

## Self-Consistent Treatment of the Frequency Spectrum of a Model Paraelectric

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The temperature dependence of the frequency spectrum of a model NaCl-structure paraelectric exhibiting soft-mode behavior at the zone center is treated self-consistently. A variational formulation is employed, yielding a set of nonlinear integral equations which are solved iteratively. The difficulties associated with perturbative treatments are avoided by starting from a renormalized phonon basis which represents a stable state of equilibrium for the crystal. In particular, the soft-mode branches, which may be imaginary in the harmonic approximation, are renormalized and treated self-consistently. The model consists of rigid anions and cations of unequal masses interacting via long-range Coulomb forces plus a short-range interaction extending to second neighbors. Anharmonicity is introduced through a parametrized quartic interaction. Calculations are carried out for a wide range of model parameters, including the situation where the phase space subtended by the imaginary harmonic frequencies may constitute a large fraction of the Brillouin zone. The importance of including the effect of the soft-mode branches is discussed in detail. It is pointed out that the self-consistent equations do not admit a zero solution for the soft-zone-center optic mode. An explanation is given of why the Curie-law dependence of the soft-zone-center frequency squared may extend to lower temperatures than one might expect on simple qualitative grounds. Attention is given to the coupling of the soft TO branch to the TA branch of the same symmetry, and the anomalous temperature dependence of the acoustic branch at finite wave vector is displayed. Finally, the temperature dependence of the intersublattice correlation function is calculated, and it is pointed out that the soft-mode branches contribute significantly to the temperature dependence of this function. The implications of the latter for a transition to an ordered phase are discussed.

### I. INTRODUCTION

Since the advent of the inelastic neutron scattering technique as a probe of the phonon dispersion curves in ferroelectric crystals, much has been learned about the dynamical aspects of the phase transitions which occur in these materials. The extensive work carried out at the neutron facilities at Brookhaven and Chalk River in the past few years has demonstrated the existence of strongly temperature-dependent low-lying TO branches in many ferroelectric and paraelectric materials. The existence of a soft optic mode of long wavelength had been predicted by Anderson<sup>1</sup> and by Cochran,<sup>2</sup> who demonstrated the connection between the strong temperature dependence of the soft mode and the dielectric anomaly observed in the paraelectric phase of many ferroelectric crystals. Anderson and Cochran proposed that in a ferroelectric material a group of modes near the zone center would be imaginary in the harmonic approximation, with anharmonic interactions providing a renormalization of the phonon self-energy such that below a certain temperature the paraelectric phase would become unstable. The qualitative correctness of this idea was demonstrated in later calculations by Silverman and Joseph,<sup>3</sup> Silverman,<sup>4</sup> and Cowley.<sup>5</sup>

The usual approach to the treatment of soft-mode systems is to employ an anharmonic perturbation expansion about a harmonic basis. However, because a group of modes will in general be imaginary in the harmonic approximation, the harmonic basis represents an unstable state of equilibrium for the crystal, and the perturbation series does not in principle exist. Faced with this difficulty, the conventional approach has been to neglect the unstable modes under the assumptions (i) that the imaginary modes encompass only a small fraction of the Brillouin zone and (ii) that the major temperature dependences will be governed by the remaining, harmonically stable modes.<sup>1,6</sup> In contrast to this approach, a more realistic treatment would require that one treat the entire frequency spectrum self-consistently, avoiding the difficulties associated with perturbative treatments by employing at the outset a renormalized phonon basis. The possibility of carrying out such a calculation in a soft-mode system was first recognized by Silverman,<sup>4</sup> who at that time pointed out the difficulty of carrying out such a procedure. Later, Boccara and Sarma<sup>7</sup> formulated variationally a self-consistent treatment of the vibrational spectrum of crystals exhibiting displacive-type transitions but did not present any numerical results.<sup>8</sup> Their formal treat-

ment represented the lowest-order approximation in what is now called the self-consistent phonon formulation of anharmonic lattice dynamics,<sup>9</sup> which recently has been employed extensively in the treatment of anharmonicity in the rare-gas solids, notably the quantum crystals of solid helium. In the light of these detailed calculations, it is now possible to extend such techniques to the treatment of soft-mode systems, and it is to this problem that we address ourselves in the present work.<sup>10</sup>

We propose to calculate the temperature dependence of the frequency spectrum of an NaCl-structure crystal which we feel should be a physically realistic model of a paraelectric exhibiting soft-mode behavior at the zone center. The treatment of the frequency spectrum is carried out within the context of the lowest-order self-consistent phonon approximation, employing a variational treatment which yields a specific set of nonlinear integral equations which are solved iteratively. The entire frequency spectrum is treated self-consistently and as such the calculation represents a significant departure from previous treatments of soft-mode systems. Contrary to the widely held view that the soft-mode branches do not make an important contribution through their implicit temperature dependence, we find that they in fact contribute significantly—both directly through their own temperature dependence and indirectly through the coupling to the acoustic branch of the same symmetry.

In Sec. II we set up a model Hamiltonian for the NaCl-structure paraelectric. The model consists of two types of ions interacting via long-range Coulomb interactions plus a short-range interaction extending to second neighbors. Anharmonicity is introduced through an effective parametrized quartic interaction. We are not of course restricted to this particular form for the anharmonic interaction. However, this simple picture emphasizes the basic physical concepts as clearly as possible. We intend to deal with the additional complexities introduced by cubic anharmonicity in a later publication. Following our discussion of the model Hamiltonian of the system, we review briefly the self-consistent phonon approach to lattice dynamics and its application to the paraelectric crystal. Having derived the set of nonlinear integral equations, we describe the methods used for solving them.

Section IIIA is devoted to a study of the conditions necessary for low-lying TO modes in the NaCl structure to exhibit soft-mode behavior. We plot the squared frequency of the renormalized zone-center TO mode as a function of temperature for a wide range of parameters. Of particular note is the fact that the Curie-law dependence of the zone-center frequency squared (and hence of the dielectric susceptibility) extends into the low-temperature regime. This is a consequence of the fact that the density of

modes with energies less than  $kT$  will be more heavily weighted at low temperatures when the frequency spectrum is treated self-consistently than it would be otherwise. It is pointed out that the soft-mode branches contribute significantly to the intersublattice correlations. Related to this is the fact that the self-consistent equations do not admit a zero solution for the soft-zone-center optic mode, thus suggesting that a transition to an ordered phase would be formally first order, even in the absence of acoustic instabilities, although with an appropriate choice of parameters it could be made very close to second order.

Following the discussion of the temperature dependence of the zone-center optic mode, the temperature dependence of the complete dispersion curves is considered. Particular attention is paid to the coupling between the optic and acoustic modes of the same symmetry. The significance of this coupling is further discussed in Sec. IIIC, where we consider the temperature dependence of the intersublattice correlation function. In this section we show that in general there exists a "transition region" in which the intersublattice correlations are dominated by the soft-mode branches.

In Sec. IV we present a final discussion of our results together with comments on the extension of the formalism to the treatment of an ordered phase.

