*Supported in part by the National Science Foundation. ¹W. J. L. Buyers and R. A. Cowley, Rev. Mod. Phys. (to be published).

²M. Butler, V. Jaccarino, and N. Kaplan, Suppl. J. Phys. (Paris) <u>32</u>, Cl-718 (1971).

³D. Hone, in *Localized Excitations in Solids*, edited by R. F. Wallis (Plenum, New York, 1968), p. 335.

⁴Yu. Izyumov, Proc. Phys. Soc. (London) <u>87</u>, 521 (1966).

^bK. Vogelsang and D. Hone, J. Appl. Phys. <u>39</u>, 1356 (1968); 40, 1118 (1969).

⁶A. Ozeroff, P. S. Pershan, and M. Kestigian, Phys. Rev. 188, 1046 (1969).

⁷P. Moch, G. Parisot, R. E. Dietz, and H. J. Guggenheim, Phys. Rev. Letters <u>21</u>, 1596 (1968).

⁸T. M. Holden, R. A. Cowley, W. J. L. Buyers, and R. W. H. Stevenson, Solid State Commun. <u>6</u>, 145 (1968);

J. Appl. Phys. <u>39</u>, 1118 (1968). ⁹W. J. De Bonte and H. B. Callen, Phys. Rev. 188,

¹⁰D. Hone, D. J. Scalapino, and R. Silberglitt, J.

Appl. Phys. <u>41</u>, 948 (1970).

¹¹Y-L. Wang and H. B. Callen, Phys. Rev. <u>160</u>, 358

PHYSICAL REVIEW B

(1967).

 12 D. Hone, H. Callen, and L. R. Walker, Phys. Rev. <u>144</u>, 283 (1966); T. Wolfram and W. Hall, *ibid*. <u>143</u>, 284 (1966).

¹³R. M. White and C. M. Hogan, Phys. Rev. <u>167</u>, 480 (1968).

¹⁴D. N. Zubarev, Usp. Fiz. Nauk <u>71</u>, 71 (1960) [Sov. Phys. Usp. <u>3</u>, 320 (1960)].

¹⁵I. M. Lifshitz, Usp. Fiz. Nauk <u>83</u>, 617 (1964) [Sov. Phys. Usp. 7, 549 (1965)].

¹⁶T. Wolfram and J. Callaway, Phys. Rev. <u>130</u>, 2207 (1963).

¹⁷L. van Hove, Phys. Rev. <u>95</u>, 1374 (1954).

¹⁸E. J. Shiles, thesis (University of California at Santa Barbara, 1970) (unpublished).

¹⁹R. J. Elliott and R. Loudon, Phys. Letters $\underline{3}$, 189 (1963).

²⁰T. Moriya, J. Phys. Soc. Japan <u>23</u>, 490 (1967); J. Appl. Phys. <u>39</u>, 1042 (1968).

²¹M. Inoue and T. Moriya, J. Phys. Soc. Japan <u>29</u>, 117 (1970).

 22 R. S. Silberglitt, thesis (University of Pennsylvania, 1968) (unpublished).

VOLUME 5, NUMBER 5

1 MARCH 1972

Phase Transitions in a Model Ferroelectric

N. S. Gillis^{*}

Sandia Laboratories, Albuquerque, New Mexico 87115

and

T. R. Koehler IBM Research Laboratory, San Jose, California 98114 (Received 5 August 1971)

A model crystal exhibiting a ferroelectric transition from a NaCl-structure phase to a distorted C_{3v}^5 phase is examined within the context of the lowest-order self-consistent phonon approximation. The difficulties associated with the usual harmonic approximation are avoided by solving a set of nonlinear integral equations for the renormalized phonon spectrum. The paraelectric phase admits a single self-consistent solution, whereas the ordered phase yields two solutions—one stable and one unstable. From the properties of these solutions several important results are obtained. In particular, for the crystal stabilized by quartic anharmonicity alone the frequency of the soft zone-center TO mode of the paraelectric phase does not vanish at the transition. Indeed, the transition from the ordered to the disordered phase takes place with a discontinuous change in the optic-mode order parameter, so that the resulting transition is distinctly first order. The implications of these results with respect to previous microscopic derivations of the Devonshire free-energy expansion are discussed.

