessarily entails the use of a

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[1] P. W. Anderson, in *Fizika Dielektrikov*, edited by G. I. Skanavi (Akademiia Nauk SSSR, Moscow, 1960).

[2] W. Cochran, Advan. Phys. **9**, 387 (1960).

[3] V. G. Vaks, V. M. Galitskii, and A. I. Larkin, Zh. Eksperim. i Teor. Fiz. **51**, 1592 (1966) [English transl.: Soviet Phys.—JETP **24**, 1071 (1967)].

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[5] B. D. Silverman and R. I. Joseph, Phys. Rev. **129**, 2062 (1963).

[6] B. D. Silverman and R. I. Joseph, Phys. Rev. **133**, A207 (1964).

[7] B. D. Silverman, Phys. Rev. **135**, A1596 (1964).

[8] S. Doniach, in *Proceedings of the International Conference on Lattice Dynamics*, edited by R. F. Wallis (Pergamon Press Ltd., London, 1965).

[9] R. A. Cowley, Phil. Mag. **11**, 673 (1965).

[10] P. C. Kwok and P. B. Miller, Phys. Rev. **151**, 387 (1966).

formidable number of parameters about which little of a quantitative nature is known *a priori* (e.g., all the significant interionic forces, their first several derivatives with respect to the crystal axes, electron-ion interactions, electronic polarizabilities etc.). Nevertheless, a formal use of lattice-dynamical theory allows the motion of the system to be cast in terms of normal modes of vibration, the translational invariance of the lattice being used to define a reciprocal-lattice wave vector. The basic simplicity of the ferroelectric system is that its dielectric properties depend directly only on the zero-wave-vector optic modes, and, of these, only a very few strongly temperature-dependent (or soft) modes contribute significantly.

The special difficulty which arises in the statistical part of the theory is that, for ferroelectrics, the long-range electrostatic dipolar interactions reduce the harmonic contributions to the "soft" mode or modes to such an extent that anharmonic contributions can become large by comparison, thereby prohibiting the use of conventional perturbation theories. Various attempts have been made to overcome this difficulty. Silverman and Joseph[5–7] have used a transformation to include a large part of the anharmonicity in the unperturbed Hamiltonian using this approach to discuss the dielectric properties of the paraelectric phase. Another line of development has been pursued by Doniach[8] who has outlined a derivation of free energy based on a variational principle. Cowley,[9] and Kwok and Miller[10] have attacked the quantum-statistical problem by use of the Green's-function techniques of many-body theory. In these theories, the many-body aspect of the problem takes the form of interactions between the zero wave-vector modes of the system and the other nonzero wave-vector modes. The description therefore includes effective-mode parameters for all phonon modes, essentially an infinite number of microscopic "unknowns."

In this paper we make use of the fact that for ordinary (not ferroelectric) systems for which dipolar forces are less important, the optic-mode frequencies are often fairly insensitive to wave vector. Thus, we postulate that in the absence of long-range dipolar interactions, many dielectric systems have optic modes which can be described essentially in terms of a single primitive cell of the lattice, i.e., the relative phase of the oscillations in neighboring primitive cells has only a minor effect on the optic mode frequencies. In this approximation, the system consists of essentially independent primitive cells, each described by the same set of optic-mode frequencies. This being so, we now include the interactions between cells in an effective-field approximation, centering our attention on one cell and replacing all others by their ensemble (thermal) averages.

This produces an approximation essentially equivalent to those of the cluster theories of magnetism, for which interactions within a certain cluster of magnetic ions are treated rigorously but the interactions between the cluster and the rest of the lattice are replaced by effective fields. The approximation is basically a high-temperature one but should give a meaningful approximation over the entire temperature range and, in view of the long range of the dipolar forces is possibly more accurate for ferroelectrics than for the analogous magnetic theories referred to.

In this description, by accepting the statistical approximations involved, we have gained very significantly in reducing the number of parameters required to describe the system. The resulting effective or "displacement" Hamiltonian consists only of a sum of effective oscillators, one for each soft mode of the primitive cell and, in particular, for ferroelectric systems which have only one grossly temperature-dependent mode of lattice vibration (lithium tantalate is a good example) we reduce the effective Hamiltonian to that of a single effective oscillator for which the "unknowns" contained therein can be overdetermined by direct comparison of theory with experiment.

We have carried out the relevant statistical calculations using classical statistics since, for this case, there is no need to limit the calculations to small anharmonicity systems or use any form of perturbation approximation. This is important because lithium tantalate (to be discussed in detail in part III) is well outside the small-anharmonicity region and also because (as discussed in part II), without limitations associated with small anharmonicity, the effective or "displacement" Hamiltonian method can be readily extended to discuss order-disorder ferroelectrics as well as displacement systems. Moreover, most ferroelectric systems are essentially classical near and above their Curie temperatures, so that the use of classical statistics gives an adequate description of the phase transition for most cases.

In Sec. 2 we describe the theoretical foundation of the displacement Hamiltonian and in Sec. 3 derive it in detail. In Sec. 4 we develop formally the classical statistical theory for the general many-mode system. In Sec. 5, quantitative calculations are performed for a system which has only one strongly temperature-dependent mode. Calculations are made of polarization (over the entire polar region), Curie temperature, susceptibilities as functions of temperature and frequency (both within and beyond the Curie-Weiss region), and the frequency dependence of the ferroelectric mode near T_c. Section 6 discusses the conditions which determine the order of the phase transition, and in Sec. 7 we calculate some nonlinear properties of the polar phase.

In the following papers, parts II and III of the present series, the theory is extended to include contributions of the soft mode to specific heat, and to remove all small anharmonicity restrictions from the results concerning soft-mode frequency. The theory is then applied in detail to the displacement ferroelectric lithium tantalate.

2. THEORETICAL FOUNDATIONS

The basic Hamiltonian which is customarily written to describe a solid is of the form

$$\mathcal{H}=\mathcal{H}_{\text{ion}}+\mathcal{H}_{\text{electron}}+\mathcal{H}_{\text{electron-ion}}\,, \tag{2.1}$$

where $\mathcal{H}_{\text{ion}}$ describes a collection of ions interacting through a potential $U(\mathbf{R}_i\mathbf{R}_j,\cdots)$ which depends only on the positions of the ion centers, $\mathcal{H}_{\text{electron}}$ describes the valence electrons, and $\mathcal{H}_{\text{electron-ion}}$ is a suitably chosen potential which is taken to represent the interactions between electrons and ions.

It is well known (see, for example, Ziman[11]) that the electronic and ionic motions can be separated to a very good approximation by use of the adiabatic principle, for which we find an effective Hamiltonian for the ionic motion in the form

$$\mathcal{H}_{\text{ion}}=\sum_i \frac{\mathbf{p}_i^2}{2M_i}+U(\mathbf{R}_i,\mathbf{R}_j,\cdots)+E(\mathbf{R}_i,\mathbf{R}_j,\cdots)\,, \tag{2.2}$$

where, in an obvious notation, the first and second terms are the kinetic and potential energy, respectively, of the ionic lattice. The last term in Eq. (2.2) is the contribution from electron-ion interactions and will vary according to the electronic state of the system. If we assume that our system remains essentially in its ground electronic state (i.e., filled electron bands and fairly large band gaps), then we can combine $U(\mathbf{R}_i,\mathbf{R}_j,\cdots)$ and $E(\mathbf{R}_i,\mathbf{R}_j,\cdots)$ to give an effective ion-ion potential $V(\mathbf{R}_i,\mathbf{R}_j,\cdots)$ which is independent of temperature, the ionic Hamiltonian reducing to

$$\mathcal{H}_{\text{ion}}=\sum_i \frac{\mathbf{p}_i^2}{2M_i}+V(\mathbf{R}_i,\mathbf{R}_j,\cdots)\,. \tag{2.3}$$

We first consider the ionic system in the absence of electrostatic dipolar interactions. The basic theory of lattice vibrations is derived from (2.3) by expanding V as a Taylor series in the small displacements $\mathbf{q}_i$ of the ions from their equilibrium positions, and making use of the translational symmetry of the lattice to diagonalize the quadratic part of the Hamiltonian. Quite formally, one obtains

$$\mathcal{H}_{\text{ion}}=\sum_{\mathbf{K},p}\mathcal{H}_0(\mathbf{K},p) + \sum_{\mathbf{K},\mathbf{K}',\cdots}\;\sum_{p,p',\cdots}\mathcal{H}'(\mathbf{K},p;\mathbf{K}',p';\cdots)\,, \tag{2.4}$$

where $\mathbf{K}$ and $\mathbf{K}'$ are reciprocal lattice vectors, p and p' label the various acoustic and optic modes of the system, $\mathcal{H}_0$ is a simple harmonic-oscillator Hamiltonian defining phonons $\mathbf{K}$, and p, and where $\mathcal{H}'$ is a potential term describing the many and varied phonon-phonon interactions for the system.

The optical modes of zero wave vector, and especially the transverse ones for which there are no depolarization forces, control the dielectric properties of the system. In fact, in the work to follow, we shall be concerned with those bulk properties of the system which can be defined in terms of $\mathbf{K}=0$ operators and are therefore uniform throughout the lattice. We think, in particular, of the ionic polarization P_{ion} and the dielectric constant ϵ, which fall into this category.

In calculating the partition function and various averages of $\mathbf{K}=0$ operators, it is only necessary to retain those terms in (2.4) which explicitly contain zero-wave-vector operators. Thus, we may reduce the Hamiltonian of interest to

$$\mathcal{H}_{\text{ion}}=\sum_p \mathcal{H}_0(0,p) + \sum_p \sum_{\mathbf{K}'p'}\cdots\mathcal{H}'(0,p;\mathbf{K}',p';\cdots)\,. \tag{2.5}$$

At this stage we make use of a Hartree approximation for which we write the interactions between any particular mode of interest $(0,p)$ and the rest of the lattice modes by replacing all operators involving the latter by their ensemble averages. In this approximation, which is in essence a perturbation approximation, best valid for systems with small anharmonicity, our Hamiltonian reduces to a set of effective Hamiltonians, one for each zero-wave-vector mode. We find

$$\mathcal{H}_{\text{ion}}=\sum_p \mathcal{H}_{\text{eff}}(0,p)\,, \tag{2.6}$$

where $\mathcal{H}_{\text{eff}}(0,p)$ contains only the canonically conjugate operators $\pi(0,p)$ and $\xi(0,p)$, which describe the generalized momentum and coordinate of the $(0,p)$ mode of lattice vibration. If we now omit the 0 label and write the conjugate coordinates π_p and ξ_p, respectively, the effective Hamiltonian for the pth mode assumes most generally the form

$$\mathcal{H}_{\text{eff}}(0,p)=\tfrac{1}{2}\pi_p^2+\tfrac{1}{2}\Omega_p^2\xi_p^2+\sum_{n=1}^{\infty}C_{np}\xi_p^n\,. \tag{2.7}$$

In this equation, the first two terms on the right-hand side are just $\mathcal{H}_0(0,p)$ from (2.5) where Ω_p^2 is the stiffness of the "isolated" p mode. The coefficients C_{np} all arise from phonon-phonon interaction terms and will all, in general, show a temperature dependence. Indeed, Anderson[1] has looked at these coefficients in more detail and, although we shall not be concerned with their detailed form in the present paper, one or two pertinent comments should be made concerning them.

Firstly, the C_2 term leads to a thermal variation of stiffness for each mode. When this variation is large the Hartree approximation is probably poor. The C_{1p} terms are the dilatation and other uniform strains. In particular, C_{1a}, where the subscript a denotes an acoustic mode, is the source of thermal expansion. The coefficients C_{np} for $n>2$ represent, of course, the anharmonic contributions to the various effective Hamiltonians.