## II. DERIVATION OF SELF-CONSISTENT EQUATIONS FOR MODEL PARAELECTRIC CRYSTAL

We begin the description of the model paraelectric by assuming that the true system Hamiltonian has the form

$$\mathcal{H} = - \sum_{l\sigma} \frac{1}{M_\sigma} (\nabla_{l\sigma})^2 + V(\{\vec{r}(l\sigma)\}) \quad , \quad (1)$$

where

$$\vec{r}(l\sigma) = \vec{R}(l\sigma) + \vec{u}(l\sigma) \quad .$$

No assumption need be made about the form of  $V$  except that of a general local interaction depending on the instantaneous positions of all the ions in the crystal.  $\vec{R}(l\sigma)$  denotes the equilibrium position vector of an ion of type  $\sigma$  in lattice cell  $l$ .  $\vec{u}(l\sigma)$  is the dynamic displacement operator associated with that ion. In general, the interaction potential in insulators and semiconductors is quite complicated and by no means expressible as a sum of pairwise interactions. Thus, in order to proceed further we specify the model in the simplest manner possible by dividing the interaction into a parametrized anharmonic short-range part together with a long-range part, the latter arising from the Coulomb interactions between the two types of ions, assumed to be rigid. If we restrict the anharmonic potential to quartic interactions only, the model Hamiltonian takes the form

$$H = - \sum_{i\sigma} \frac{1}{M_\sigma} (\nabla_{i\sigma})^2 + V_0 + \frac{1}{2!} \sum_{i1',\sigma1',\alpha\beta} u_\alpha(i\sigma) [C_{\alpha\beta}^{\sigma\sigma'}(l1') + R_{\alpha\beta}^{\sigma\sigma'}(l1')] u_\beta(l'\sigma') \\ + \frac{1}{4!} \sum_{l_1 \cdots l_4, \sigma_1 \cdots \sigma_4, \alpha_1 \cdots \alpha_4} u_{\alpha_1}(l_1\sigma_1) u_{\alpha_2}(l_2\sigma_2) R_{\alpha_1 \cdots \alpha_4}^{\sigma_1 \cdots \sigma_4}(l_1 \cdots l_4) u_{\alpha_3}(l_3\sigma_3) u_{\alpha_4}(l_4\sigma_4). \quad (2)$$

As mentioned previously, we need not restrict ourselves to this form for the model Hamiltonian. Terms cubic and higher order in the anharmonic interaction may also be included. Since we do not have a well-defined functional form for the potential, however, the simple form (2) allows us to keep the number of model parameters down to a manageable few. One can also treat self-consistently possible distortions of the lattice by introducing an appropriate set of order parameters. This will be discussed in Sec. IV. In expression (2),  $R_{\alpha\beta}^{\sigma\sigma'}(l1')$  represents the harmonic part of the short-range interaction extending to second neighbors, while  $R_{\alpha_1 \cdots \alpha_4}^{\sigma_1 \cdots \sigma_4}(l_1 \cdots l_4)$  represents the quartic anharmonic contribution to the short-range interaction, assumed to be nonzero for nearest-neighbor pairs only. Finally,  $C_{\alpha\beta}^{\sigma\sigma'}(l1')$  represents the contribution to the interaction energy arising from the long-range Coulomb interactions. We treat the Coulomb interaction harmonically instead of self-consistently. This simplification should not alter the qualitative features of the model since the short-range forces usually dominate the anharmonicity. Further, we neglect the polarizability of the ions, specifying the Coulomb interaction through some effective charge  $Z^*$  which determines the splitting between the LO and TO modes at the zone center. For specific comparisons with actual materials it is important to allow for the polarizability of the ions and possibly important to treat the Coulomb interactions anharmonically.

The techniques used in dealing with the Coulomb contribution to the dynamical matrix are well known.<sup>11</sup> Thus, we confine ourselves to a discussion of the short-range part. Employing the symmetry properties appropriate to a cubic crystal, together with the requirement of translational invariance, we write the nearest-neighbor contribution to the short-range interaction as

$$V_{\text{SR}} = \frac{1}{2} \sum [\varphi_L x^2 + \varphi_T (y^2 + z^2)] + \sum [\Phi_{11} x^4 + \Phi_{22} (y^4 + z^4) \\ + \Phi_{12} x^2 (y^2 + z^2) + \Phi_{23} y^2 z^2], \quad (3)$$

where we have used  $x$ ,  $y$ ,  $z$  to symbolically denote the corresponding Cartesian components of the relative displacement between nearest-neighbor ion pairs. The summation implies a single sum over the  $N$  unit cells in the crystal together with a sixfold permutation over the octahedral environment of nearest-neighbor pairs. The coefficients  $\varphi$  and  $\Phi$  depend, of course, on the nearest-neighbor

pair considered. However, any  $\varphi$  (or  $\Phi$ ) may be obtained from a single reference  $\varphi$  (or  $\Phi$ ) through an appropriate symmetry operation. In what follows,  $\varphi_L$ ,  $\varphi_T$ ,  $\Phi_{11}$ , etc. will be taken to mean  $\varphi_L(100)$ ,  $\varphi_T(100)$ ,  $\Phi_{11}(100)$ , etc. The second-neighbor interaction, which is to be treated harmonically, will be discussed in Sec. III.

Within the spirit of the self-consistent phonon formalism we assume that the dynamics of the phonon excitations are well described by some trial harmonic Hamiltonian. For the case of the paraelectric crystal, this assumption implies the following form for the trial Hamiltonian:

$$H_t = - \sum_{i\sigma} \frac{1}{M_\sigma} (\nabla_{i\sigma})^2 + \frac{1}{2} \sum_{i1',\sigma1',\alpha\beta} u_\alpha(i\sigma) C_{\alpha\beta}^{\sigma\sigma'}(l1') u_\beta(l'\sigma') \\ + \frac{1}{2} \sum_{i1',\sigma1',\alpha\beta} u_\alpha(i\sigma) \tilde{\varphi}_{\alpha\beta}^{\sigma\sigma'}(l1') u_\beta(l'\sigma'). \quad (4)$$

Within the context of the model, the last term of (4) will take the form  $\frac{1}{2} \sum [\tilde{\varphi}_L x^2 + \tilde{\varphi}_T (y^2 + z^2)]$ .  $\tilde{\varphi}_L$  and  $\tilde{\varphi}_T$  denote the renormalized nearest-neighbor force constants, to be determined variationally from a minimization of the free energy

$$F = \text{Tr}[\rho_t (\mathcal{H} + \beta^{-1} \ln \rho_t)] \quad (5)$$

In the above  $\mathcal{H}$  is to be approximated by the model Hamiltonian (2).  $\rho_t$  denotes the trial density matrix, having the canonical form

$$\rho_t = e^{-\beta H_t} / \text{Tr}(e^{-\beta H_t}). \quad (6)$$

Expression (5) represents the lowest-order term in a cumulant expansion<sup>9</sup> of the exact free energy in powers of  $\mathcal{H} - H_t$ . Minimization of the free energy with respect to the parameters of the trial Hamiltonian yields the by now well-known result  $\tilde{\varphi} = \langle \nabla \nabla V \rangle$ , which relates the trial force-constant matrix to the thermal average [with respect to the density matrix (6)] of the second derivative of the true potential.<sup>12</sup> We are now in a position to explain the physical reasoning behind our model. If we note that the force matrix obtained from the Coulomb interaction alone is not positive definite, then we see that if  $\tilde{\varphi}_L$  and  $\tilde{\varphi}_T$  are smaller than the equivalent components of this matrix, a certain number of frequencies will be imaginary in the harmonic approximation. However, the renormalized force matrix possesses not only a temperature-independent term from the harmonic part of  $V$  but also a temperature-dependent term from the thermal average of higher derivatives of  $V$ . At high enough temperatures the amplitude of thermal mo-

tion ultimately will be such that the renormalized force matrix will be positive definite. This must happen if the crystal itself is stable. Thus, at high enough temperature all of the frequencies will be positive. However, as the temperature is lowered, the thermal motion decreases and  $\langle \nabla \nabla V \rangle$  will approach the harmonic value. Hence, a frequency such as the zone-center TO frequency, which in the absence of renormalization would be imaginary, should be quite temperature dependent and will decrease in value and perhaps go to zero as the temperature is lowered. We will find out in fact that this frequency does not go to zero.