I. INTRODUCTION

The single most useful approach to the treatment of phase transitions in ferroelectric crystals of the displacive type has been to employ a Landau free-energy expansion in powers of the macroscopic polarizations and strains of the ordered phase. From a practical point of view, the expansion is usually introduced as a phenomenological expression with coefficients to be determined from the experimental properties of the crystal.¹ On the other hand, such a free-energy expression can, in principal, be derived from a microscopic basis employing anharmonic lattice dynamics.^{2,3} Kwok and Miller³ have shown that by starting with a complete set of order parameters associated with each normal mode a free-energy functional may be derived which formally reduces to the phenomenological expression in the special case where the paraelectric phase may be characterized by a single soft optical branch. A primary drawback of the usual microscopic derivation, however, is the fact that it rests on the validity of a perturbation expansion about a harmonic basis—a basis which, in general, represents an unstable state of equilibrium for the crystal. Since the frequencies associated with the unstable modes are imaginary, those frequencies must be excluded from all normal-mode sums. When this is done the meaning of the coefficients in the microscopic free-energy expansion becomes obscure.

A more realistic approach to the problem is that which was employed in a previous work⁴ (henceforth referred to as I), where a self-consistent calculation of the frequency spectrum of a model paraelectric was carried out employing a renormalized phonon basis which represented a stable state of equilibrium for the crystal. The problem was formulated variationally, yielding a set of nonlinear integral equations which were solved iteratively. The present work extends the model of I to a treatment of a hypothetical ordered ferroelectric phase. We consider the case of a NaCl-structure crystal undergoing a distortion to a rhombohedral ordered phase of C_{3v} symmetry.⁵ As in I, we assume a model of anions and cations of unequal masses interacting via long-range Coulomb forces plus an anharmonic short-range interaction extending to nearest neighbors. The treatment of the ordered phase is accomplished through the introduction of an order parameter η associated with the optic modes at zone center. This order parameter is then determined self-consistently within the context of the approximation.

Section II introduces the model Hamiltonian from which the crystal free energy is derived. We then proceed to the derivation of the self-consistent equations for the frequency spectrum. As in I, we confine ourselves to the case of the crystal being stabilized by quartic anharmonicity alone. If we limit ourselves to ordered phases whose point groups are subgroups of O_h , then the NaCl structure may transform continuously into either a rhombohedral structure of C_{3v} symmetry or a C_{4v} tetragonal structure.⁶ We further specialize to the case where only the longitudinal component of the quartic interaction is nonzero. Choosing this component to be positive then favors a rhombohedral distortion. The solutions for both ordered and disordered phases are displayed graphically. It is found that in a temperature interval $0 \le T \le T_0$ there exist two solutions for the ordered phaseone stable and one unstable. For $T > T_0$, no physical solutions exist for the ordered phase. On the other hand, the paraelectric phase yields one physical solution at all temperatures and this solution can be shown to always represent at least a local minimum of the free energy. The freeenergy functional which we derive resembles a conventional Devonshire expansion in its explicit

dependence on η . However, the self-consistency conditions impose an additional implicit dependence on η which does not permit an expansion about $\eta = 0$. In general, the free-energy curves for the ordered and disordered phases cross at a temperature $T_c < T_0$, so that the temperature interval T_c $< T < T_0$ represents a region of metastability for the ordered phase.

Several sets of parameters from the cases treated in I are employed and the character of the transition between the paraelectric and ferroelectric phases is examined by calculating self-consistently the free-energy difference between the two phases. It was suggested in I that a transition between ordered and disordered phases must be first order in a model which includes guartic anharmonicity self-consistently. This conjecture is verified in the present work by demonstrating explicitly that a transition occurs discontinuously from a state with $\eta = 0$ to a state with $\eta \neq 0$. The frequency of the soft zone-center TO mode is plotted as a function of temperature for both the ordered and disordered phases and the discontinuous change in this frequency at the transition is displayed.