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[11] J. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, 1960).

We shall discuss in the following sections the details of the statistical mechanics of displacement type ferroelectrics using the basic representation (2.6), (2.7). We are now required to incorporate the long-range electrostatic dipolar interactions into the Hamiltonian. In principle, this can be done rigorously by finding a canonical coordinate transformation from (π_p,ξ_p) to (π_p',ξ_p') in terms of which the dipolar contribution transforms to a negative stiffness contribution (quadratic in ξ_p'). All the problems connected with a resultant small quadratic term then follow.

We attempt to avoid these problems by going back to (2.7) and, as explained in the introduction, reinterpreting π_p and ξ_p as operators referring to a single primitive cell, say the ith. The dipolar interactions are then of a form involving the products $\xi_p(i)\xi_{p'}(j)$. We now make a statistical approximation, replacing all primitive cells except the ith by their ensemble averages. The dipolar contributions then become proportional to $\xi_p(i)\langle\xi_{p'}\rangle$, giving terms linear in the primitive-cell normal-mode parameter $\xi_p(i)$, where angle brackets denote an ensemble average. The resulting Hamiltonian for the motion can now be examined statistically and the thermal average $\langle\xi_p\rangle$ determined in a self-consistent fashion. First steps, in the spirit of this approximation, have already been taken by Aizu.[12]

This statistical approximation neglects any effects resulting from short-range correlations between cells and is therefore most accurate when the intercell interactions (or, more accurately, those intercell interactions which depend strongly upon wave vector) are of long range. It is also most accurate at higher temperatures, where there is sufficient thermal energy to excite optic phonons over a reasonably large volume of the Brillouin zone. The degree of accuracy in magnetic theory (very short range interactions) is well known. It should be rather better for ferroelectrics.

In the following section we deduce the detailed form of the statistically approximated dipolar energy. We do this in terms of a model which replaces ions by effective charges and electronic polarizabilities. There is reason to believe, however (part III), that the general form of the resulting effective or displacement Hamiltonian is considerably more general than the model used to construct it. That is to say, the microscopic parameters of the displacement Hamiltonian could also be related to the detailed structure of a more sophisticated model.

Our immediate aim is to use the resulting displacement Hamiltonian to demonstrate that, for at least some displacement ferroelectrics, the dielectric properties can be explained quantitatively in terms of surprisingly few microscopic parameters. We shall hope (and find for the case of lithium tantalate) that these parameters are not grossly temperature-dependent so that a surprisingly good interpretation of experimental results is obtained even with completely temperature-independent parameters.

In the present paper we consider systems with a centrosymmetric nonpolar phase, describing the ferroelectric phase in terms of deviations from it. Thus, from symmetry arguments, ξ_p cannot enter into (2.7) in odd powers for optic modes. The Hamiltonian (2.7) therefore reduces to

$$\mathcal{H}_{\text{eff}}=\sum_p\left(\tfrac{1}{2}\pi_p^2+\tfrac{1}{2}\Omega_p^2\xi_p^2+\sum_{n=1}^{\infty}C_{np}\xi_p^{2n}\right), \qquad (2.8)$$

where Σ_p runs over optic modes of the primitive cell.

For many ferroelectric systems, only one or two modes contribute significantly to ferroelectric properties. Also, we often need retain only one or two anharmonic terms to describe adequately the motion of these modes.

3. DISPLACEMENT HAMILTONIAN IN DETAIL

In the statistical approximation to be used, we replace all cells of the system except one by their thermal averages. It follows that the electrostatic interactions between the cell of interest and the rest of the environment can be expressed in terms of effective fields.

We now set up the effective Hamiltonian to be used for the statistical mechanical calculations and we shall allow for an external electric (Maxwell) field **E**. Let **P** be the total polarization per unit volume, and let $\mathbf{E}_{\text{loc}}^b$ be the local electric field at site b of the primitive cell in question. The local field is related to the thermally averaged polarization $\langle\mathbf{P}\rangle$ via a Lorentz-field tensor γ_b which varies widely from site to site.[13]

We write

$$\mathbf{E}_{\text{loc}}^b=\mathbf{E}+\gamma_b\langle\mathbf{P}\rangle. \qquad (3.1)$$

The total polarization **P** is determined by the local field, and the displacement $\mathbf{q}_b$ of the ionic charge e_b from its equilibrium position by the equation

$$\mathbf{P}=\frac{1}{v}\sum_b\left(\boldsymbol{\alpha}_b\mathbf{E}_{\text{loc}}^b+e_b\mathbf{q}_b\right), \qquad (3.2)$$

where v is the volume of a primitive cell, $\boldsymbol{\alpha}_b$ is the electronic polarizability of the bth ion, and Σ_b runs over all ions in a single primitive cell. It is convenient to label the separate contributions of $\mathbf{E}_{\text{loc}}^b$ and $\mathbf{q}_b$ to **P** as the electronic and ionic polarizations $\mathbf{P}_{\text{elec}}$ and $\mathbf{P}_{\text{ion}}$, respectively. The total contribution to the system Hamiltonian from the long-range dipolar forces, and the external field is

$$V'=\frac{-1}{v}\sum_b\left[e_b\mathbf{q}_b\cdot\mathbf{E}_{\text{loc}}^b+\tfrac{1}{2}\boldsymbol{\alpha}_b(\mathbf{E}_{\text{loc}}^b)^2\right]. \qquad (3.3)$$

We shall be concerned with the equation of motion for $\mathbf{q}_b$ and, since the $\boldsymbol{\alpha}_b$ terms in (3.3) are independent of

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[12] K. Aizu, J. Phys. Soc. Japan **21**, 1240 (1966).

[13] J. C. Slater, Phys. Rev. **78**, 748 (1950).

$\mathbf{q}_b$, we need not retain them. Hence

$$V'=\frac{-1}{v}\sum_b e_b\mathbf{q}_b\cdot\mathbf{E}_{\mathrm{loc}}{}^b=\frac{-1}{v}\sum_b e_b\mathbf{q}_b\cdot[\mathbf{E}+\gamma_b\langle\mathbf{P}\rangle]. \quad (3.4)$$

We can write this equation in terms of $\langle\mathbf{P}_{\mathrm{ion}}\rangle$ by using (3.2) to relate $\langle\mathbf{P}_{\mathrm{ion}}\rangle$ to $\langle\mathbf{P}\rangle$. We find, for the latter,

$$\langle\mathbf{P}_{\mathrm{ion}}\rangle=\langle\mathbf{P}\rangle-\frac{1}{v}\sum_b \boldsymbol{\alpha}_b(\mathbf{E}+\gamma_b\langle\mathbf{P}\rangle), \quad (3.5)$$

from which it follows that

$$\langle\mathbf{P}\rangle=\boldsymbol{\eta}'(\langle\mathbf{P}_{\mathrm{ion}}\rangle+\boldsymbol{\alpha}\mathbf{E}), \quad (3.6)$$

where

$$\boldsymbol{\alpha}=\frac{1}{v}\sum_b \boldsymbol{\alpha}_b, \quad (3.7)$$

$$\boldsymbol{\eta}'=\left(1-\frac{1}{v}\sum_b \boldsymbol{\alpha}_b\gamma_b\right)^{-1}. \quad (3.8)$$

In terms of $\langle\mathbf{P}_{\mathrm{ion}}\rangle$, the potential V' is now expressed as

$$V'=\frac{-1}{v}\sum_b e_b\mathbf{q}_b\cdot(\boldsymbol{\eta}_b\mathbf{E}+\boldsymbol{\lambda}_b\langle\mathbf{P}_{\mathrm{ion}}\rangle), \quad (3.9)$$

where

$$\boldsymbol{\eta}_b=\gamma_b\boldsymbol{\eta}'\boldsymbol{\alpha}+1, \quad (3.10)$$

$$\boldsymbol{\lambda}_b=\gamma_b\boldsymbol{\eta}'. \quad (3.11)$$

Since the purpose of this section is solely to demonstrate the form of the effective ion Hamiltonian required to describe dielectric properties in both polar and nonpolar states, only the form of (3.9) is of concern to us. The detailed expressions for the coefficients involved will not concern us further in this paper.

The ionic Hamiltonian for our system now takes the form

$$\mathcal{H}_{\mathrm{ion}}=\frac{1}{v}\left(\sum_b\frac{\mathbf{p}_b{}^2}{2M_b}+V(\mathbf{q}_b,\mathbf{q}_{b'},\cdots)\right)+V', \quad (3.12)$$

where $V(\mathbf{q}_b,\mathbf{q}_{b'},\cdots)$ is now the effective interionic potential energy but excluding the contributions from intercell dipolar forces; it concerns, therefore, the effects of dominantly short-range forces.

Expanding V as a Taylor series in the **q**'s, we may readily diagonalize that part of $\mathcal{H}_{\mathrm{ion}}$ involving terms up to quadratic in **q**. The required transformation to new conjugate coordinates π_p and ξ_p is familiar from any standard text on lattice vibrations, and may be written

$$\pi_p=\sum_b \mathbf{u}_{bp}\cdot\mathbf{p}_b, \qquad \xi_p=\sum_b M_b\mathbf{u}_{bp}\cdot\mathbf{q}_b, \quad (3.13)$$

$$\mathbf{p}_b=M_b\sum_p \mathbf{u}_{bp}\pi_p, \quad \mathbf{q}_b=\sum_p \mathbf{u}_{bp}\xi_p, \quad (3.14)$$

where $(M_b)^{1/2}\mathbf{u}_{bp}$ is the bth component of the pth normalized eigenvector, and satisfies

$$\sum_b M_b\mathbf{u}_{bp}\cdot\mathbf{u}_{bp'}=\delta_{pp'}. \quad (3.15)$$

In the new coordinate system, the ionic Hamiltonian per unit cell, up to quadratic terms, is

$$v\mathcal{H}_{\mathrm{ion}}=\sum_p [\tfrac{1}{2}\pi_p{}^2+\tfrac{1}{2}\Omega_p{}^2\xi_p{}^2 -\boldsymbol{\eta}_p\mathbf{S}_p\xi_p(\mathbf{E}+\gamma_p\langle\mathbf{P}_{\mathrm{ion}}\rangle)]+\cdots, \quad (3.16)$$

where the formalisms $(\boldsymbol{\eta}_p\mathbf{S}_p)\mathbf{E}$ and $(\boldsymbol{\eta}_p\mathbf{S}_p)(\gamma_p\langle\mathbf{P}_{\mathrm{ion}}\rangle)$ imply scalar products, and where

$$\mathbf{S}_p=\sum_b e_b\mathbf{u}_{bp}, \quad (3.17)$$

$$\boldsymbol{\eta}_p\mathbf{S}_p=\sum_b \boldsymbol{\eta}_b{}^\dagger e_b\mathbf{u}_{bp}, \quad (3.18)$$

and

$$\gamma_p{}^\dagger\boldsymbol{\eta}_p\mathbf{S}_p=\sum_b \boldsymbol{\lambda}_b{}^\dagger e_b\mathbf{u}_{bp}. \quad (3.19)$$

Once again, we shall not be particularly concerned with the relationships between the relevant parameters and the fundamental properties of the lattice. We shall treat these parameters simply as quantities to be estimated by comparing with experiment the relevant results of a statistical theory using this Hamiltonian. Thus, we have not written out explicitly the matrix equation for eigenvalues $\Omega_p{}^2$, we shall not use it.