Returning now to the model, the general self-consistent equations become

$$\bar{\varphi}_L = \varphi_L + 12\Phi_{11}F_{11}(100) + 4\Phi_{12}F_{22}(100) \quad (7a)$$

$$\bar{\varphi}_T = \varphi_T + 2\Phi_{12}F_{11}(100) + (12\Phi_{22} + 2\Phi_{23})F_{22}(100) \quad (7b)$$

where

$$F_{\alpha\alpha}(100) \equiv \langle [u_\alpha(A) - u_\alpha(B)]^2 \rangle,$$

and the thermal average is with respect to the density matrix (6).  $u_\alpha(A) - u_\alpha(B)$  denotes the  $\alpha$  component of the relative displacement between nearest-neighbor  $A$  and  $B$  atoms located at  $(0, 0, 0)$  and  $(1, 0, 0)$ , respectively.  $F_{\alpha\alpha}$ , of course, depends implicitly on  $\bar{\varphi}_L$  and  $\bar{\varphi}_T$ . Within the framework of the approximation the general equal-time-displacement correlation function  $\langle u_\alpha(l\sigma)u_\beta(l'\sigma') \rangle$  may be decomposed via a normal-mode representation in terms of the renormalized frequencies and eigenvectors,<sup>13</sup> i. e.,

$$\begin{aligned} \langle u_\alpha(l\sigma)u_\beta(l'\sigma') \rangle &= \frac{1}{2N} \sum_{q\lambda} \frac{1}{\omega(q, \lambda)} \\ &\times \coth\left[\frac{1}{2}\beta\omega(q, \lambda)\right] e^{-i\vec{q}\cdot[\vec{R}(l\sigma) - \vec{R}(l'\sigma')]} \\ &\times (M_\sigma M_{\sigma'})^{-1/2} \epsilon_\alpha^\sigma(q, \lambda) \epsilon_\beta^{\sigma'}(q, \lambda). \quad (8) \end{aligned}$$

The frequencies  $\omega(q, \lambda)$  and eigenvectors  $\epsilon_\alpha^\sigma(q, \lambda)$  are obtained from a diagonalization of the trial Hamiltonian (4). Equation (8) together with Eqs. (7a) and (7b) and the harmonic dispersion relation determining  $\omega(q, \lambda)$  and  $\epsilon_\alpha^\sigma(q, \lambda)$  constitute the set of self-consistent equations which must be solved in general. Since the equations are not amenable to analytic solution, they must be solved iteratively on a computer. One begins the solution with a guess for the correlation functions  $F_{11}$  and  $F_{22}$ . This yields force constants  $\bar{\varphi}_L$  and  $\bar{\varphi}_T$  which, when inserted in (4), permit the calculation of a set of frequencies  $\omega(q, \lambda)$  and eigenvectors  $\epsilon_\alpha^\sigma(q, \lambda)$ . These in turn allow us to calculate a new set of correlation functions using Eq. (8). The procedure is then repeated until convergence is achieved. In carrying out the sum in wave-vector space indicated in (8), 1000 points in the first

Brillouin zone were employed.

In practice one is usually interested in the case of a freely expanding crystal at constant pressure. If one minimizes the free energy with respect to the internal strain tensor, one obtains for the case of a cubic crystal an expression for the equilibrium pressure. In the presence of cubic anharmonicity the zero-pressure condition then yields an expression for the thermal strain. In the present case where cubic anharmonicity is neglected the zero-pressure condition takes the form of a stability criterion placing a constraint on the unrenormalized nearest-neighbor force constant  $\varphi_T$ . Indeed, we must have<sup>11</sup>

$$\varphi_T = \frac{1}{3}\epsilon_c, \quad (9)$$

where  $\epsilon_c$  is the Coulomb energy per particle. In the presence of second-neighbor forces this criterion must, in general, be modified.

### III. TEMPERATURE DEPENDENCE OF FREQUENCY SPECTRUM

#### A. Zone-Center TO Mode

In this section we consider the variation with temperature of the renormalized zone-center TO mode for various values of the model parameters. We choose a set of units such that neither the reduced mass nor the parameters of the dipolar interaction enter into the expressions for the frequencies at the zone center. A squared frequency  $\omega^2$  will be expressed in units of  $M_R^{-1}[4\pi(Z^*e)^2/2r_0^3]$ , where  $M_R$  is the reduced mass of an  $AB$  ion pair,  $Z^*e$  is the zone-center effective charge, and  $r_0$  is the nearest-neighbor distance. In these units the splitting between the zone-center optic modes is normalized to unity, i. e.,

$$\omega_{LO}^2(\Gamma) - \omega_{TO}^2(\Gamma) = 1. \quad (10)$$

Similarly, harmonic force constants will be expressed in units of  $4\pi(Z^*e)^2/2r_0^3$  and quartic force constants in units of  $r_0^{-2}[4\pi(Z^*e)^2/2r_0^3]$ . With this choice of units the expression for the zone-center TO-mode frequency squared takes the form

$$\begin{aligned} \omega_{TO}^2(\Gamma) &= 2\left[\varphi_L + 2\varphi_T - \frac{1}{6} + (4\Phi_{12} + 12\Phi_{11})F_{11}(100) \right. \\ &\quad \left. + (4\Phi_{12} + 24\Phi_{22} + 4\Phi_{23})F_{22}(100)\right]. \quad (11) \end{aligned}$$

It should be borne in mind that  $\varphi_T$  in the above expression is fixed by condition (9) and as such is always negative. The units we have chosen render the long-wavelength properties relatively independent of the dipolar parameters, the masses of the two types of ions, and the atomic volume. The detailed features of the full dispersion curves will, of course, depend on the value of these quantities. For definiteness, we have in the present treatment made the choice of assigning values to  $M_A$ ,  $M_B$ ,

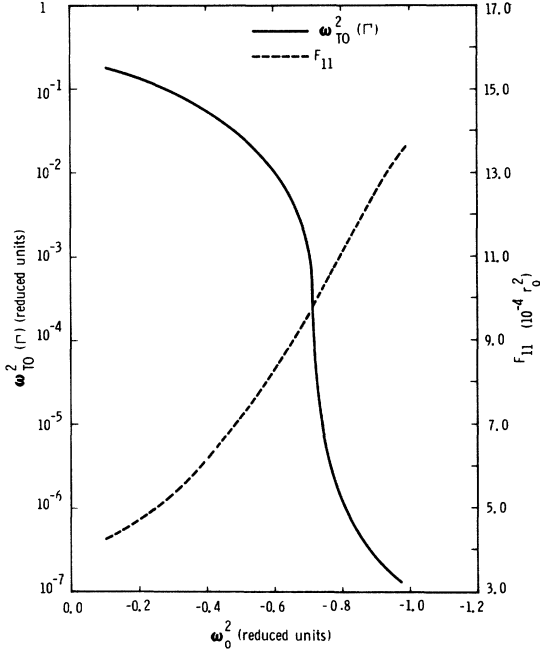


FIG. 1.  $\omega_{\text{TO}}^2(\Gamma)$  and  $F_{11}$  vs the unrenormalized zone-center TO frequency squared for fixed quartic anharmonicity ( $\Phi_{11} = 30.0$ ).

$Z^*$ , and  $\nu_0^3$  appropriate to SnTe, a semiconductor of the NaCl structure which exhibits soft-mode behavior at the zone center.<sup>14,15</sup> We do not pretend that the present rigid-ion model describes at all accurately the detailed features of the interactions in this material. As such we do not attempt a comparison with the available experimental data, even though a wide range of behavior for the temperature dependence of the zone-center mode may be obtained in our model without resorting to a more sophisticated description of the interatomic forces.

The accepted criterion for soft-mode behavior at the zone center is that the unrenormalized  $\omega_{\text{TO}}^2(\Gamma)$  [i.e., Eq. (11) with the quartic force constants set equal to zero] be negative or small and positive. This results from a cancellation between the dipolar and the short-range forces, a cancellation which does not occur for the LO mode. In the conventional way of looking at soft-mode behavior, a negative value for the harmonic TO frequency squared (which we henceforth denote by  $\omega_0^2$ ) would imply that the renormalized frequency given by Eq. (11) would vanish at some finite temperature. This is no longer true when the spectrum is treated self-consistently.