In Sec. III we discuss the implications of our results, the limitations of the model, and the possibility of improvements on the theory.

II. SELF-CONSISTENT EQUATIONS OF ORDERED PHASE

The properties of the ordered ferroelectric phase are most easily treated within the context of the self-consistent phonon approximation by introducing a complete set of microscopic order parameters representing deviations of the mean positions of the ions from their equilibrium positions in the symmetric (paraelectric) phase. The true crystal Hamiltonian has the form

$$\begin{aligned} W &= -\sum_{l\sigma} \frac{1}{M_{\sigma}} (\nabla_{l\sigma})^{2} \\ &+ V \left(\tilde{\mathbf{r}}(l_{1} \sigma_{1}), \ \tilde{\mathbf{r}}(l_{2} \sigma_{2}), \ \dots, \ \tilde{\mathbf{r}}(l_{N} \sigma_{N}) \right) , \end{aligned}$$
(1)

where the instantaneous positions of the ions are given by

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

 $\vec{R}(l\sigma)$ is the equilibrium position of an ion of type σ in unit cell l of the symmetric phase, while $\vec{\eta}(l\sigma)$ is the order parameter representing the displacement which that ion undergoes in the transition to the ordered phase. Finally, $\vec{u}(l\sigma)$ is the dynamic displacement of ion $(l\sigma)$ from the mean position $\vec{R}(l\sigma) + \vec{\eta}(l\sigma)$. Although we have not allowed for the possibility of a homogeneous deformation, such distortions may be treated by introducing the six independent strain components as an additional set of order parameters. The effect of including the strain parameters will not be considered here, al-

1926

though we will return to discuss this point briefly in Sec. III.

We follow essentially the arguments of I. Thus we postulate that for each value of the mean ionic position $\vec{R}(l\sigma) + \hat{\eta}(l\sigma)$ the dynamics of the phonon excitations will be well described by a trial harmonic Hamiltonian of the form

$$H_{t} = -\sum_{l\sigma} \frac{1}{M_{\sigma}} (\nabla_{l\sigma})^{2} + \frac{1}{2} \sum_{ll', \sigma\sigma', \alpha\beta} u_{\alpha}(l\sigma) C_{\alpha\beta}^{\sigma\sigma'}(ll') u_{\beta}(l'\sigma') + \frac{1}{2} \sum_{ll', \sigma\sigma', \alpha\beta} u_{\alpha}(l\sigma) \tilde{\varphi}_{\alpha\beta}^{\sigma\sigma'}(ll') u_{\beta}(l'\sigma') .$$
(2)

As in I, $C^{\sigma\sigma'}_{\alpha\beta}(ll')$ represents the Coulomb contribution to the dynamical matrix, to be treated harmonically, and $\tilde{\varphi}^{\sigma\sigma'}_{\alpha\beta}(ll')$ represents the trial force constant matrix, which for cubic symmetry and in the nearest-neighbor approximation has only longitudinal and transverse components $\tilde{\varphi}_L$ and $\tilde{\varphi}_T$. Both

 $ilde{\varphi}$ and the order parameters $ilde{\eta}(l\sigma)$ are to be determined variationally from a minimization of the trial free energy

$$F_t = \operatorname{Tr}\left[\rho_t (\mathcal{K} + \beta^{-1} \ln \rho_t)\right] , \qquad (3)$$

where ρ_t is the canonical density matrix based on the Hamiltonian (2). We employ the approximations of I, i.e., the Coulomb forces are to be treated harmonically while the nearest-neighbor shortrange part of the interaction potential in (1) is to include anharmonicity through a quartic contribution only. Furthermore, we will introduce only a single order parameter $\bar{\eta}$, independent of the cell indices l and σ , representing the relative displacement of sublattices A and B from their positions in the symmetric phase. As such, $\bar{\eta}$ may be identified as the order parameter corresponding to the optic modes at zone center.