It is now evident, by comparing Eqs. (3.16) and (2.8), that our final effective Hamiltonian per unit cell for the dielectric properties of a ferroelectric will take the form

$$v\mathcal{H}_{\mathrm{eff}}=\sum_p \{\tfrac{1}{2}\pi_p{}^2+\tfrac{1}{2}\Omega_p{}^2\xi_p{}^2+\sum_{n=1}^{\infty} C_{np}\xi_p{}^{2n} -\boldsymbol{\eta}_p\mathbf{S}_p\xi_p(\mathbf{E}+\gamma_p\langle\mathbf{P}_{\mathrm{ion}}\rangle)\}. \quad (3.20)$$

We shall retain anharmonic terms only up to ξ^6 in the subsequent calculations, this being the least number of anharmonic terms which can reasonably be hoped to describe free ferroelectric crystals. To treat free, as opposed to clamped systems it is, in general, necessary to go beyond ξ^4, since this lowest-order anharmonic term can be negative in free ferroelectric crystals[13,14] (as we shall see, this may or may not lead to a first-order transition), and the lattice must necessarily be stabilized in the polar state by some higher-order anharmonicity. We shall combine the C_{1p} quadratic term into the temperature-independent term $\frac{1}{2}\Omega_p{}^2\xi_p{}^2$, recognizing that it will lend some temperature dependence to the stiffness.

Thus, the Hamiltonian which we shall use is

$$v\mathcal{H}_{\mathrm{eff}}=\sum_p \{\tfrac{1}{2}(\pi_p{}^2+\omega_p{}^2\xi_p{}^2)+A_p\xi_p{}^4+B_p\xi_p{}^6 -\boldsymbol{\eta}_p\mathbf{S}_p\xi_p(\mathbf{E}+\gamma_p\langle\mathbf{P}_{\mathrm{ion}}\rangle)\}, \quad (3.21)$$

where we have written $C_{2p}=A_p$, $C_{3p}=B_p$, and $\Omega_p{}^2+2C_{1p}=\omega_p{}^2$. This is our displacement Hamiltonian, which we suggest is adequate for describing the dielectric properties of displacement-type ferroelectric systems. It

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[14] A. F. Devonshire, Phil. Mag. 40, 1040 (1949); 42, 1065 (1951).

is to be used to determine the temperature dependence of polarization, linear and nonlinear susceptibility, etc. of ferroelectrics in exactly the same spirit that an exchange Hamiltonian is used in magnetism to determine the temperature dependence of bulk magnetic properties for spin-ordered systems.

However, one practical limitation is obvious. Since we have no less than five "unknown parameters" per mode, namely, ω^2, A, B, $\boldsymbol{\eta}\mathbf{S}$, and $\boldsymbol{\gamma}$, we can only expect any success in determining them quantitatively from our statistical mechanical relationships alone if we can find systems which have, to a good approximation, only one soft mode. We can proceed quite formally through the classical statistics retaining all the modes p of Eq. (3.21) and this we shall do. However, when we perform actual numerical calculations we shall restrict the discussion to the one soft-mode case.

4. FORMAL CLASSICAL STATISTICS FOR THE MANY-MODE CASE

Since

$$\mathbf{P}_{\mathrm{ion}}=\frac{1}{v}\sum_b e_b\mathbf{q}_b\,,$$

we can express the thermal average $\langle\mathbf{P}_{\mathrm{ion}}\rangle$ in terms of $\langle\xi_p\rangle$ by use of the transformation equation, (3.14), giving

$$\langle\mathbf{P}_{\mathrm{ion}}\rangle=\frac{1}{v}\sum_p \mathbf{S}_p\langle\xi_p\rangle. \tag{4.1}$$

Thus, an implicit equation for ionic polarization can immediately be written in the form

$$\langle\mathbf{P}_{\mathrm{ion}}\rangle=\frac{1}{v}\sum_p\left(\mathbf{S}_p\int_{-\infty}^{\infty}\xi_p\exp\left(-\frac{V_p}{kT}\right)\frac{d\xi_p}{Z_p}\right), \tag{4.2}$$

where

$$V_p=\tfrac{1}{2}\omega_p{}^2\xi_p{}^2+A_p\xi_p{}^4+B_p\xi_p{}^6 -\boldsymbol{\eta}_p\mathbf{S}_p\xi_p(\mathbf{E}+\boldsymbol{\gamma}_p\langle\mathbf{P}_{\mathrm{ion}}\rangle)\,, \tag{4.3}$$

and where Z_p is the partition function

$$Z_p=\int_{-\infty}^{\infty}\exp\left(-\frac{V_p}{kT}\right)d\xi_p. \tag{4.4}$$

For the case of zero external field, we may calculate the ferroelectric Curie temperature by expanding the exponentials in (4.2) for the limit $\langle\mathbf{P}_{\mathrm{ion}}\rangle\rightarrow 0$. We find a temperature T_c, given by

$$kT_c=\sum_p\left[\frac{\eta_p\gamma_pS_{pz}{}^2}{v}\int_{-\infty}^{\infty}\xi_p{}^2\exp\left(-\frac{U_p}{kT_c}\right)d\xi_p \div\int_{-\infty}^{\infty}\exp\left(-\frac{U_p}{kT_c}\right)d\xi_p\right], \tag{4.5}$$

where

$$U_p=\tfrac{1}{2}\omega_p{}^2\xi_p{}^2+A_p\xi_p{}^4+B_p\xi_p{}^6\,, \tag{4.6}$$

where S_{pz} is the component of S_p in the direction of the spontaneous polarization, and where we have written $(\boldsymbol{\eta}_p\mathbf{S}_p)(\boldsymbol{\gamma}_p\langle\mathbf{P}_{\mathrm{ion}}\rangle)=\eta_p\gamma_pS_{pz}\langle P_{\mathrm{ion}}\rangle$.

Thus, in principle at least, we have calculated the spontaneous ionic polarization as a function of temperature. The total polarization $\langle\mathbf{P}\rangle$ is related to the ionic polarization through Eq. (3.6). In particular, for the case of zero external field, there is a direct proportionality.

The static susceptibility follows in a straightforward manner from the expression (4.2) for polarization. For simplicity we shall restrict ourselves to directions of external field $\mathbf{E}$ for which the susceptibility is scalar, i.e., $\mathbf{E}$ parallel to an axis of symmetry of the crystal which may, or may not, be the direction of spontaneous polarization. If we define an ionic susceptibility $\chi_{\mathrm{ion}}=\partial\langle\mathbf{P}_{\mathrm{ion}}\rangle/\partial\mathbf{E}$ when $\mathbf{E}\rightarrow 0$, then a direct differentiation of (4.2) with respect to $\mathbf{E}$ gives

$$\chi_{\mathrm{ion}}=\sum_p(1+\gamma_{pE}\chi_{\mathrm{ion}})\frac{\eta_{pE}S_{pE}{}^2}{kTv}(\langle\xi_p{}^2\rangle-\langle\xi_p\rangle^2)\,, \tag{4.7}$$

where we define S_{pE} as the component of $\mathbf{S}_p$ in the direction of the applied field, where $\eta_{pE}=\mathbf{S}_p\boldsymbol{\eta}_p{}^\dagger\mathbf{E}/S_{pE}E$ and $\gamma_{pE}=\mathbf{S}_p\boldsymbol{\eta}_p{}^\dagger\boldsymbol{\gamma}_p\mathbf{E}/\eta_{pE}S_{pE}E$, and where the angle brackets refer to ensemble averages of the form

$$\langle\xi_p{}^n\rangle=\int_{-\infty}^{\infty}\xi_p{}^n\exp\left(-\frac{V_p}{kT}\right)d\xi_p\Big/\int_{-\infty}^{\infty}\exp\left(-\frac{V_p}{kT}\right)d\xi_p. \tag{4.8}$$

For the particular case of applied field $\mathbf{E}$ being parallel to $\langle\mathbf{P}_{\mathrm{ion}}\rangle$, we write η_{pE} and γ_{pE} simply as η_p and γ_p, respectively. We also note, in connection with (4.7) that $\langle\xi_p\rangle=0$ in the paraelectric phase.

The dynamic susceptibility is readily calculated by examining the equation of motion of the classical distribution function. Details of such a calculation for $T\approx T_c$ have been given by Aizu[12] and need not be repeated here, although it should be stressed, despite Aizu's contrary implication, that these results are strictly valid only in the limit of small anharmonicity. We calculate a frequency-dependent susceptibility, in this limit, of the form

$$\chi_{\mathrm{ion}}(\omega)=\sum_p[1+\gamma_{pE}\chi_{\mathrm{ion}}(\omega)] \times\frac{\eta_{pE}S_{pE}{}^2}{kTv}\frac{\omega_p{}^2}{\omega_p{}^2-\omega^2}[\langle\xi_p{}^2\rangle-\langle\xi_p\rangle^2]. \tag{4.9}$$

The ionic susceptibility is directly related to the total susceptibility $\chi(\omega)$ through Eq. (3.6) by differentiation with respect to E. We find

$$\chi(\omega)=\boldsymbol{\eta}'[\chi_{\mathrm{ion}}(\omega)+\boldsymbol{\alpha}]. \tag{4.10}$$

For directions of applied field perpendicular to the spontaneous polarization, the soft modes which are responsible for the ferroelectricity of the system will contribute little. For the other modes of the crystal lattice, anharmonic effects are less important, and we find $\langle\xi_p\rangle^2 \ll \langle\xi_p^2\rangle$, and $\langle\xi_p^2\rangle$ approximately proportional to temperature. This leads us to anticipate a largely temperature-independent perpendicular electric susceptibility.

For applied field parallel to the direction of spontaneous polarization, the situation is quite different. Let T_c' be the temperature at which, for an applied field of frequency ω, the parallel susceptibility becomes infinite. It follows that

$$kT_c' = \sum_p \frac{\eta_p\gamma_p S_{pz}^2}{v} \frac{\omega_p^2}{\omega_p^2-\omega^2} \Phi_p(T_c'), \tag{4.11}$$

where we have written $\Phi_p(T_c')$ for the value of $\langle\xi_p^2\rangle - \langle\xi_p\rangle^2$ at the temperature T_c'. Using (4.11) and considering temperatures close to T_c', retaining terms only to first order in $(T-T_c')/T_c'$, we find that the equation for ionic (parallel) susceptibility reduces to

$$\sum_p \eta_p\gamma_p S_{pz}^2 \frac{\omega_p^2}{\omega_p^2-\omega^2} \Phi_p(T_c') \times\left[\frac{1}{\gamma_p\chi_{\text{ion}}} + (\lambda_p-1)\frac{T-T_c'}{T_c'}\right] = 0, \tag{4.12}$$

where we have written

$$\frac{\Phi_p(T)-\Phi_p(T_c')}{\Phi_p(T_c')} = \frac{\lambda_p(T-T_c')}{T_c'}, \tag{4.13}$$

as the equation defining the parameter λ_p (again retaining only the first-order term in an expansion in terms of temperature deviations from T_c'). This parameter has different values in the polar and nonpolar states, in particular, $\lambda_p \to 1$ for hard modes, being greater than unity in the polar state and less than unity in the nonpolar state.