In order to simplify our discussion as much as possible, we initially consider the case where only  $\Phi_{11}$ , the longitudinal component of the quartic interaction, is nonzero. This will permit us to

parametrize our results in terms of the two quantities  $\varphi_L$  (or, alternatively,  $\omega_0^2$ ) and  $\Phi_{11}$ . From a central-force point of view one expects the radial component of the quartic interaction to be by far the strongest. Even if the forces deviate appreciably from centrality as one might expect in real materials, it is probably reasonable to assume that  $\Phi_{11}$  would still be the dominant component. A further motivation for keeping only  $\Phi_{11}$  nonzero is that in this approximation the elastic constant  $C_{44}$  is rigorously temperature independent (since only  $\tilde{\varphi}_T$  contributes to  $C_{44}$ ). This will facilitate the discussion of mode coupling at finite wave vector at a later point in this section. Finally, as we discuss in Sec. IV, this choice for the quartic interaction favors a transition to a rhombohedrally distorted NaCl-structure ordered phase such as is observed in the IV-VI semiconductor GeTe.<sup>16</sup>

In Fig. 1 we plot the zero-temperature squared frequency of the renormalized zone-center TO mode for fixed quartic anharmonicity and as a function of the bare frequency  $\omega_0^2$ . As  $\omega_0^2$  becomes increasingly negative,  $\omega_{\text{TO}}^2(\Gamma)$  decreases as expected. At the same time, however,  $F_{11}$  increases in such a way that  $\omega_{\text{TO}}^2(\Gamma)$  only asymptotically approaches zero. Similar behavior would arise if one were to fix  $\omega_0^2$  and decrease  $\Phi_{11}$ . The set of self-consistent equations may be thought of as a set of nonlinear equations determining  $F_{11}$ . We can see this as follows. Equation (8) defines  $F_{11}$  as a nonlinear but single-valued function of  $\tilde{\varphi}_L$  at each temperature. So defined,  $F_{11}$  has the property that at any given temperature,  $\infty > F_{11} > 0$  for  $\tilde{\varphi}_{\text{min}} < \tilde{\varphi}_L < \infty$ , where  $\tilde{\varphi}_{\text{min}}$  is the value of  $\tilde{\varphi}_L$  at which  $\omega_{\text{TO}}^2(\Gamma)$  would vanish, i.e.,

$$\tilde{\varphi}_{\text{min}} = \frac{1}{6} - 2\varphi_T.$$

Furthermore, in the interval  $\tilde{\varphi}_{\text{min}} < \tilde{\varphi}_L < \infty$  one can show<sup>17</sup> that  $dF_{11}/d\tilde{\varphi}_L < 0$  and  $d^2F_{11}/d\tilde{\varphi}_L^2 > 0$ . One can now think of plotting a set of temperature-parametrized curves of  $F_{11}$  vs  $\tilde{\varphi}_L$  using Eq. (8). The self-consistent solutions for  $F_{11}$  will then be given by the intersection of the straight line (7a) (with  $\Phi_{12} = 0$ ) with the appropriate curve at each temperature. Since  $\varphi_L < \tilde{\varphi}_{\text{min}}$  (this must be so if  $\omega_0^2 < 0$ ) and  $\Phi_{11} > 0$ , a little reflection will reveal that there is one and only one self-consistent solution at each temperature. Furthermore, the solution  $\omega_{\text{TO}}^2(\Gamma) = 0$  corresponds at any temperature to an intersection at  $\tilde{\varphi}_L = \tilde{\varphi}_{\text{min}}$  (and  $F_{11} = \infty$ ) and can only be achieved in the limit  $\Phi_{11} \rightarrow 0$  (fixed  $\omega_0^2$ ) or  $\omega_0^2 \rightarrow -\infty$  (fixed  $\Phi_{11}$ ). Thus,  $\omega_{\text{TO}}^2(\Gamma) = 0$  is not a physically realizable solution except in an asymptotic sense.

If in the long-wavelength region of phase space the low-lying TO-mode frequencies are of the same order of magnitude as the TA-mode frequencies, then the long-wavelength contributions to  $F_{11}$

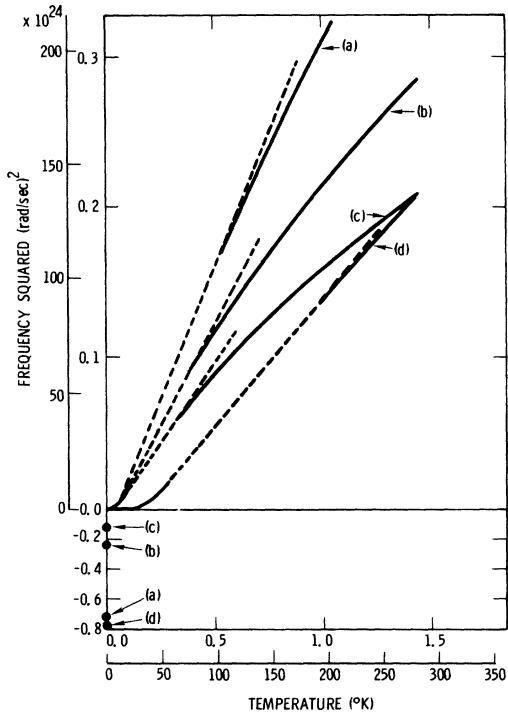


FIG. 2. Temperature dependence of the renormalized zone-center TO frequency squared for different values of  $\omega_0^2$  and  $\Phi_{11}$ . The values of  $\omega_0^2$  are indicated on the negative ordinate for the various cases, whereas the values of  $\Phi_{11}$  are (a) 30.0, (b) 10.0, (c) 5.0, and (d) 15.0. The inner-temperature and squared-frequency scales are in reduced units.

will be dominated by the modes of opticlike character. This can be verified from the normal-mode decomposition of  $F_{11}$ —indeed, the contribution from the acoustic modes will be down by a factor of  $q^2$  from the optic contribution. Suppose at  $T=0$  we were to follow the complete dispersion curves as a function of  $\omega_0^2$ . Then, in Fig. 1 the region  $\omega_0^2 \gtrsim -0.65$  would mark the domain of acoustic dominance, whereas for  $\omega_0^2 \lesssim 0.75$  optic character dominates. In the interval  $-0.65 \gtrsim \omega_0^2 \gtrsim -0.75$  the coupling between TO and TA branches of the same symmetry reaches a critical value and the branch which was acousticlike in character becomes opticlike and vice versa. The branches do not cross, of course; rather, the polarity of the eigenvectors changes such that the low-lying branch changes from acoustic to opticlike character.

In Fig. 2 the squared frequency of the renormalized zone-center TO mode is plotted as a function of temperature for various sets of parameters labeled (a)–(d). On the negative ordinate we have indicated the value that the unrenormalized squared frequency would have for the various cases (note the change of scale). The dotted portions of the curves represent the essentially linear portions of

each plot. Starting with case (a) ( $\Phi_{11} = 30$ ,  $\omega_0^2 = -0.721571$ ), for which  $\omega_{TO}^2$  has the value  $1.822 \times 10^{-4}$  at  $T=0$ , we decrease the value of the quartic anharmonicity in cases (b) and (c), keeping the zero-temperature value of  $\omega_{TO}^2$  constant. Since  $\omega_{TO}^2$  is quite small at  $T=0$ , we see from Eq. (11) that the ratio of the quartic force constant to the unrenormalized TO force constant remains essentially constant in cases (a)–(c). In going from case (c) to case (d) we have kept the value of  $\omega_{TO}^2$  at the high-temperature end constant and decreased the ratio of the quartic interaction to the unrenormalized TO force constant. It is to be noted that the most extensive linear temperature region is that yielded by cases (a) and (d). In all cases, however, the linear region extends to lower temperatures than one might at first expect from an expansion of (8) for  $\hbar\omega/kT \ll 1$ . The point is that by treating all modes self-consistently, the density of modes with  $\hbar\omega \ll kT$  is weighted more heavily at low temperatures than if the contribution from the optic branches of long wavelength had been neglected. It is, of course, observed experimentally<sup>18</sup> that the Curie-law dependence of the soft-mode frequency squared extends to lower temperatures than one would expect on simple qualitative considerations.