In analogy to Eq. (3) of I, the short-range part of the interaction potential may be written in the present case as

$$V_{\rm SR}(\vec{\eta}) = \frac{1}{2} \sum \left\{ \varphi_L(x+\eta_1)^2 + \varphi_T[(y+\eta_2)^2 + (z+\eta_3)^2] \right\} + \sum \left\{ \Phi_{11}(x+\eta_1)^4 + \Phi_{22}[(y+\eta_2)^4 + (z+\eta_3)^4] + \Phi_{12}(x+\eta_1)^2[(y+\eta_2)^2 + (z+\eta_3)^2] + \Phi_{23}(y+\eta_2)^2(z+\eta_3)^2 \right\} .$$
(4)

The notation is identical to that which was employed in I, the summation being over all unit cells and nearest neighbors, while x, y, and z denote the corresponding Cartesian components of the relative displacement between nearest-neighbor A and B ion pairs. The evaluation of the free energy per unit cell is straightforward, yielding

$$F = F_{0} + 3(\varphi_{L} - \tilde{\varphi}_{L})F_{11} + 6(\varphi_{T} - \tilde{\varphi}_{T})F_{22} + 6[3\Phi_{11}F_{11}^{2} + (6\Phi_{22} + \Phi_{23})F_{22}^{2} + 2\Phi_{12}F_{11}F_{22}] + [\varphi_{L} + 2\varphi_{T} - (2\pi/3a)(Z^{*})^{2} + 4(3\Phi_{11} + \Phi_{12})F_{11} + 4(6\Phi_{22} + \Phi_{12} + \Phi_{23})F_{22}](\eta_{1}^{2} + \eta_{2}^{2} + \eta_{3}^{2}) + 2(\Phi_{11} + 2\Phi_{22})(\eta_{1}^{4} + \eta_{2}^{4} + \eta_{3}^{4}) + 2(\Phi_{23} + 2\Phi_{12})(\eta_{1}^{2}\eta_{2}^{2} + \eta_{1}^{2}\eta_{3}^{2} + \eta_{2}^{2}\eta_{3}^{2}) , \qquad (5)$$

where

$$F_0 = -(1/N)\beta^{-1} \ln[tr(e^{-\beta H_t})]$$
.

In the above, Z^* is the zone-center effective charge, *a* is the nearest-neighbor distance in a.u., and F_{11} and F_{22} are the longitudinal and transverse components of the nearest-neighbor displacementdisplacement correlation function as defined in I. The resulting free energy is in Ry.

Since the second-order terms in (5) are independent of the direction of η , the direction of the order parameter is determined by the condition that the fourth-order terms be a minimum for a given absolute value of η . This gives rise to two possibilities: η directed along one of the Cartesian axes if $\Phi_{11} + 2\Phi_{22} < \Phi_{12} + \frac{1}{2}\Phi_{23}$, or η directed along a cube diagonal if the opposite inequality holds. ⁶ We restrict ourselves to the case where the only nonzero component of the quartic interaction is Φ_{11} , so that the condition $\Phi_{11} > 0$ favors a rhombohedral distortion. With $\bar{\eta} = (1/\sqrt{3})(\eta, \eta, \eta)$ the free energy then takes the form⁷

$$F = F_0 + 3(\varphi_L - \tilde{\varphi}_L)F_{11} + 18\Phi_{11}F_{11}^2 + [\varphi_L + 2\varphi_T - (2\pi/3a)(Z^*)^2 + 12\Phi_{11}F_{11}]\eta^2 + \frac{2}{3}\Phi_{11}\eta^4 .$$
(6)