From (4.12) we can calculate χ_{ion} explicitly. It takes the form of a Curie-Weiss law $\chi_{\text{ion}} = CT_c'/(T-T_c')$, where C is temperature-independent and given by

$$C = \sum_p \eta_p S_{pz}^2 \frac{\omega_p^2}{\omega_p^2-\omega^2} \Phi_p(T_c') \Big/ \sum_p \eta_p S_{pz}^2 \frac{\omega_p^2}{\omega_p^2-\omega^2} \gamma_p(1-\lambda_p)\Phi_p(T_c'). \tag{4.14}$$

Thus, for any frequency of applied field, the parallel electric susceptibility obeys a Curie-Weiss law about T_c'. In general, Eq. (4.11) has two solutions for T_c', one on either side of T_c, which we may denote by T_c'(ferro) and T_c'(para), respectively. Since $\Phi_p(T)$ is not analytic at $T=T_c$ (having a discontinuity in slope at this point), Eq. (4.13) is valid only for $T > T_c'$(para) and for $T < T_c'$(ferro). Therefore, in the general case, the system will display a Curie-Weiss susceptibility below T_c'(ferro) and above T_c'(para). These temperatures are frequency-dependent, but will not in practice be distinguishable from the real Curie point for applied frequencies small with respect to typical optical-phonon values.

For a fixed temperature T, the parallel susceptibility will diverge for a value of frequency which makes $T_c' = T$. Using (4.11), for the case $\omega^2 \ll \omega_p^2$, we may readily show that this so called "soft mode" or "ferroelectric mode" has a frequency ω_s given by

$$\omega_s^2(\text{ferro}) = C_1(T_c - T), \quad \omega_s^2(\text{para}) = C_2(T - T_c), \tag{4.15}$$

where C_1 and C_2 are temperature-independent if the parameters in our starting displacement Hamiltonian are not dependent on temperature. We note that Eqs. (4.15) involve the real Curie temperature T_c, so that the ferroelectric-mode frequency comes down to zero (from both sides) at the Curie point, whereas the parallel susceptibility diverges at two temperatures, usually very close to T_c but separated from it by small frequency-dependent amounts.

Thus, even using a formalism which retains the full complexity of the multimode system, we are able to deduce a few qualitative features of the ferroelectric transition. For quantitative work, however, we shall move to the other extreme, and consider in detail the dielectric properties of a displacement ferroelectric using the "single-mode" approximation.

5. SINGLE-MODE APPROXIMATION

We now consider a system which has only one strongly temperature-dependent mode. For such a system, $\langle\mathbf{P}_{\text{ion}}\rangle \| \mathbf{S}$ and, for $\mathbf{E} \| \langle\mathbf{P}_{\text{ion}}\rangle$, we can dispense with all vector and tensor notation and write the effective Hamiltonian

$$v\mathcal{H}_{\text{eff}} = \tfrac{1}{2}(\pi^2 + \omega_0^2\xi^2) + A\xi^4 + B\xi^6 - \eta S\xi(E + \gamma\langle P_{\text{ion}}\rangle), \tag{5.1}$$

where we have retained a subscript only for ω_0 to distinguish it from the frequency variable ω, which will be used later in connection with the dynamic susceptibility.

From Sec. 4 we can write down the statistical estimates for T_c, and for $\langle P_{\text{ion}}\rangle$ as a function of temperature, in the form

$$kT_c = \frac{\eta\gamma S^2}{v}\int_{-\infty}^{\infty} \xi^2 \exp(-U/kT_c)d\xi \Big/ \int_{-\infty}^{\infty} \exp(-U/kT_c)d\xi, \quad E=0, \tag{5.2}$$

$$\langle P_{\text{ion}}\rangle = \frac{S}{v}\int_{-\infty}^{\infty} \xi \exp(-V/kT)d\xi \Big/ \int_{-\infty}^{\infty} \exp(-V/kT)d\xi, \tag{5.3}$$

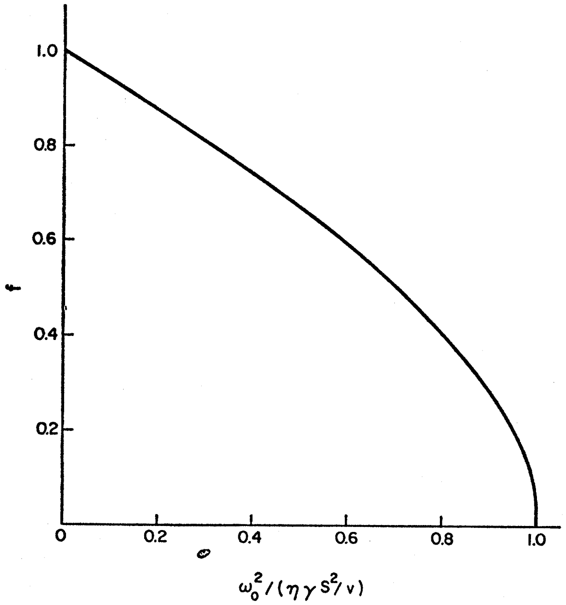

FIG. 1. The function f of Eq. (5.7), plotted as a function of $\beta/\alpha=\omega_0^2/(\eta\gamma S^2/v)$ which measures the ratio of contributions to harmonic energy from short-range and long-range (dipolar) forces, respectively.

where

$$U=\tfrac{1}{2}\omega_0^2\xi^2+A\xi^4+B\xi^6, \tag{5.4}$$

$$V=U-\eta\xi S(E+\gamma\langle P_{\text{ion}}\rangle). \tag{5.5}$$

In cases where the coefficient A is positive, the effects of the ξ^6 term is probably negligible. This case, and the limit $\eta\gamma S^2 \gg v\omega_0^2$, was the system discussed by Aizu.[12] We shall also consider this positive-A case, but without any restrictions on the parameter magnitudes (except to neglect the ξ^6 anharmonicity). This serves as a simple introduction to the more general situation, where we allow A to be negative; a case which often appears to be important for free crystals. For example, this helps to explain the first-order ferroelectric transition observed for $BaTiO_3$. However, we shall find that a negative value for the coefficient A does not necessarily lead to a first-order transition, and that systems may have a negative value of A and yet still show a second-order phase transition. Study of the dielectric properties of $LiNbO_3$[15] and $LiTaO_3$ (Part III), indicate that these are examples of the latter. Such "negative-A" systems must, of course, have their ferroelectric displacement limited by terms higher than fourth order in anharmonicity. We shall assume that our systems are stabilized in such cases by sixth-order terms.

A. Positive-A Case

Neglecting ξ^6 terms, and transforming to the dimensionless variable $x=(A/kT)^{1/4}\xi$, our problem can be neatly cast in terms of the dimensionless parameters $\alpha=(kTA)^{1/2}/\omega_0^2$ and $\beta=(kTA)^{1/2}/(\eta\gamma S^2/v)$. With this nomenclature we find, from (5.2),

$$\beta_c=\int_{-\infty}^{\infty} x^2\exp\left(-\frac{x^2}{2\alpha_c}-x^4\right)dx \Bigg/ \int_{-\infty}^{\infty}\exp\left(-\frac{x^2}{2\alpha_c}-x^4\right)dx, \tag{5.6}$$

where the subscript c refers to the case $T=T_c$. The integrals involved have been evaluated numerically to give β_c as a function of α_c, which in turn gives β_c as a function of $\beta/\alpha=\omega_0^2/(\eta\gamma S^2/v)$. The Curie temperature follows as

$$kT_c=(1/A)(0.338\eta\gamma S^2 f/v)^2, \tag{5.7}$$

where f, as a function of $\omega_0^2/(\eta\gamma S^2/v)$, is shown in Fig. 1. To quite a good approximation, we find $f^2\approx 1-\omega_0^2/(\eta\gamma S^2/v)$, in which case

$$kT_c\approx 0.114(\eta\gamma S^2/vA)[(\eta\gamma S^2/v)-\omega_0^2]. \tag{5.8}$$

The ionic polarization is computed from (5.3) which, in terms of the variable x, and for the case of zero external field, may be written

$$\Gamma=\int_{-\infty}^{\infty} x\exp\left(-\frac{x^2}{2\alpha}-x^4+\frac{\Gamma x}{\beta}\right)dx \Bigg/ \int_{-\infty}^{\infty}\exp\left(-\frac{x^2}{2\alpha}-x^4+\frac{\Gamma x}{\beta}\right)dx, \tag{5.9}$$

where

$$\Gamma=\langle P_{\text{ion}}\rangle(v/S)(A/kT)^{1/4}. \tag{5.10}$$

Again we compute the integrals numerically to give Γ as a function of α and β. These results can be more conveniently recast in the form $\langle P_{\text{ion}}\rangle$ as a function of T for various values of $\beta/\alpha=\omega_0^2/(\eta\gamma S^2/v)$. Finally, noting that

$$\langle P_{\text{ion}}\rangle_{T=0}=\frac{S}{v}\left[\frac{1}{4A}\left(\frac{\eta\gamma S^2}{v}-\omega_0^2\right)\right]^{1/2} \tag{5.11}$$

is the ionic polarization at $T=0$, obtained by minimizing H_{eff} with respect to ξ, and using (5.7) for T_c, we may plot curves of reduced polarization $P/P_0=\langle P_{\text{ion}}\rangle/\langle P_{\text{ion}}\rangle_{T=0}$ against reduced temperature T/T_c (where P is the total polarization, and P_0 its value at absolute zero). These curves, as functions of β/α are shown in Fig. 2.

A few interesting observations can be made at this juncture. First, from (5.11), the condition for ferroelectricity in the one-mode approximation, for the case where lattice stabilization is produced by fourth-order anharmonicity, is $\eta\gamma S^2/v\omega_0^2>1$; i.e., $\beta/\alpha<1$. Secondly, the phase transition for this case is always of second order. Thirdly, the polarization curve shapes, particularly for the strongly ferroelectric case ($\beta/\alpha\ll 1$) are very similar to the classical Brillouin curve of magnetism

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[15] M. E. Lines (unpublished).

theory. The latter, familiar from the simple effective-field theory of magnetism in insulators, describes the shape of magnetization curves for the limit of classical spins; it lies fractionally outside the $\beta/\alpha=0.3$ curve of Fig. 2. Finally by expanding (5.9) in powers of Γ to order Γ^3, it is not difficult to show that $\langle P_{\text{ion}}\rangle$ varies as $(T_c-T)^{1/2}$ when T approaches the Curie temperature. Again, a corresponding result is familiar from the effective-field theory of magnetism. There is, however, a very significant difference between this result, as deduced for magnetism, and for ferroelectricity. In the former case it represents a relatively crude approximation, in the latter case it seems, experimentally, to be an extremely good one. In both systems, the broken-symmetry character of the ordered state makes convenient a description in terms of an order parameter. In the present paper this is introduced by representing long-range dipolar interactions by a Lorentz field; for effective-field theories of magnetism, by replacing very short-range exchange interactions by a molecular field. The existence of short-range-order correlations in the respective systems obviously affects the latter approximation much more seriously than the former.