Cases (a) and (d) are distinguished by the value of the ratio of the quartic force constant to the unrenormalized TO force constant—in (a) this ratio is relatively large, whereas in (d) the ratio is relatively small. Thus, this ratio has its dominant effect in controlling the rate of increase of  $\omega_{TO}^2$  with temperature. It is to be noted that in both (a) and (d) the value of the unrenormalized frequency squared has the largest negative values—indeed, in these two cases the phase space subtended by the imaginary harmonic frequencies encompasses essentially the entire Brillouin zone. Thus, quite reasonable temperature dependences for the soft-zone-center mode may be obtained without restrictive assumptions being made about the unrenormalized state of the system—in particular, one need not assume that only a small group of modes near the zone center are imaginary in the harmonic approximation.

Case (a) of Fig. 2 is replotted in Fig. 3. Also plotted in Fig. 3 is a case which differs from case (a) in that a small component of second-neighbor interaction has been introduced between the “anions”. The second-neighbor interaction has been chosen to be central and purely longitudinal so that the stability criterion (9) is left unchanged. In the units introduced previously the second derivative of the pair potential between second-neighbor  $B$  ions has the value 0.1493 for case (b) in Fig. 3. The introduction of a second-neighbor interaction between anions has the effect of stiffening the acoustic modes near the zone center as well as stiffening the

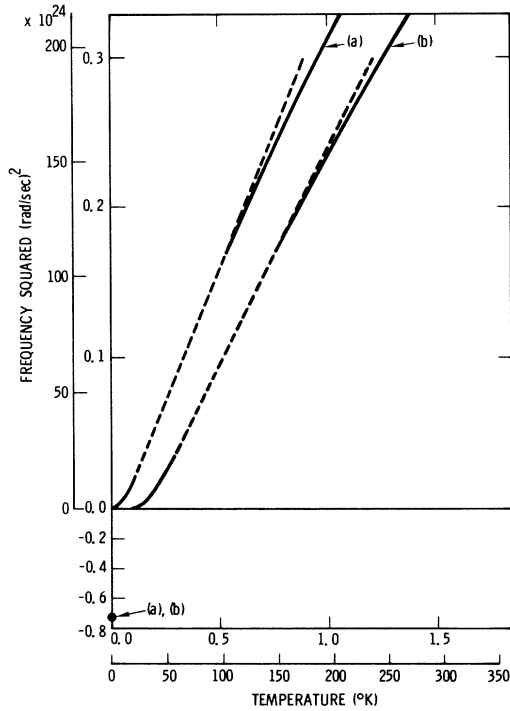


FIG. 3. Temperature dependence of the renormalized zone-center TO frequency squared with values of  $\omega_0^2$  and  $\Phi_{11}$  identical to those of case (a) in Fig. 2. Case (b) differs from case (a) in that a component of a second-neighbor interaction has been introduced.

optic modes at the zone boundary. Equation (11) is unchanged by the introduction of second-neighbor forces. The value of the zero-temperature  $\omega_{\text{TO}}^2(\Gamma)$  is reduced from a value of  $1.822 \times 10^{-4}$  in case (a) to a value of  $1.300 \times 10^{-7}$  in case (b), with the entire temperature plot having the appearance of being shifted bodily to the right along the temperature axis.

Figure 4 presents a  $\omega_{\text{TO}}^2(\Gamma)$ -vs- $T$  plot for two cases differing from the ones already considered. The plot labeled (a) includes short-range interactions through nearest neighbors only, with  $\Phi_{11} = 5.0$  and  $\omega_0^2 = -0.449552$ . In going from plot (a) to plot (b),  $\Phi_{11}$  and  $\omega_0^2$  are kept invariant while a second-neighbor interaction is introduced between the anions. Again, as in Fig. 3, the introduction of second-neighbor forces essentially shifts the plot of case (a) to the right along the temperature axis. The striking feature of Fig. 4, of course, is that on the scale of the frequencies considered in the plot the impression is given of a vanishing mode frequency at finite temperature.

#### B. Mode Coupling at Finite Wave Vector

It is of interest to examine in some detail the temperature dependence of the complete dispersion curves for the two cases plotted in Fig. 3—in par-

ticular, we will be interested in considering the coupling which occurs between the strongly temperature-dependent TO branch and the TA branch of the same symmetry. Figure 5 displays the complete dispersion curves at 84 K for case (a) of Fig. 3. The strong repulsion of the acoustic and optic branches of the same symmetry along the [110] symmetry direction is to be noted. In Fig. 6 we have replotted the transverse branches along [100] and [110] at 84 K together with these same branches at 0 K. It is to be pointed out that the slope at  $q = 0$  of the TA branch along [100] is rigorously independent of temperature, so that the coupling with the soft optic branch occurs only at finite wave vector.<sup>19</sup> Indeed, in going from 84 to 0 K the TA-mode frequency at  $(0.2, 0, 0)$  decreases by 35%. This is illustrated even more dramatically along [110], where the low-lying TA-mode frequency at  $(0.2, 0.2, 0)$  decreases by 75% and actually develops a dip at  $(0.1, 0.1, 0)$ . It should be borne in mind, however, that the elastic constant  $C_{11} - C_{12}$  associated with this mode is not rigorously independent of temperature as was  $C_{44}$ , since it depends upon the renormalized longitudinal force constant  $\varphi_L$ . The complete dispersion curves for case (b) of Fig. 3 are plotted in Fig. 7 for the temperature 112 K. It is to be noted in comparing Figs. 7 and 5 that the introduction of second-neighbor forces produces a strong upward dispersion in the low-lying TO branch as a function of wave vector. The transverse branches for this case are plotted at the three temperatures 112, 56, and 28 K in Fig. 8. The TA-

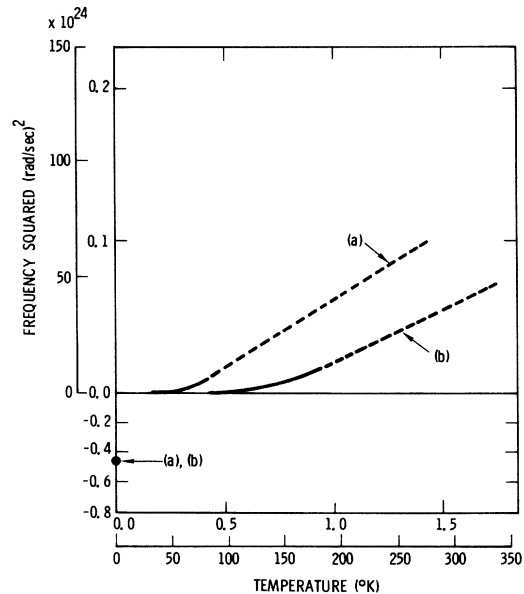


FIG. 4. Temperature dependence of the renormalized zone-center TO frequency squared with  $\Phi_{11} = 5.0$  and  $\omega_0^2 = -0.449552$ . Case (b) differs from case (a) through the introduction of a second-neighbor interaction.

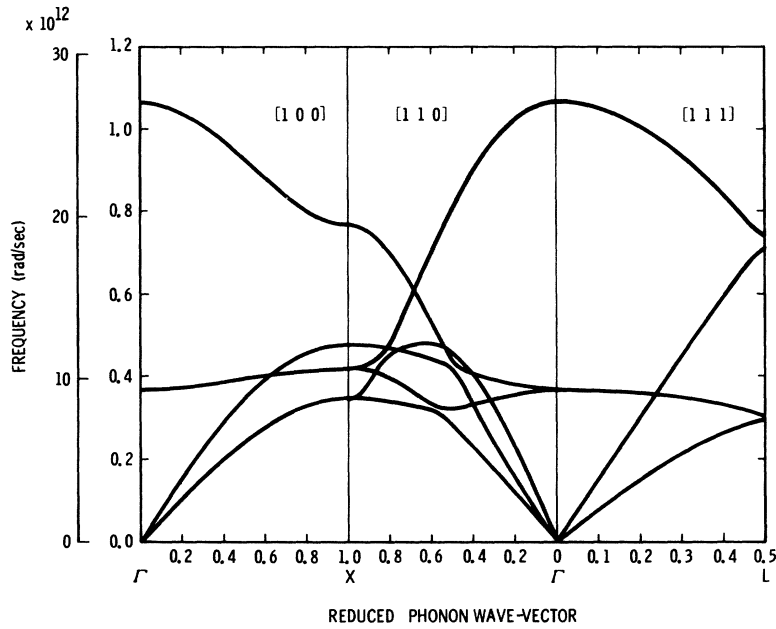


FIG. 5. Complete dispersion curves at 84 K for case (a) of Fig. 3.

mode frequency at  $(0.2, 0, 0)$  decreases by 45% in going from 112 to 28 K, while the low-lying TA-mode frequency at  $(0, 2, 0, 2, 0)$  decreases by 70% in this same temperature interval. Again, we note the appearance of a dip in the TA branch at  $(0.1, 0.1, 0)$  at the temperature 28 K.