Minimization of (6) with respect to $\tilde{\varphi}_L$ and η yields the two coupled equations

$$\begin{split} \tilde{\varphi}_L &= \varphi_L + 12\Phi_{11}F_{11} + 4\Phi_{11}\eta^2 , \\ \eta^2 &= -(3/4\Phi_{11})[\varphi_L + 2\varphi_T - (2\pi/3a)(Z^*)^2 + 12\Phi_{11}F_{11}] . \end{split}$$

$$\tag{7}$$

Renormalized frequencies and eigenvectors $\omega(q\lambda)$ and $\epsilon^{\sigma}_{\alpha}(q\lambda)$ are determined from a diagonalization of the trial Hamiltonian (2). This permits an implicit equation for F_{11} in terms of $\tilde{\varphi}_L$ to be obtained through the normal-mode decomposition

$$F_{11} = \frac{1}{2N} \sum_{\vec{q}\lambda} \frac{1}{\omega(q\lambda)} \operatorname{coth}\left(\frac{\beta\omega(q\lambda)}{2}\right) \left(\frac{1}{M_1} \left[\epsilon_1^1(\vec{q}\lambda)\right]^2\right)$$

5



FIG. 1. Graphical solution of the coupled Eqs. (7) and (8). The curved lines represent plots of Eq. (8) at the four temperatures 0, 56, 84, and 112 K. The set of linear plots (a)-(c) and the set (a')-(c') represent plots of Eqs. (10a) and (10b), respectively, for different values of Φ_{11} and φ_L . For the various cases the relevant values of Φ_{11} are (a) and (a'), 30; (b) and (b'), 15; (c) and (c'), 5. The parameter φ_L is chosen such that the zero-temperature paraelectric phase solution remains unchanged in cases (a)-(c).

$$+\frac{1}{M_2}\left[\epsilon_1^2(\vec{q}\lambda)\right]^2 - \frac{2}{(M_1M_2)^{1/2}}\left[\epsilon_1^1(\vec{q}\lambda)\epsilon_1^2(\vec{q}\lambda)\right]\cos q_1\right)$$
(8)

Self-consistent solutions for F_{11} follow from the simultaneous solution of (7) and (8). The squared frequency of the renormalized zone-center TO mode is then given simply as

$$\omega_{\rm TO}^2(\Gamma) = 2(\varphi_L + 2\varphi_T - \frac{1}{6} + 12\Phi_{11}F_{11} + 4\Phi_{11}\eta^2) \quad , \qquad (9)$$

where we have employed units such that Z^* and the reduced mass do not appear explicitly.⁸

We recall from I that the stability of the paraelectric phase required that φ_T be eliminated in terms of the Coulomb energy per particle [see Eq. (9) of I]. Thus it is clear that once the parameters M_1, M_2 , and Z^* are specified, Eq. (8) provides a single-valued equation for F_{11} as a function of $\tilde{\varphi}_L$ at each temperature. In Fig. 1 we have plotted F_{11} as a function of $\tilde{\varphi}_L$ at four temperatures. It is clear that F_{11} is a monotonically decreasing function of $\tilde{\varphi}_L$, so that $(dF_{11}/d\tilde{\varphi}_L) < 0$ over the interval $\infty > F_{11} > 0$, for which $\tilde{\varphi}_{min} < \tilde{\varphi}_L < 0$. $\tilde{\varphi}_{min}$ is defined as the value of $\tilde{\varphi}_L$ for which $\omega_{TO}(\Gamma)$ vanishes; i.e.,

$$\tilde{\varphi}_{\min} = \frac{1}{6} - 2\varphi_T = 0.259378.$$

The self-consistent solutions may be obtained from the iterative solution of Eqs. (7) and (8). For the case where Φ_{11} is the only nonzero quartic component, however, the qualitative features of these solutions are most easily displayed graphically. Equation (7) expresses $\tilde{\varphi}_L$ as a linear function of F_{11} ; in the paraelectric phase we have

$$\tilde{\varphi}_L = \varphi_L + 12\Phi_{11}F_{11}$$
 , (10a)

whereas in the ordered phase we have

$$\tilde{\varphi}_L = -2\varphi_L + 3\varphi_{\min} - 24\Phi_{11}F_{11} \quad . \tag{10b}$$