The ionic susceptibility for the single-mode approximation follows from Eq. (4.9), and may be written, for E parallel to the ferroelectric axis, as

$$\frac{\gamma\chi_{\text{ion}}(\omega)}{1+\gamma\chi_{\text{ion}}(\omega)}=\frac{\eta\gamma S^2}{kTv}\,\frac{\omega_0^2}{\omega_0^2-\omega^2}(\langle\xi^2\rangle-\langle\xi\rangle^2). \quad (5.12)$$

Let us consider the case $T\approx T_c$, for which $\Gamma/\beta\ll 1$. Transforming to dimensionless variables, we find

$$\frac{\gamma\chi_{\text{ion}}(\omega)}{1+\gamma\chi_{\text{ion}}(\omega)}=\frac{\omega_0^2}{\omega_0^2-\omega^2}\left(\frac{T_c}{T}\right)^{1/2}\frac{1}{\beta_c}[\langle x^2\rangle-\langle x\rangle^2]. \quad (5.13)$$

We may expand $\langle x^2\rangle$ and $\langle x\rangle^2$ in powers of Γ to order Γ^2, to obtain

$$\langle x^2\rangle=\langle x^2\rangle_0+\tfrac{1}{2}(\Gamma/\beta)^2[\langle x^4\rangle_0-\langle x^2\rangle_0^2], \quad (5.14)$$

$$\langle x\rangle^2=(\Gamma/\beta)^2\langle x^2\rangle_0^2, \quad (5.15)$$

where $\langle x^n\rangle_0$ denotes an average for the case $\Gamma=0$, i.e.,

$$\langle x^n\rangle_0=\int_{-\infty}^{\infty}x^n\exp\left(-\frac{x^2}{2\alpha}-x^4\right)dx\bigg/\int_{-\infty}^{\infty}\exp\left(-\frac{x^2}{2\alpha}-x^4\right)dx. \quad (5.16)$$

Using Eqs. (5.14) and (5.15), we find values of $\langle x^2\rangle-\langle x\rangle^2$ in the paraelectric and in the ferroelectric phases to be $\langle x^2\rangle_0$ and $\langle x^2\rangle_0+(\Gamma/\beta)^2[\frac{1}{2}\langle x^4\rangle_0-\frac{3}{2}\langle x^2\rangle_0^2]$, respectively. We can eliminate Γ from the latter expression by making use of Eq. (5.9), which, when expanded to second order in Γ, becomes

$$(\Gamma/\beta)^2=6(\beta-\langle x^2\rangle_0)(\langle x^4\rangle_0-3\langle x^2\rangle_0^2)^{-1}. \quad (5.17)$$

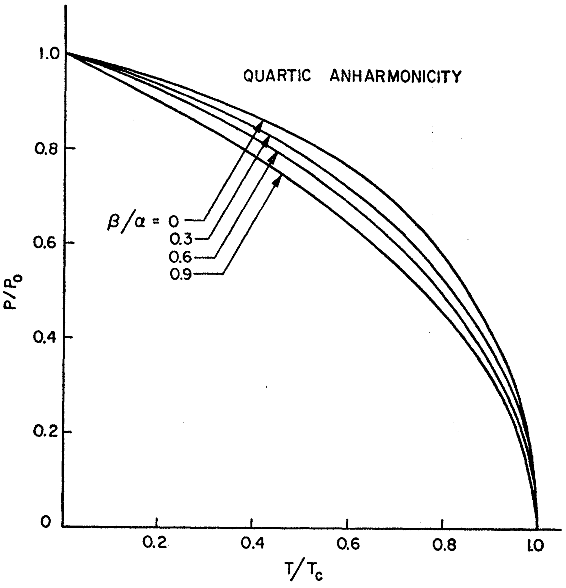

FIG. 2. Reduced polarization P/P_0, shown as a function of reduced temperature T/T_c for a number of values of the parameter β/α. The curves refer to a ferroelectric stabilized by quartic anharmonicity, for which $T_c\to 0$ as $\beta/\alpha\to 1$.

It follows that $\langle x^2\rangle-\langle x\rangle^2$ in the ferroelectric phase just below T_c can be written $\langle x^2\rangle_0+3(\beta-\langle x^2\rangle_0)$.

Now $\langle x^2\rangle_0$ is a continuous function of T near T_c so that, noting that the value of $\langle x^2\rangle_0$ at T_c is just β_c, we may write

$$\langle x^2\rangle_0=\beta_c[1+\mu(T-T_c)/T_c], \quad (5.18)$$

for values of temperature not too far removed from T_c. Making use of these results to expand the ionic susceptibility about the Curie temperature, we obtain

$$\gamma\chi_{\text{ion}}^p(\omega)[1+\gamma\chi_{\text{ion}}^p(\omega)]^{-1}=[\omega_0^2/(\omega_0^2-\omega^2)]\times[1-(\tfrac{1}{2}-\mu)(T-T_c)/T_c] \quad (5.19)$$

for the paraelectric state (superscript p denoting this nonpolar phase), and

$$\gamma\chi_{\text{ion}}^f(\omega)[1+\gamma\chi_{\text{ion}}^f(\omega)]^{-1}=[\omega_0^2/(\omega_0^2-\omega^2)]\times[1+2(\tfrac{1}{2}-\mu)(T-T_c)/T_c] \quad (5.20)$$

for the ferroelectric state.

Consider the paraelectric state. The susceptibility diverges at T_p' for which

$$[\omega_0^2/(\omega_0^2-\omega^2)][1+(\tfrac{1}{2}-\mu)(T_c-T_p')/T_c]=1. \quad (5.21)$$

Combining (5.19) and (5.21), we find, to first order in $(T-T_p')/T_c$, $(T_p'-T_c)/T_c$, and $1/\gamma\chi_{\text{ion}}^p(\omega)$, the result

$$\gamma\chi_{\text{ion}}^p(\omega)=T_c[(\tfrac{1}{2}-\mu)(T-T_p')]^{-1}. \quad (5.22)$$

By an analogous calculation it follows that

$$\gamma\chi_{\text{ion}}^f(\omega)=T_c[2(\tfrac{1}{2}-\mu)(T_f'-T)]^{-1}, \quad (5.23)$$

where T_f', the temperature for which $\chi_{\text{ion}}^f(\omega)$ diverges, is given by

$$[\omega_0^2/(\omega_0^2-\omega^2)][1-2(\tfrac{1}{2}-\mu)(T_c-T_f')/T_c]=1. \quad (5.24)$$

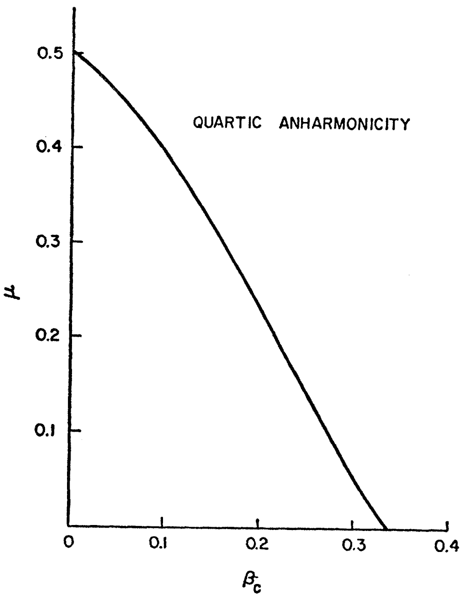

FIG. 3. The parameter μ of Eq. (5.18), which determines the Curie constant and soft-mode frequency near T_c, plotted as a function of β_c (which controls the Curie temperature) for the quartic-anharmonicity case.

Near T_c, the total susceptibility is related to the ionic susceptibility by $\chi(\omega)=\eta'\chi_{\text{ion}}(\omega)$ [see Eq. (4.10) with $\chi_{\text{ion}}(\omega)\gg\alpha$]. Thus, both paraelectric and ferroelectric susceptibility follow a Curie-Weiss law near T_c, and there is a factor-two difference in the Curie constants between the two cases. This result does not depend on the specific form used for our potential function V_p of Eq. (4.3) so long as the nonpolar state is centrosymmetric and the transition is of second order, and it is a result that is familiar from the thermodynamic theory of ferroelectricity.[16]

The paraelectric susceptibility diverges when $T=T_p'$, where T_p' is a function of frequency. Expanding T_p' by use of (5.21), we find that for a fixed temperature T a little larger than T_c, the susceptibility diverges at a frequency of applied field ω_p, where

$$\omega_p^2=\omega_0^2(\tfrac{1}{2}-\mu)(T-T_c)/T_c. \qquad (5.25)$$

This is the frequency of the "Cochran mode" or "ferroelectric mode" of the nonpolar phase. There is, of course, an exactly equivalent result for the ferroelectric phase, where we find a polar soft mode of frequency ω_f where

$$\omega_f^2=2\omega_0^2(\tfrac{1}{2}-\mu)(T_c-T)/T_c. \qquad (5.26)$$

The behavior of susceptibility and soft-mode frequency near the Curie temperature can therefore be described quantitatively as soon as μ has been computed in terms of the basic parameters of the single-mode Hamiltonian. Using (5.16) and (5.18), we have computed μ as a function of β_c for the "positive-A" case of the present section; it is shown in Fig. 3. The parameter β_c is related to the more fundamental parameter $\beta/\alpha=\omega_0^2/(\eta\gamma S^2/v)$ through the equation $\beta_c=0.338f$ where f, as a function of β/α is shown in Fig. 1.

It is, of course, possible to compute susceptibilities directly from (5.13), and to calculate deviations from Curie-Weiss behavior as one moves away from the Curie temperature. We have done this only for the nonpolar phase, since the computations are far easier when $\langle x\rangle=0$. We have

$$\frac{\gamma\chi_{\text{ion}}^{p}(\omega)}{1+\gamma\chi_{\text{ion}}^{p}(\omega)}=\frac{\omega_0^2}{\omega_0^2-\omega^2}\left(\frac{T_c}{T}\right)^{1/2}\frac{\langle x^2\rangle_0}{\beta_c}, \qquad (5.27)$$

where $\langle x^2\rangle_0/\beta_c$ as a function of T/T_c has been computed for various values of β_c and is shown in Fig. 4.

There is, of course, a simple relationship between the parameter μ of the present section and the parameter λ of Sec. 4 [Eq. (4.13)]. The latter takes different values in the polar and nonpolar phases, and may be related to μ, for the single-mode approximation, by comparing (5.22) and (5.23), in turn, with the single-mode form of (4.14), viz., $C=1/[\gamma(1-\lambda)]$.

One final observation for the quartic-anharmonicity case can be made by comparing Eqs. (5.8) and (5.11), for T_c and $\langle P_{\text{ion}}\rangle$ at $T=0$, respectively. We note that a very simple relationship exists between these two quantities, namely,

$$kT_c\approx 0.45\eta\gamma v\langle P_{\text{ion}}\rangle_{T=0}^2, \qquad (5.28)$$

or, more accurately,

$$kT_c=0.45\rho\eta\gamma v\langle P_{\text{ion}}\rangle_{T=0}^2, \qquad (5.28')$$

where ρ is plotted as a function of β/α in Fig. 5.

Note added in proof. Relationships of the form (5.28) are particularly interesting when considered in con-

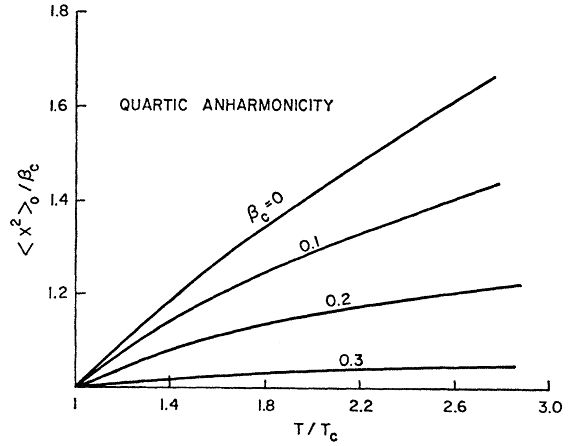

FIG. 4. The ratio $\langle x^2\rangle_0/\beta_c$, which is a direct measure of ionic susceptibility in the nonpolar phase [via Eq. (5.27)], shown as a function of reduced temperature for a ferroelectric stabilized by quartic anharmonicity.