Axe, Harada, and Shirane<sup>19</sup> have suggested that the coupling at finite wave vector between the TO and TA modes of the same symmetry in centrosymmetric crystals could be responsible for a finite wave-vector acoustic instability before a dielectric instability occurs. These authors have, in fact, observed the development of a dip in the low-lying [100] TA branch of  $\text{KTaO}_3$  at low temperatures. This anomalous dispersion of the low-lying acoustic branch in  $\text{KTaO}_3$  is similar to that which occurs along the [110] direction in the model calculations of Figs. 6 and 8, although no acoustic instability actually occurs.

### C. Intersublattice Correlations

In the Introduction the claim was made that the soft-mode branches contribute significantly to the intersublattice correlations. Here, we wish to substantiate this claim by displaying the temperature dependence of the correlation function of Eq. (8) for various intersublattice spacings. The intersublattice correlation function is obtained from the general formula (8) by setting  $\sigma = A$ ,  $\sigma' = B$ . We consider the correlation function for  $A$  and  $B$  ions at nearest-neighbor separations and at eighth-neighbor separations. This corresponds to setting  $\vec{R}(l\sigma) - \vec{R}(l'\sigma')$  equal to  $r_0(1, 0, 0)$  and  $r_0(3, 0, 0)$ , respectively, in Eq. (8).

In Figs. 9 and 10 we plot the longitudinal and transverse components of the intersublattice correlation function associated with case (a) of Fig. 4. The solid curve is for  $A$  and  $B$  atoms at nearest-neighbor separations, whereas the dashed curve is

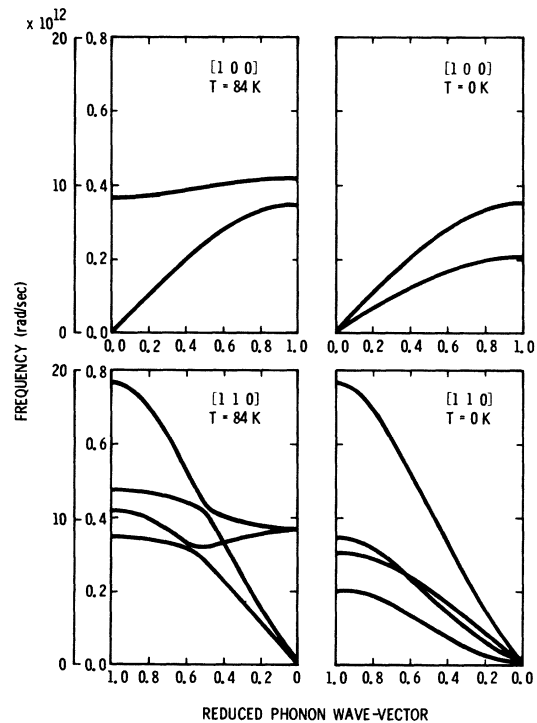


FIG. 6. Transverse branches along selected symmetry directions at 84 and 0 K for case (a) of Fig. 3.



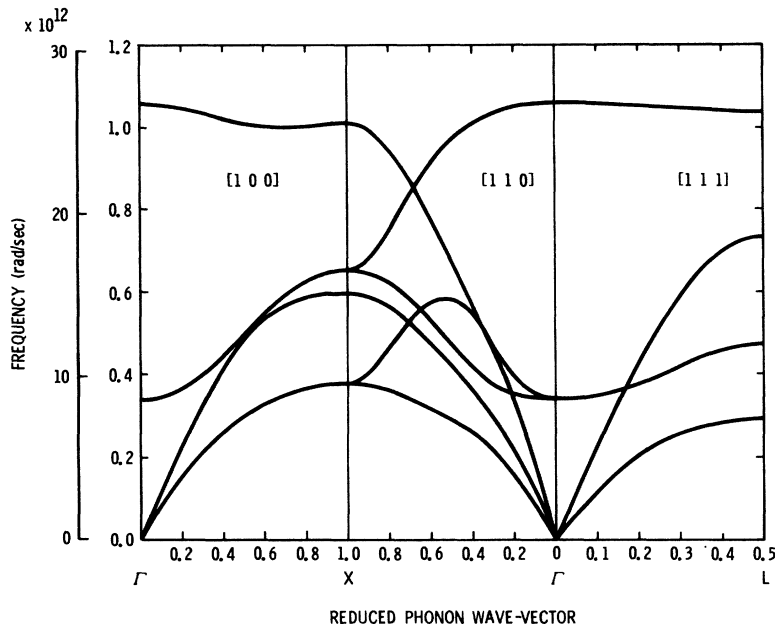


FIG. 7. Complete dispersion curves at 112 K for case (b) of Fig. 3.

for eighth-neighbor separations. At high and intermediate temperatures the strongest temperature dependence is that yielded by the nearest-neighbor correlation function as expected. At temperatures less than 80 K there is a dramatic decrease in both near- and far-neighbor correlation functions and the plots essentially coincide in this region. The point at which the plots cross the abscissa and the correlation function becomes negative marks the beginning of the region in which the temperature dependence is dominated by low-lying modes of opticlike

character. It is easily seen from Eq. (8) that the intersublattice correlation function will be essentially positive if modes of acoustic character are weighted more heavily than opticlike modes. As the soft TO branch drops with temperature, however, the coupling with the TA branch of the same symmetry increases to the point where the polarities of the eigenvectors associated with the TO and TA branches are interchanged and the correlation function changes sign. This clearly points to the importance of the implicit temperature dependence

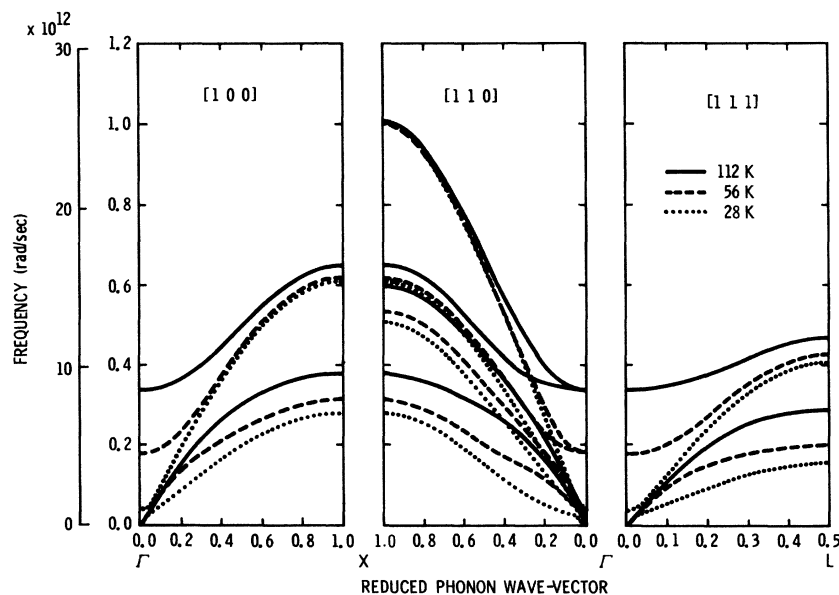


FIG. 8. Transverse branches of case (b) of Fig. 3 at the three temperatures 112, 56, and 28 K.