Thus the allowable self-consistent solutions will be given by the intersections of the straight lines (10a) and (10b) with the temperature-parametrized curves of F_{11} vs $\tilde{\varphi}_L$ obtained from (8). We have illustrated these solutions in Fig. 1 for three cases which were considered in $I.^9$ In cases (a), (b), and (c), Φ_{11} and φ_L are varied in such a way that the zero-temperature value of $\omega_{TO}^2(\Gamma)$ for the paraelectric phase solution¹⁰ remains constant at the value 1.822×10^{-4} . Focusing attention first on the paraelectric phase solutions, it is clear from Fig. 1 that one feature which is independent of the particular examples considered here is that the effect of varying Φ_{11} and φ_L is merely to change the intersection and slope of the line (10a) with respect to the Cartesian axes. The solution $\omega_{TO}^2(\Gamma) = 0$ corresponds at any temperature to an intersection at infinity and hence can only be achieved in the limit $\Phi_{11} \rightarrow 0$ or $\varphi_L \rightarrow -\infty$. This was pointed out in I. We can also verify that the paraelectric solution represents a minimum of the free energy at all temperatures. Indeed, we have

$$(\delta^2 F / \delta \tilde{\varphi}_L^2) = -3(\delta F_{11} / \delta \tilde{\varphi}_L) + 36\Phi_{11} (\delta F_{11} / \delta \tilde{\varphi}_L)^2 > 0$$

for positive Φ_{11} . The paraelectric solution may or may not, however, represent an absolute minimum of the free energy with respect to the ordered solution. This point will be examined in what follows.



FIG. 2. Plots of the free energy as a function of temperature for the ordered phase solutions and disordered phase solutions of Fig. 1. The plots (a)-(c) refer to the paraelectric phase solutions of Fig. 1. These solutions exist at all temperatures. The plots (a')-(c') refer to the stable ordered phase solutions and terminate at T_0 . The inner scale on the abscissa is in reduced temperature units.

The self-consistent ordered phase solutions depicted in Fig. 1 exhibit several interesting features. For given values of the parameters φ_L and Φ_{11} there will, in general, be a limiting temperature T_0 below which two distinct ordered solutions exist; above T_0 no such solutions can be found.¹¹ Of the two ordered solutions obtained below T_0 , one solution corresponds to a minimum of the free energy with η^2 decreasing with increasing temperature; this is the physical solution. For the remaining solution the opposite is found to be true, i.e., η^2 increases with increasing temperature and the free energy exhibits a maximum. $^{12,13}\,$ If we denote by T_c the temperature at which the free-energy curves for the paraelectric and ferroelectric solutions cross, then in general $T_c < T_0$ and the temperature interval $T_c < T < T_0$ will represent a region of metastability for the ordered phase. Figure 2 displays the free energies of the two phases as functions of temperature for the three cases illustrated in Fig. 1. The corresponding transition temperatures T_c for the three cases are approximately 20, 36, and 97 K. Plotted in Fig. 3 are the self-consistent values of η^2 over the entire temperature range for which the ordered solutions exist. The dotted portions of the curves represent the extrapolation of the η^2 solutions into the region of metastability. We see that η^2 increases rapidly below the transition and then levels off as one approaches zero temperature. It is clear from the plots of Fig. 3 that the transition to an ordered phase is distinctly first order. The first-order character of the transition is further emphasized in Fig. 4 where the frequency of the renormalized zone-center TO mode is plotted as a function of temperature. In each case the solid line represents the value of the TO mode frequency for the absolutely stable phase, with the dashed line denoting the extrapolation into the metastable region. The qualitative features of Figs. 1-4 clearly indicate that as the magnitude of the quartic anharmonicity decreases, the transition temperature



FIG. 3. Plots of the order parameter squared as a function of temperature. The labeling of the plots corresponds to the different cases of Fig. 1.