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

junction with the recent suggestion of Abrahams, Kurtz and Jamieson, Phys. Rev. **172**, 551 (1968) that T_c and $\langle P\rangle_{T=0}{}^2$ may be correlated over a range of displacive ferroelectrics.

B. Negative-A Case

If the coefficient A in the single-mode effective Hamiltonian (5.1) is negative, then the ferroelectric system must be stabilized by a positive higher-order anharmonicity. We shall assume that our system is stabilized by a positive sixth-order term. It is then of interest to compute the various dielectric properties for this case also; they will, of course, vary considerably as a function of the relative magnitudes of the fourth- and sixth-order anharmonic terms.

To evaluate (5.2) and (5.3) for Curie temperature and ionic polarization, it is again convenient to introduce a dimensionless variable. This time we write $y=(B/kT)^{1/6}\xi$, in terms of which (5.2) and (5.3) transform to

$$\beta_c'=\int_{-\infty}^{\infty} y^2\exp\left(-\frac{y^2}{2\alpha_c'}+\frac{y^4}{\delta_c}-y^6\right)dy\bigg/\int_{-\infty}^{\infty}\exp\left(-\frac{y^2}{2\alpha_c'}+\frac{y^4}{\delta_c}-y^6\right)dy, \tag{5.29}$$

and

$$\Gamma'=\int_{-\infty}^{\infty} y\exp\left(-\frac{y^2}{2\alpha'}+\frac{y^4}{\delta}-y^6+\frac{\Gamma' y}{\beta'}\right)dy\bigg/\int_{-\infty}^{\infty}\exp\left(-\frac{y^2}{2\alpha'}+\frac{y^4}{\delta}-y^6+\frac{\Gamma' y}{\beta'}\right)dy, \tag{5.30}$$

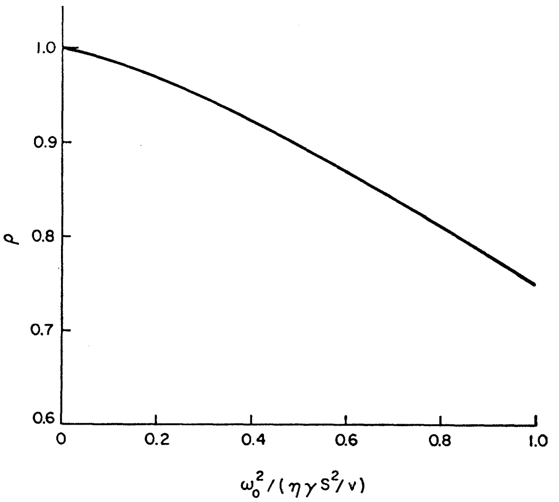

FIG. 5. The parameter ρ, which relates Curie temperature to ionic polarization via Eq. (5.28′), plotted as a function of β/α for a quartic-anharmonicity system.

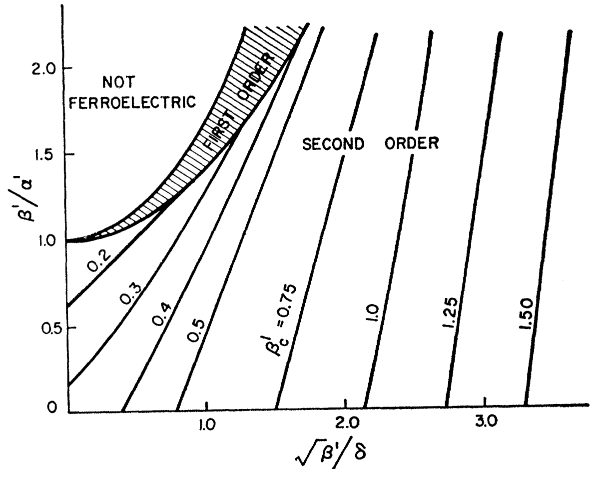

FIG. 6. The parameter β_c', which controls the Curie temperature through Eq. (5.32), shown as a function of β'/α' and $\sqrt{\beta'}/\delta$, the two dimensionless temperature-independent quantities in terms of which the more general sixth-order-anharmonicity problem is most conveniently described. Calculations of β_c' have been performed only for the system which exhibits a second-order phase transition, although the regions of β'/α', $\sqrt{\beta'}/\delta$ space for which first-order transitions, or no transition at all, would occur are also marked in the figure.

where α', β', Γ', and δ are dimensionless parameters defined by

$$\alpha'=(Bk^2T^2)^{1/3}/\omega_0^2,\quad \beta'=(Bk^2T^2)^{1/3}/(\eta\gamma S^2/v), \tag{5.31}$$

$$\Gamma'=(v/S)(B/kT)^{1/6}\langle P_{\text{ion}}\rangle,\ \delta=(B^2kT)^{1/3}/(-A), \tag{5.31'}$$

and a subscript c refers to values for the case $T=T_c$. The ratios $\beta'/\alpha'=\omega_0^2/(\eta\gamma S^2/v)$, and $(\beta')^{1/2}/\delta=-A/(B\eta\gamma S^2/v)^{1/2}$ are temperature-independent, and are the parameters in terms of which the system is most conveniently described. We compute

$$kT_c=(1/B)^{1/2}(\eta\gamma S^2/v)^{3/2}(\beta_c')^{3/2}, \tag{5.32}$$

where β_c' as a function of β'/α' and $(\sqrt{\beta'})/\delta$ is shown in Fig. 6. This expression for T_c is valid only if the phase transition is of second order, since it has been evaluated from the condition $\langle P_{\text{ion}}\rangle\rightarrow 0$. In Fig. 6 we have also sketched those regions of β'/α', $(\sqrt{\beta'})/\delta$ space for which a first-order transition, or no ferroelectric transition would occur. The second-order–first-order boundary will be discussed later, but the boundary between ferroelectric and nonferroelectric systems can be calculated easily (in the one-mode approximation) as follows.

Minimizing the effective Hamiltonian (5.1) with respect to ξ, and writing $\langle P_{\text{ion}}\rangle=(S/v)\xi$, we readily calculate the ionic polarization at $T=0$ as

$$\langle P_{\text{ion}}\rangle_{T=0}=(S/v)(1/6B)^{1/2}\times(-2A+\{4A^2+6B[(\eta\gamma S^2/v)-\omega_0^2]\}^{1/2})^{1/2}. \tag{5.33}$$

Thus, the system can be polar at $T=0$ for the negative-A case if

$$4A^2+6B[(\eta\gamma S^2/v)-\omega_0^2]>0, \tag{5.34}$$

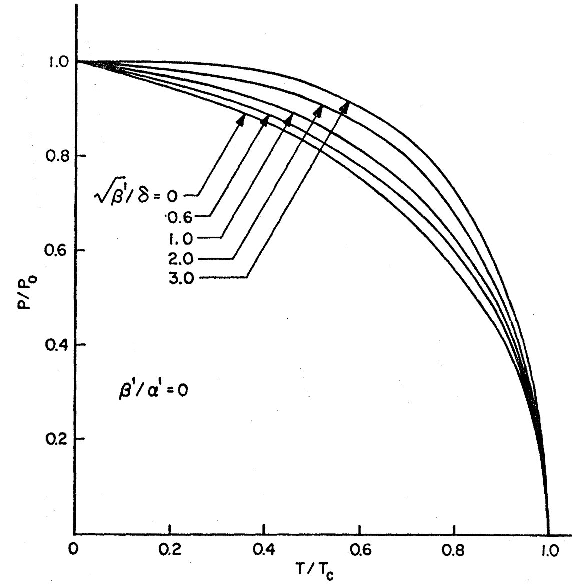

FIG. 7. Reduced polarization P/P_0, plotted as a function of reduced temperature T/T_c for various values of the parameter $\sqrt{\beta'}/\delta$, which measures the (negative) quartic-anharmonicity contribution to a ferroelectric system stabilized by sixth-order anharmonic terms. The curves $\sqrt{\beta'}/\delta \to \infty$ converge very rapidly to a limit barely outside the $\sqrt{\beta'}/\delta=3$ curve of the figure. The curves are computed for the case $\beta'/\alpha'=\omega_0^2/(\eta\gamma S^2/v)=0$.

which, in terms of the dimensionless parameters is

$$\beta'/\alpha' < 1+2\beta'/3\delta^2. \tag{5.34'}$$

We say "can be" because the first-order region calculated from the above includes metastable ferroelectrics for which the effective ion potential energy has a local, but not absolute, minimum for a nonzero value of P_{ion} at $T=0$. Details of the metastable-stable boundary will be discussed in a future publication on first-order ferroelectrics, in which region the boundary occurs.

Curves of P/P_0 versus T/T_c have been computed from (5.30) for many values of β'/α' and $\sqrt{\beta'}/\delta$. Some typical results are shown in Figs. 7–9. Again, these curves have been computed only for systems showing a second-order phase transition, and one readily verifies that $\langle P_{\mathrm{ion}}\rangle^2 \propto T_c - T$ as the temperature approaches the Curie point.

A few interesting observations can be made. First, in the limit $A\to 0$, the curves of Fig. 9 are almost identical with those of Fig. 2 for the case of quartic anharmonicity alone. They do, however, fall off with T fractionally faster, the difference being most pronounced for larger β'/α' ratios. Secondly, for a fixed value of β'/α', the curves (Figs. 7 and 8) become rapidly more steplike as the negative quartic anharmonicity increases, but they eventually become insensitive to further increase beyond $\sqrt{\beta'}/\delta \approx 3$. The limiting curve shape for $\sqrt{\beta'}/\delta > 3$ is independent of β'/α'. Finally, a rather surprising feature; the curve shapes become less steplike as the second-order–first-order phase boundary is approached.

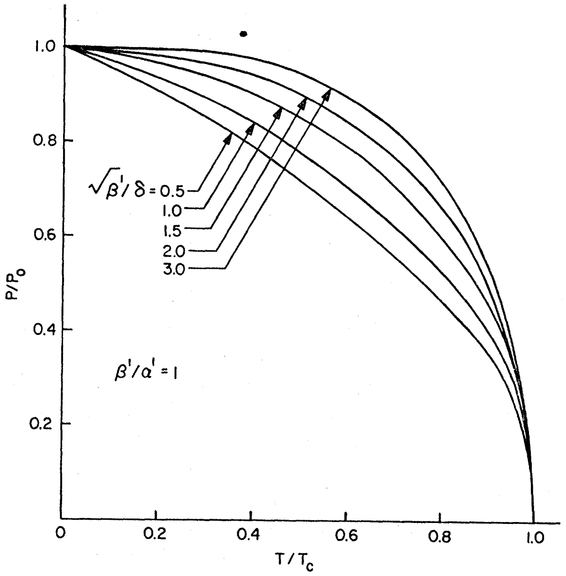

FIG. 8. As Fig. 7, but for $\beta'/\alpha'=1$. Again, all curves $\sqrt{\beta'}/\delta \to \infty$ converge very rapidly to a limit barely outside the $\sqrt{\beta'}/\delta=3$ curve.