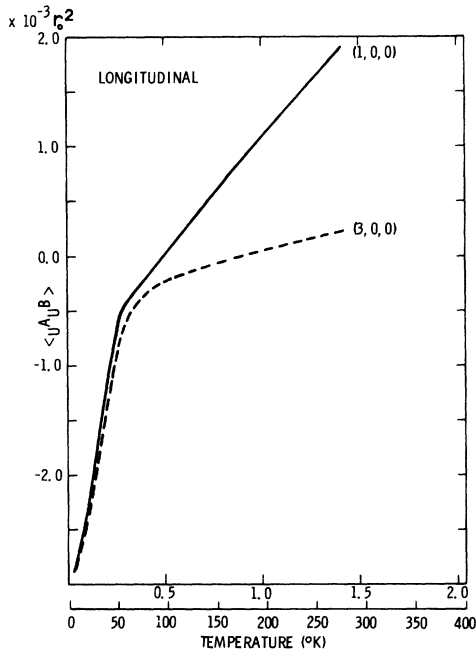


FIG. 9. Longitudinal component of the intersublattice correlation function of case (a) of Fig. 4 vs temperature. The solid line is for nearest-neighbor separations, the dashed line for eighth-neighbor separations.

of the renormalized eigenvectors. In the region less than 80 K in Figs. 9 and 10 the values of the near- and far-neighbor correlation functions merge, thus indicating that the governing optic modes are of long wavelength, causing sublattice *A* to move as a whole out of phase with sublattice *B*. It is tempting to suggest that a transition to an ordered phase probably occurs in this temperature regions, although verification of such speculation must await a free-energy calculation for both ordered and disordered phases.

The correlation functions associated with case (b) of Fig. 3 are plotted as functions of temperature in Fig. 11. It is seen that the plots are qualitatively similar to those of Figs. 9 and 10, although less dramatic in the changeover from acoustic to optic-like behavior.

#### IV. DISCUSSION

In previous sections a detailed study of the temperature dependence of the frequency spectrum of a model paraelectric was carried out within the framework of the lowest-order self-consistent phonon approximation. Several important conclusions were reached. It was found that for a paraelectric crystal stabilized by quartic anharmonicity alone, the self-consistent equations did not admit a zero solution for the soft-zone-center optic mode. This implied that a transition to an ordered phase would always be first order, although it could probably be

made close to second order<sup>20</sup> with the proper choice of model parameters. The question arises as to what the effect would be of including cubic anharmonic terms to second order in the calculation of the phonon self-energy. The cubic correction typically enters with a sign opposite to that of the quartic correction. It is clear, then, that if one were to calculate the cubic correction based on frequencies and eigenvectors derived from the lowest-order self-consistent phonon approximation, one could with an appropriate choice of parameters cause the real part of the phonon self-energy to vanish at any temperature. On the other hand, if one were to determine the renormalized frequencies to the same order of approximation, i.e., as the positions of the resonances in the true self-consistent one-phonon Green's function including damping, then it is unlikely that the real part of the self-energy would in fact vanish for any choice of parameters.<sup>21</sup> The implications of these two levels of approximation including cubic anharmonicity are being investigated.

With the proper choice of model parameters, the Curie-law behavior of the zone-center TO frequency squared was found to extend over a wide range of temperature—for example, case (a) of Fig. 3, which qualitatively resembles the temperature dependence of the zone-center squared frequency in  $\text{K}\alpha\text{TaO}_3$ ,<sup>18</sup> both in the deviation from Curie-law behavior at high temperature as well as in the extension of the linear region into the low-temperature regime.

The answer to the question of whether a transition

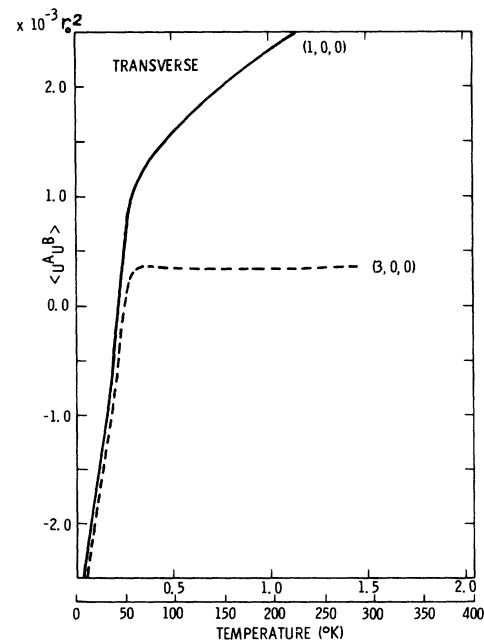


FIG. 10. Same as Fig. 9 but for the transverse component.

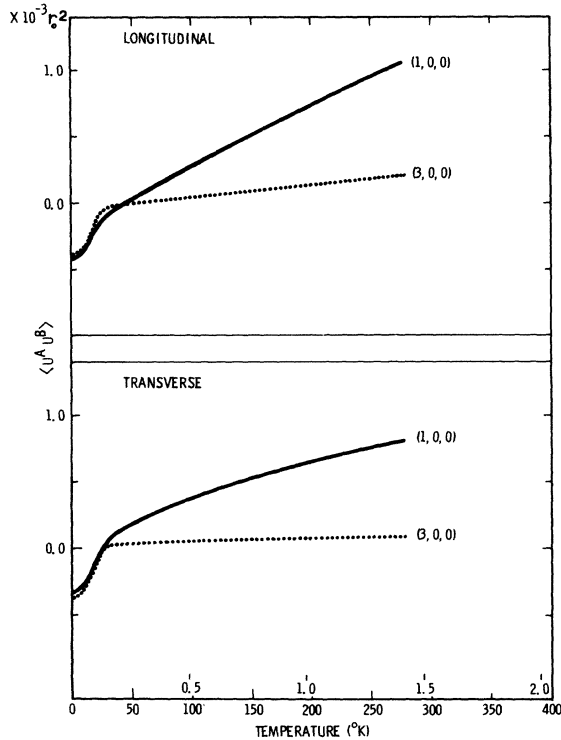


FIG. 11. Temperature dependence of the longitudinal and transverse components of the intersublattice correlation function of case (b), Fig. 3. The solid line is for nearest-neighbor separations, the dotted line for eighth-neighbor separations.

occurs from the paraelectric phase to an ordered ferroelectric phase depends of course on a comparison of the free energy of the disordered NaCl phase with the free energy of possible ordered phases. Such a calculation is currently being investigated and we would like to close this section with a brief discussion of the important qualitative points associated with such a treatment.

A distortion to an ordered phase may be described through the introduction of a complete set of order parameters associated with each normal mode.<sup>22</sup> As an example, consider the simple case of a long-wavelength relative displacement  $\vec{\eta}$  occurring between the *A* and *B* sublattices of the NaCl structure. In this case  $\vec{\eta}$  may be identified as the order param-

eter corresponding to the zone-center optic modes. Simple considerations show that  $\vec{\eta}$  will be directed along a body diagonal if  $\Phi_{11} + 2\Phi_{22} > \Phi_{12} + \frac{1}{2}\Phi_{23}$  and along one of the Cartesian axes if the opposite inequality holds. For the case of a rhombohedral distortion,  $\vec{\eta} = (1/\sqrt{3})(\eta, \eta, \eta)$ , and the free energy has the form

$$F(\eta) = F(0) + [\varphi_L + 2\varphi_T - \frac{1}{6} + 12\Phi_{11}F_{11}(100)]\eta^2 + \frac{2}{3}\Phi_{11}\eta^4, \quad (12)$$

with  $\eta$  being determined self-consistently from

$$\eta^2 = - (3/4\Phi_{11}) [\varphi_L + 2\varphi_T - \frac{1}{6} + 12\Phi_{11}F_{11}(100)]. \quad (13)$$

The renormalized force constant  $\tilde{\varphi}_L$  is given by

$$\tilde{\varphi}_L = \varphi_L + 12\Phi_{11}F_{11}(100) + 4\Phi_{11}\eta^2 \quad (14)$$

and the zone-center optic mode by

$$\omega_{\text{TO}}^2(\Gamma) = 2 [\varphi_L + 2\varphi_T - \frac{1}{6} + 12\Phi_{11}F_{11}(100) + 4\Phi_{11}\eta^2]. \quad (15)$$