FIG. 4. Plots of the frequency of the zone-center TO mode as a function of temperature. The labeling of the curves refers to the solutions in Fig. 1.

decreases with the transition itself becoming more second order in character. It is equally clear, however, that the transition will become truly second order only in the asymptotic limit $\Phi_{11} \rightarrow 0$.

We summarize in Fig. 5 the properties of the ordered and disordered solutions discussed above by plotting the qualitative behavior of the free energy [Eq. (6)] as a function of the order parameter. At all temperatures the paraelectric solution $(\eta = 0)$ represents at least a local minimum of the free energy. In the temperature interval $0 \le T < T_0$ the stable and unstable ordered solutions are represented by a local minimum and a local maximum of the free energy at finite η . At $T = T_0$ the unstable and stable ordered solutions merge to form a point of inflection in the free-energy curve. These general features can be compared with what one would predict on the basis of a conventional Landau expansion of the free energy to fourth order in η .¹⁴ Within the context of Landau theory the free energy would exhibit for $T < T_c$ a local maximum at $\eta = 0$ and an absolute minimum at finite η . At $T = T_c$ the two extremal points would merge to

form a single absolute minimum at $\eta = 0$ and the transition from the ordered to the disordered phase would be second order.

III. DISCUSSION

Section II examined the qualitative features of the phase transition exhibited by a model ferroelectric crystal. The particular structural transition considered was that of an NaCl-structure crystal undergoing a deformation to a rhombohedral ordered phase of C_{3v}^5 symmetry. The fundamental assumption of the model was that the low-lying excitation spectrum of the crystal was dominated by collective behavior which was phononlike in character. This assumption permitted the use of a trial harmonic Hamiltonian for the description of the dynamics of the renormalized phonon spectrum. Since the spectrum was treated self-consistently, the difficulties associated with imaginary frequencies in the harmonic approximation were avoided. Anharmonicity was restricted to quartic interactions only. This yielded an expression for the free energy which, in terms of the explicit dependence on the optic-mode order parameter, resembled a Devonshire expansion. However, it was pointed out that in addition to the explicit dependence on the order parameter there was an implicit dependence resulting from the self-consistency conditions. This had the important consequence that the transition from the paraelectric to the ferroelectric phase was distinctly first order and remained so for any choice of parameters. Thus, when treated self-consistently, the model ferroelectric crystal stabilized by quartic anharmonicity alone does not exhibit a vanishing zone-center optic mode and the transition from ordered to disordered phases takes place with a discontinuous change in the optic-mode order parameter. The effects of strain deformations and their coupling to the optic-mode order parameter were not included in the present treatment. It is expected, however, that the inclusion of a strain deformation will not alter the qualitative conclusions of the model. Indeed, coupling to the strains should in fact increase the first-order character of the transition.

The present calculation can be compared with the treatment employed recently by Kwok and Miller³ in a formal derivation of the Devonshire free-energy expansion. The formalism employed by these authors allowed for the possibility of treating the problem self-consistently. However, in order to obtain a free-energy expansion which was *formally* identical to the Devonshire expression, they found it sufficient to employ a linear anharmonic approximation in which the phonon self-energy was renormalized through quartic anharmonicity in a non-self-consistent fashion, with





ORDER PARAMETER

the unstable soft modes being neglected. In the absence of sixth-order terms and strains, the Kwok-Miller result for the perovskite structure would predict a second-order transition and a vanishing mode frequency. On the other hand, the central result of the present work indicates that linear quartic anharmonicity does not contain the physics necessary for producing a second-order transition. It should be emphasized that this latter result is essentially model independent, i.e., we would have reached the same conclusion if we had treated the perovskite structure selfconsistently with a realistic description of the interatomic forces. The implication is that a higherorder renormalization is needed in order to obtain a second-order transition. This higher-order renormalization may be introduced through an extension of the Kwok-Miller formalism or by means of the more recently developed self-consistent techniques. We reserve for a future publication an investigation of the approximation in which cubic anharmonicity to second order is treated self-consistently.