We can again write an equation of the form (5.28′) relating T_c and $\langle P_{\mathrm{ion}}\rangle$. Writing $\rho'=0.45\rho$, the parameter ρ' is a function of β'/α' and $\sqrt{\beta'}/\delta$ and is shown in Fig. 10. For a fixed value of $(\eta\gamma S^2/v)$ and of B, both T_c and $\langle P_{\mathrm{ion}}\rangle$ at $T=0$ increase as A increases or as ω_0^2 decreases. This is true both in the first-order and in the second-order transition regions, so that for systems with comparable values of $\eta\gamma S^2/v$ and B, those exhibiting second-order transitions are likely to have higher transition temperatures and larger values of spon-

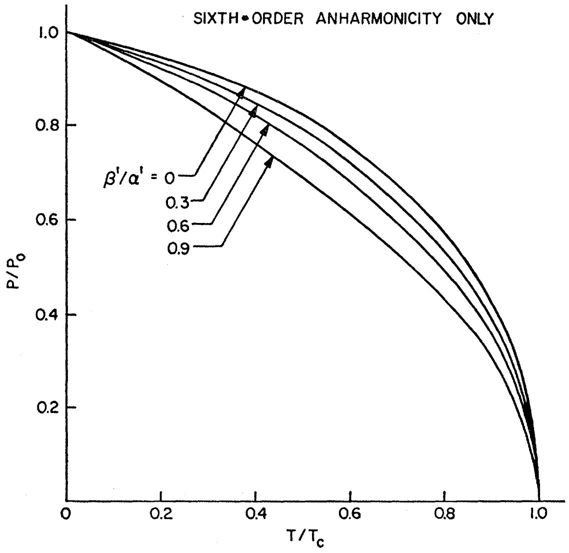

FIG. 9. Reduced polarization as a function of reduced temperature for a number of values of the parameter β'/α'. The curves are computed for a ferroelectric having only sixth-order anharmonicity, for which $T_c\to 0$ and $\beta'/\alpha'\to 1$.

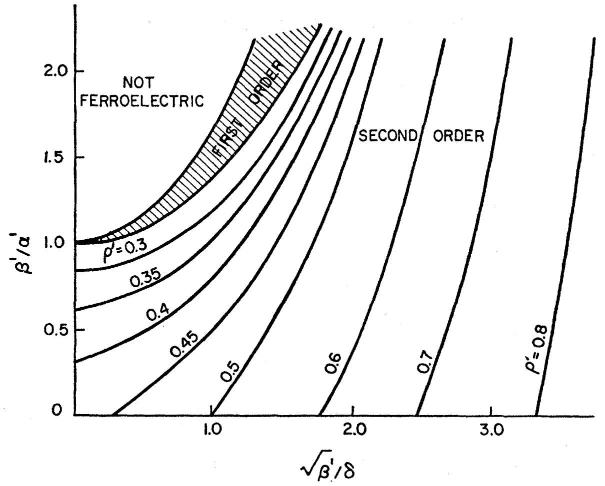

FIG. 10. The parameter $\rho'=0.45\rho$, which relates Curie temperature to ionic polarization via Eq. (5.28′), shown as a function of β'/α' and $\sqrt{\beta'}/\delta$.

taneous polarization than those with first-order transitions.

The results obtained earlier in this section relating $\chi_{\text{ion}}(\omega)$ in the paraelectric and ferroelectric states (for $T\approx T_c$) still hold when the quartic anharmonicity is negative. Thus, for this case, we need only compute for the easier paraelectric case. In the present notation we find

$$\frac{\gamma\chi_{\text{ion}}(\omega)}{1+\gamma\chi_{\text{ion}}(\omega)}=\frac{\omega_0^2}{\omega_0^2-\omega^2}\left(\frac{T_c}{T}\right)^{2/3}\frac{\langle y^2\rangle_0}{\beta_c'}, \tag{5.35}$$

where

$$\langle y^2\rangle_0=\int_{-\infty}^{\infty}y^2\exp\left(-\frac{y^2}{2\alpha'}+\frac{y^4}{\delta}-y^6\right)dy\Bigg/\int_{-\infty}^{\infty}\exp\left(-\frac{y^2}{2\alpha'}+\frac{y^4}{\delta}-y^6\right)dy. \tag{5.36}$$

Computing $\langle y^2\rangle_0/\beta_c'$ directly as a function of T/T_c, we find, numerically, that it seems to depend rather accurately on β_c' alone. The resulting curves are shown in Fig. 11. In analogy with (5.18), we define a parameter μ' by writing

$$\langle y^2\rangle_0=\beta_c'[1+\mu'(T-T_c)/T_c], \tag{5.37}$$

for temperatures $T\approx T_c$. With this notation, Eqs. (5.19)–(5.26) still hold if $\mu=\mu'-\frac{1}{6}$. We have computed μ' as a function of β_c' in Fig. 12.

6. FIRST- OR SECOND-ORDER TRANSITION?

We noted in Sec. 5 that ferroelectric systems stabilized by fourth-order anharmonicity always exhibit a second-order phase transition, whereas systems stabilized by sixth-order terms might exhibit first- or second-order transitions. The most direct way to determine the character of the phase transition is to examine the free

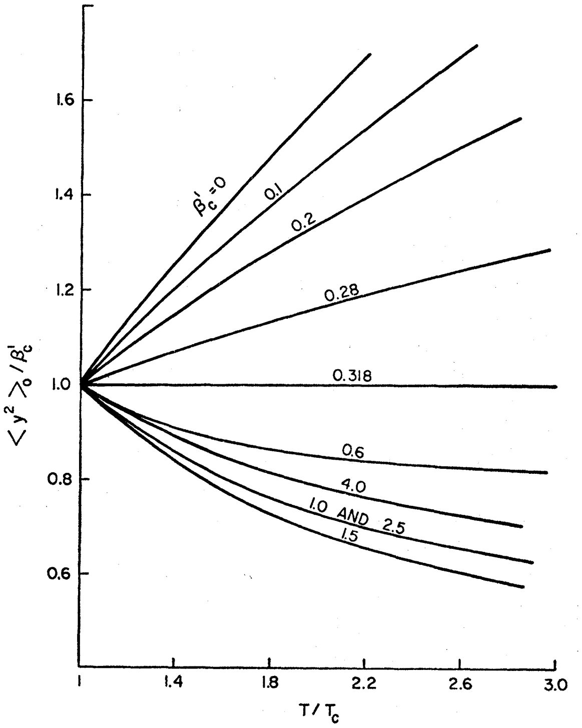

FIG. 11. The ratio $\langle y^2\rangle_0/\beta_c'$, which is a direct measure of ionic susceptibility in the nonpolar phase [via Eq. (5.35)], computed as a function of reduced temperature. It is found to depend rather accurately on β_c' alone.

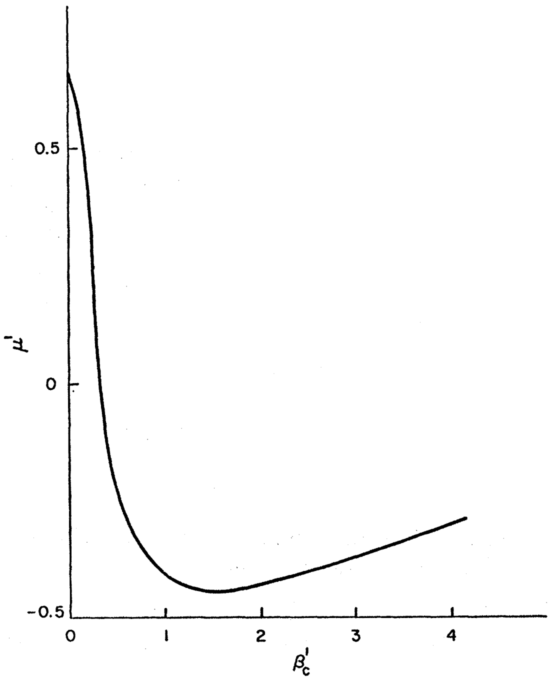

FIG. 12. The parameter μ' of Eq. (5.37), which determines the Curie constant and soft-mode frequency near T_c, shown as a function of β_c' (which controls the Curie temperature).

energy $F(P,T)$ expressed as a function of polarization and temperature alone.

The familiar statistical mechanical relationship for free energy, viz., $F=-kT\ln(\text{p.f.})$ where p.f. is the partition function, does not calculate $F(P,T)$. It calculates rather the free energy $F(E_{\text{loc}},T)$, defined as

$$F(E_{\text{loc}},T)=U-TS'-P_{\text{ion}}E_{\text{loc}}, \tag{6.1}$$

where U is internal energy and S' is entropy. Using the energy equation

$$TdS'=dU-E_{\text{loc}}dP_{\text{ion}}, \tag{6.2}$$

we find

$$dF(E_{\text{loc}},T)=-S'dT-P_{\text{ion}}dE_{\text{loc}}, \tag{6.3}$$

justifying the notation. Thus, from $F(E_{\text{loc}},T)$, by differentiation, can be obtained the ionic polarization and entropy functions of the system.

The function $F(P,T)$ is defined by the equation

$$F(P,T)=F(E_{\text{loc}},T)+\eta P_{\text{ion}}(E+\tfrac{1}{2}\gamma P_{\text{ion}}), \tag{6.4}$$

as may be verified as follows. Using (6.1), together with the fact that $E_{\text{loc}}=\eta(E+\gamma P_{\text{ion}})$, we find

$$F(P,T)=U-TS'-\tfrac{1}{2}\eta\gamma P_{\text{ion}}^2. \tag{6.5}$$

Differentiating and using (6.2), we have

$$dF(P,T)=-S'dT+\eta EdP_{\text{ion}}, \tag{6.6}$$

which is the required relationship.

For the ferroelectric system in the one-mode approximation, we may write

$$F(E_{\text{loc}},T)=-NkT\ln\left\{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\exp\left(\frac{-v\mathcal{H}_{\text{eff}}}{kT}\right)d\pi\, d\xi\right\}, \tag{6.7}$$

where $\mathcal{H}_{\text{eff}}$ is given by (5.1). The ξ integration involved in (6.7) can be performed analytically only in the limit of small anharmonicity. We accept this unfortunate restriction and proceed to calculate $F(P,T)$ within this limitation.

Introducing the dimensionless variable $w=\omega_0\xi/(kT)^{1/2}$, we write

$$-v\mathcal{H}_{\text{eff}}/kT=-(\pi^2/2kT)-\tfrac{1}{2}w^2-aw^4-bw^6+gw, \tag{6.8}$$

where

$$a=AkT/\omega_0^4,\quad b=Bk^2T^2/\omega_0^6,$$

and

$$g=SE_{\text{loc}}/\omega_0(kT)^{1/2}.$$

We can now integrate (6.7) directly if $a\ll 1$ and $b\ll 1$ to obtain, to first order in a and b

$$F(E_{\text{loc}},T)=-NkT[\ln(kT/\hbar\omega_0)-3a-15b+\tfrac{1}{2}g^2(1-12a-90b)-g^4(a+15b)-bg^6]. \tag{6.9}$$

P_{ion} follows as $-\partial F(E_{\text{loc}},T)/\partial E_{\text{loc}}$ and may be checked for consistency with (5.3) evaluated in the same approximation. This equation for P_{ion} as a function of E_{loc} can be solved for E as a function of P_{ion}. We find

$$\eta SE/\omega_0=pz+4qz^3+6rz^5, \tag{6.10}$$

where

$$z=vP_{\text{ion}}\omega_0/S,$$

and

$$p=1-(\eta\gamma S^2/v\omega_0^2)+12(AkT/\omega_0^4)+90(Bk^2T^2/\omega_0^6), \tag{6.11}$$

$$q=(A/\omega_0^4)+15(BkT/\omega_0^6),\quad r=B/\omega_0^6. \tag{6.12}$$

The free energy $F(P,T)$ now follows as $\int\eta EdP_{\text{ion}}$ and is

$$vF(P,T)=\tfrac{1}{2}pz^2+qz^4+rz^6. \tag{6.13}$$

The ferroelectric transition is of first order if $F(P,T)$ and its derivative with respect to z are simultaneously zero for a nonzero value of z; that is, if

$$\begin{aligned}p+2qz^2+2rz^4&=0,\\ p+4qz^2+6rz^4&=0.\end{aligned} \tag{6.14}$$

For a positive value of B (and hence r), a solution exists if q is negative, p is positive, and $q^2=2rp$. The boundary between first- and second-order transition regions is $p_c=q_c=0$ [$p_c=p(T=T_c)$, etc.], which is

$$1-(\eta\gamma S^2/v\omega_0^2)=2A^2/5B\omega_0^2, \tag{6.15}$$

or, in terms of the dimensionless parameters of Fig. 5 [compare Eq. (5.34')],

$$\beta'/\alpha'=1+2\beta'/5\delta^2, \tag{6.15'}$$

which is the boundary curve drawn in Fig. 6 to separate first- and second-order regions. The boundary value of β_c' (and hence transition temperature) follows as

$$\beta_c'=(15)^{-2/3}(\beta'/\alpha')^{2/3}(\beta'/\delta^2)^{1/3}. \tag{6.16}$$

The above theory is valid only in the limit of small anharmonicity, and this condition can be reduced to $\beta'/\alpha'\approx 1$, $\sqrt{\beta'}/\delta\ll 1$, so that the boundary curve of Fig. 5 may not be exact beyond this rather limited domain.