In its explicit dependence on  $\eta$ , expression (12) for the free energy formally resembles a conventional Landau expansion in  $\eta$ . However, it is important to note that in addition to the explicit dependence on  $\eta$  displayed here, there is an implicit dependence [since  $F_{11}(100)$  and  $F(0)$  depend implicitly on  $\eta$  through (14)] which does not permit an expansion about  $\eta=0$ . Thus, it is possible for a transition to occur at finite  $\eta$  (hence, first order) even though the crystal is stabilized by quartic anharmonicity alone. Finally, we should note that the expression occurring in the square brackets of (12) and (13) is formally identical to the expression for  $\omega_{\text{TO}}^2(\Gamma)$  in the symmetric phase. This last observation completes the formal identification of (12) with a Devonshire expansion of the free energy<sup>23</sup> up to fourth order in the optic-mode order parameters. It is significant, however, to note that the microscopic interpretation of the coefficients in the expansion differs considerably from the interpretation usually ascribed to them. Indeed, the coefficients in expansion (12) are determined self-consistently, rather than being evaluated by employing a conventional perturbation expansion about a harmonic basis.<sup>5,22</sup> The implications of the present formalism when applied to a more detailed consideration of the Devonshire expansion will be the subject of a future publication.

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<sup>1</sup>P. W. Anderson, in *Fizika Dielektrikov*, edited by G. I. Skanavi (Akademika Nauk SSSR Fisicheskii Inst. im P. N. Lebedeva, Moscow, 1960).

<sup>2</sup>W. Cochran, *Advan. Phys.* **9**, 387 (1960).

<sup>3</sup>B. D. Silverman and R. I. Joseph, *Phys. Rev.* **129**, 2062 (1963); R. I. Joseph and B. D. Silverman, *ibid.* **133**, A207 (1964).

<sup>4</sup>B. D. Silverman, *Phys. Rev.* **135**, A1596 (1964).

<sup>5</sup>R. A. Cowley, *Phil. Mag.* **11**, 673 (1965).

<sup>6</sup>Recently, several authors have recognized the importance of treating the soft-mode problem self-consistently. See A. A. Maradudin, in *Ferroelectricity*, edited by E. F. Weller (Elsevier, Amsterdam, 1967); P. C. Kwok and P. B. Miller, *Phys. Rev.* **151**, 387 (1966). However, in proceeding beyond the formal aspects of the problem these authors revert to the approximation of (a) replacing all

renormalized frequencies by their harmonic counterparts and (b) neglecting the unstable modes.

<sup>7</sup>N. Boccara and G. Sarma, *Physics* **1**, 219 (1965).

<sup>8</sup>Unpublished numerical work based on the formalism of Ref. 7 has recently been performed; N. Boccara (private communication).

<sup>9</sup>See N. R. Werthamer [*Phys. Rev. B* **1**, 572 (1970)] for a review of the relevant literature; also, N. R. Werthamer, *Am. J. Phys.* **37**, 763 (1969).

<sup>10</sup>A preliminary account of this work has been given in N. S. Gillis and T. R. Koehler, *Bull. Am. Phys. Soc.* **16**, 415 (1971).

<sup>11</sup>E. W. Kellermann, *Phil. Trans. Roy. Soc. London* **238**, 513 (1940); see also N. S. Gillis, *Phys. Rev. B* **3**, 1482 (1971).

<sup>12</sup>Since the thermal average is with respect to a harmonic density matrix, the thermally averaged potential  $\langle V \rangle$  may be evaluated in closed form; see N. S. Gillis, N. R. Werthamer, and T. R. Koehler, *Phys. Rev.* **165**, 951 (1968).

<sup>13</sup>N. S. Gillis, N. R. Werthamer, and T. R. Koehler, *Phys. Rev.* **165**, 951 (1968); N. R. Werthamer, *Phys. Rev. B* **1**, 572 (1970).

<sup>14</sup>G. S. Pawley, W. Cochran, R. A. Cowley, and G. Dolling, *Phys. Rev. Letters* **17**, 753 (1966).

<sup>15</sup>E. R. Cowley, J. K. Darby, and G. S. Pawley, *J. Phys. C* **2**, 1916 (1969).

<sup>16</sup>J. N. Bierly, L. Muldower, and O. Beckman, *Acta Met.* **11**, 447 (1963); E. F. Steigmeier and G. Harbeke,

*Solid State Commun.* **3**, 1275 (1970).

<sup>17</sup>As the longitudinal force constant  $\bar{\varphi}_L$  is increased, the frequencies increase also. From Eq. (8) it then follows that  $dF_{11}/d\bar{\varphi}_L < 0$  and  $d^2F_{11}/d\bar{\varphi}_L^2 > 0$ .

<sup>18</sup>G. Shirane, R. Nathans, and V. J. Minkiewicz, *Phys. Rev.* **157**, 396 (1967).

<sup>19</sup>J. D. Axe, J. Harada, and G. Shirane, *Phys. Rev. B* **1**, 1227 (1970).

<sup>20</sup>By "close to second order" we mean in the present context that the value of the inverse dielectric susceptibility [or, alternatively,  $\omega_{\text{TO}}^2(\Gamma)$ ] at the transition is much less than its value far from the transition.

<sup>21</sup>The statement that the phonon frequency may not vanish identically in this higher level of approximation is speculative at this point, since the complexity of the fully self-consistent second-order equations (see Ref. 9) precludes a tractable analytical treatment. However, the question of whether the phonon energy vanishes is somewhat academic for real systems, since other complications occur. Indeed, as the phonon energy decreases in magnitude, overdamping may cause the mode of phononlike character to exhibit a purely relaxation-type behavior [see Y. Yamada, G. Shirane, and A. Linz, *Phys. Rev.* **177**, 848 (1969)]. Furthermore, coupling to the strains may also destroy the purely dielectric character of the instability.

<sup>22</sup>P. C. Kwok and P. B. Miller, *Phys. Rev.* **151**, 387 (1966).

<sup>23</sup>A. F. Devonshire, *Advan. Phys.* **3**, 85 (1954).

## Origin of the Linear Term in the Expression for the Approach to Saturation in Ferromagnetic Materials\*

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There has been confusion for many years over the origin of the  $a/H$  term in the expression for the approach to saturation,  $M/M_s = 1 - a/H - b/H^2 + cH$ , observed in many ferromagnetic materials. A calculation is presented which suggests that residual internal strain contributes significantly to this term. Internal strain has previously been thought to contribute only to the  $b/H^2$  term. It is further suggested that the  $a/H$  term has been overemphasized and has validity only over a limited region of the  $H$  axis. The effect of internal strain is deduced from consideration of a problem concerning nonhydrostatic strains induced in slightly porous magnetic material subject to external hydrostatic pressure. A comparison with recent experimental work supports the calculation.

### I. INTRODUCTION

There has been continued interest for many years in explaining the various terms which occur in the expression for the approach to saturation observed experimentally in many ferromagnetic materials:

$$\frac{M}{M_s} = 1 - \frac{a}{H} - \frac{b}{H^2} + cH. \quad (1)$$

The  $cH$  term has been adequately explained in terms of paraprocesses. The constant in the  $b/H^2$  term has been shown to be

$$b = \frac{8}{105} \frac{K^2}{M_s^2} + \frac{3}{5} \frac{\lambda_s^2 \langle \sigma_i^2 \rangle_{\text{av}}}{M_s^2}, \quad (2)$$

where the first part is due to crystalline anisotropy,<sup>1</sup> and the second part, derived by Becker and Polley,<sup>2</sup> is considered to be the influence of internal strain on the approach to saturation.

The origin of the  $a/H$  term is not well understood. Calculations by Brown<sup>3</sup> have shown that dislocation effects can contribute to this term, while Néel<sup>4</sup> has concluded that stray fields due to nonuniform magnetization may bring about forces