The free energy $F(P,T)$ is of particular interest since it is the "Devonshire" free energy as used in the thermodynamic theories of ferroelectricity (see, for example, Jona and Shirane[16]). We note that the quartic coefficient q of the polarization series (6.13) for this free energy is not temperature-independent, even for a clamped system. Thus, a negative value for A does not ensure a negative q or a first order phase transition. Quite generally, the present theory leads to temperature-dependent Devonshire coefficients which are algebraically related to the microscopic parameters only in the limit of small anharmonicity.

7. NONLINEAR PROPERTIES OF THE FERROELECTRIC STATE

We have described, in this paper, dielectric properties of a ferroelectric system in terms of distortions from a centrosymmetric paraelectric state. In the nonpolar state, the effective Hamiltonian for the system contains no odd-order terms in optical-mode variables. In the ferroelectric state, on the other hand, the symmetry is broken when the system distorts to one or other of the minimum-energy positions in the familiar double-minimum free energy. In such a distorted state, the environment ceases to be centrosymmetric.

The effective Hamiltonian of the many-mode system is given in (3.21). It is a sum of independent contributions from each optical-phonon mode p. We shall expand the effective ionic potential V_p of each mode about that value of ξ_p which minimizes it. Thus, this value $\xi_p{}^0$ is given by

$$\omega_p{}^2\xi_p{}^0+4A_p(\xi_p{}^0)^3+6B_p(\xi_p{}^0)^5 -\boldsymbol{\eta}_p\mathbf{S}_p(\mathbf{E}+\boldsymbol{\gamma}_p\langle\mathbf{P}_{\text{ion}}\rangle)=0. \tag{7.1}$$

Let $\theta_p=\xi_p-\xi_p{}^0$ be the new variable, in terms of which we find

$$V_p=V_p{}^0+P_p\theta_p{}^2+Q_p\theta_p{}^3+R_p\theta_p{}^4+\cdots, \tag{7.2}$$

where $V_p{}^0$ is independent of θ_p, and where

$$P_p=\tfrac{1}{2}\omega_p{}^2+6A_p(\xi_p{}^0)^2+15B_p(\xi_p{}^0)^4, \tag{7.3}$$

$$\begin{aligned}Q_p&=4A_p\xi_p{}^0+20B_p(\xi_p{}^0)^3,\\ R_p&=A_p+15B_p(\xi_p{}^0)^2.\end{aligned} \tag{7.4}$$

The equation of motion for θ_p follows immediately, and is

$$\ddot{\theta}_p+2P_p\theta_p+3Q_p\theta_p{}^2+4R_p\theta_p{}^3+\cdots=0. \tag{7.5}$$

It is a simple anharmonic oscillator equation of the type very frequently taken as a model to discuss the nonlinear optical properties of solids.[17–19] The application of a sinusoidal field $\mathbf{E}=\mathbf{E}_0e^{i\omega t}+\mathbf{E}_0{}^*e^{-i\omega t}$ to the system adds a term $-\boldsymbol{\eta}_p\mathbf{S}_p(\xi_p{}^0+\theta_p)\mathbf{E}$ to the potential-energy function of the pth mode. This, in turn, leads to a term $(\boldsymbol{\eta}_p\mathbf{S}_p)\mathbf{E}$ on the right-hand side of the equation of motion (7.5). The linear properties will be controlled by the first-order term in θ_p and the nonlinear properties will, in general, be dominated by the quadratic term. We shall therefore neglect higher-order terms and write the equation of motion for the pth mode

$$\ddot{\theta}_p+\Omega_p{}^2\theta_p+3Q_p\theta_p{}^2=(\boldsymbol{\eta}_p\mathbf{S}_p)\mathbf{E}, \tag{7.6}$$

where $\Omega_p{}^2=2P_p$ is now the frequency of the optic mode p at low temperatures (a more accurate evaluation of $\Omega_p{}^2$, when p is the soft mode, is given in Part II of the present series).

We may now write down quite formally the linear and nonlinear ionic susceptibilities for the system described by (7.6). For the linear susceptibilitiy parallel to $\langle\mathbf{P}_{\text{ion}}\rangle$ we find

$$\chi_{\text{ion}}{}^{(1)}(\omega)=\sum_p\frac{\eta_pS_{pz}{}^2/v}{\Omega_p{}^2-\omega^2}. \tag{7.7}$$

The first-order nonlinear solution has Fourier components at 2ω and 0. We have

$$\chi_{\text{ion}}{}^{(2)}(2\omega;\,\omega,\omega)=\sum_p\frac{-(3Q_p\eta_p{}^2S_{pz}{}^3/v)}{(\Omega_p{}^2-\omega^2)(\Omega_p{}^2-4\omega^2)}, \tag{7.8}$$

$$\chi_{\text{ion}}{}^{(2)}(0;\,\omega,\omega)=\sum_p\frac{-2(3Q_p\eta_p{}^2S_{pz}{}^3/v)}{(\Omega_p{}^2-\omega^2)\Omega_p{}^2}. \tag{7.9}$$

For ferroelectric systems, Q_p is large only for those soft modes which dominate the ferroelectric properties. Thus, for a system with only one or two soft modes, the above expressions simplify accordingly. Quite generally, however, by use of Eqs. (7.1), (7.3) and (7.4), we can express the optical-phonon frequencies and the various nonlinear susceptibilities of interest directly in terms of the ionic polarization. For the one-mode approximation, these may, in turn, be related directly to the pertinent parameters of the effective Hamiltonian.

It should be noted that the above results are derived for the ionic motion of a ferroelectric, and are therefore of direct relevance only to infrared nonlinear properties. Even here, as pointed out by Garrett,[19] an adequate discussion of nonlinear effects requires, at the very least, the use of an anharmonic vibronic oscillator model, allowing simultaneously for ionic and electronic anharmonicity. This involves the use of four anharmonic third-order parameters in the expression for the potential energy of each vibronic oscillator, of which Q_p of Eq. (7.2) is only one. Even so, coupled with some knowledge of optical anharmonicities, calculations along the lines of the present section must shed some light on the dependence of nonlinear effects on polarization in ferroelectrics.

8. CONCLUSIONS

An effective Hamiltonian has been developed to describe the nondissipative dielectric properties of displacement ferroelectrics. It is suggested that this displacement Hamiltonian might be used for some dielectrics in the same spirit that a spin Hamiltonian is used for an analysis of magnetic properties, i.e., as a convenient stepping stone between the "tossing sea of Cause and Theory and the firm ground of Result and Fact."

Although some broad features of the dielectric properties of ferroelectrics have been outlined, even for the general "many-soft-mode" systems, it is evident that the real value of the displacement Hamiltonian is for ferroelectrics which have, to at least a fair

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approximation, only one strongly temperature-dependent optical-phonon mode. For such a system we have described many dielectrics properties quantitatively in terms of the parameters of the displacement Hamiltonian. These properties include polarization, soft-mode frequency, and linear and nonlinear static and dynamic susceptibilities, all as functions of temperature both near to and away from the Curie temperature.

A comparison of theory with experiment for some or all of these dielectric properties is sufficient to determine the relevant parameters of the displacement Hamiltonian. These parameters are microscopic and are very much more closely related to the fundamental forces of the system than are the parameters of a thermodynamic theory. In part III we actually determine them for lithium tantalate, and proceed to show how they can be used to elucidate less obvious features of detailed microscopic behavior and to support, or to reject, particular microscopic models.

The accuracy that can be achieved in any such undertaking probably depends most significantly on the validity of the "one-soft-mode" approximation for the particular ferroelectric concerned. A quantitative assessment of the number and degree of softness of the various optic modes can be made by direct measurement of the infrared or Raman spectra as a function of temperature.

The hope is that for a number of displacement ferroelectrics (and possibly even order-disorder ferroelectrics; see part II) the use of the displacement Hamiltonian and classical statistics will allow for a fairly quantitative description of nondissipative dielectric properties in terms of relatively few microscopic parameters which can themselves, as a result, be estimated with reasonable accuracy. In this way, less emphasis need be placed on thermodynamic (macroscopic) theories and explanations of experimental data can perhaps, more frequently, be given directly in terms of microscopic theory.

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Statistical Theory for Displacement Ferroelectrics. II. Specific-Heat and Soft-Mode-Frequency Calculations

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

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The effective field theory for displacement ferroelectrics which was developed in part I of the present series of papers is extended to include specific-heat, energy-of-ordering, and more detailed soft-mode-frequency calculations. Numerical results are computed for a simple one-soft-mode system in preparation for a test of the theory on the displacement ferroelectric $LiTaO_3$ (which is presented in the following paper). Detailed shapes of the specific-heat curves are computed and the discontinuity at the Curie temperature is displayed. The soft-mode-frequency calculations are extended beyond the small-anharmonicity region discussed in part I, thereby removing the last small-anharmonicity restriction from the method. Freed from all small-anharmonicity restrictions, it is demonstrated that the present approach is no longer confined to displacement systems, but is equally applicable for order-disorder ferroelectrics and goes over quite smoothly from one class of ferroelectric to the other.

1. INTRODUCTION

In part I of the present series of papers,[1] an attempt was made to construct a workhorse theory for displacement ferroelectrics bearing a resemblance in spirit to the molecular-field theory (or, more closely, the cluster theories) of magnetism. In the theory, advantage is taken of the relative insensitivity of optic-mode frequencies to wave vector, in the absence of long-range electrostatic forces, to write an effective Hamiltonian for their motion in terms of a single primitive cell of the crystal lattice. The long-range dipolar interactions are then accommodated in an effective-field approximation by replacing all the other cells of the system by their thermal (ensemble) averages. The latter statistical approximation is basically a high-temperature one (neglecting short-range correlations between cells), but is one which is likely, in view of the long range of the dipolar forces, to give quite a good description of the system over the entire temperature range.

The great advantage which accrues from accepting the statistical mechanical restrictions associated with the use of an effective-field theory is the ability to describe at least some ferroelectric systems in terms of comparatively few parameters associated with an effective Hamiltonian; few enough, in particular, for these "unknowns" to be comfortably overdetermined by a comparison of theory with experiment for dielectric properties alone.

In part I, quantitative statistical calculations were performed for a particularly simple case; that of a displacement ferroelectric which has only one grossly

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