With respect to possible applications to real materials, the present model is most directly suited to a treatment of a paraelectric such as SnTe.¹⁵ Although we cannot hope to duplicate the detailed features of the interactions in such a material by means of the simple rigid-ion model employed here, some of the qualitative features of the frequency spectrum such as the temperature dependence of the soft mode, mode coupling, etc., can be adequately explained. Indeed, we saw in I that many of the qualitative features of the frequency spectrum of the paraelectric KTaO₃ can be duplicated in this simple model. As we have already emphasized, however, the details of a transition close to second order such as occurs in SrTiO₃ and GeTe are outside the scope of an approximation in which only linear quartic anharmonicity is included. In

addition to yielding only a first-order transition, this approximation is essentially a low-temperature approximation, whereas most real transitions occur at relatively high temperatures. However, recent improvements of the self-consistent phonon approximation¹⁶ provide some hope of treating an actual transition realistically. Goldman, Horton, and Klein¹⁶ have pushed the self-consistent calculations close to the melting temperature in the rare-gas solids with good results. In materials such as $SrTiO_3$ and GeTe, where the melting temperature is considerably higher than the transition temperature, it should be possible to improve on the present treatment with the more sophisticated techniques now available-although with a considerable increase in labor.

In summary, it appears that from a microscopic viewpoint the ferroelectric transition in displacive crystals is considerably more complicated than the simple Devonshire expression would lead one to

 $\ast Work$ supported by the U.S. Atomic Energy Commission.

¹A. F. Devonshire, Advan. Phys. <u>3</u>, 85 (1954).

²R. A. Cowley, Phil. Mag. <u>11</u>, 673 (1965).

³P. C. Kwok and P. B. Miller, Phys. Rev. <u>151</u>, 387 (1966).

⁴N. S. Gillis and T. R. Koehler, Phys. Rev. B <u>4</u>, 3971 (1971).

⁵The structural transformation $O_h^5 \rightarrow C_{3v}^5$ occurs in the IV-VI compound GeTe; see J. Goldak, D. Innes, W. Youdelis, and C. S. Barrett, J. Chem. Phys. <u>44</u>, 3323 (1966). Soft-mode behavior associated with this transformation has also been observed; see E. F. Steigmeier and G. Harbeke, Solid State Commun. <u>8</u>, 1275 (1970).

⁶L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Addison-Wesley, Reading, Mass., 1960), pp. 88-89.

⁷Although (6) resembles a Landau expansion in its explicit dependence on η , it is important to note that F_0 and F_{11} implicitly depend on η through the equations of self-consistency.

⁸As in Ref. 4, ω^2 is in units of $M_R^{-1}[4\pi(Z^*e)^2/(2r_0^3)]$, φ is in units of $4\pi(Z^*e)^2/(2r_0^3)$, and Φ is in units of $r_0^{-2} \times 4\pi(Z^*e)^2/(2r_0^3)$. M_R is the reduced mass and r_0 is the nearest-neighbor distance.

⁹See cases (a)-(c) of Fig. 1, Ref. 4.

 $^{10}\,{\rm The}\,\,{\rm zero-temperature}\,{\rm value}\,\,{\rm of}\,\,\omega^2_{\rm TO}(\Gamma)$ in the paraelec-

expect. It is known experimentally that the thermodynamic theory introduced by Devonshire appears to be qualitatively correct as long as the coefficients in the formal free-energy expansion are treated phenomenologically. However, when examined theoretically on a microscopic basis, the extent to which the coefficients are renormalized by anharmonic interactions is not completely clear. Quartic renormalization treated self-consistently implies a first-order transition, even in the absence of strain instabilities. Thus, the achievement of a vanishing mode frequency and a secondorder transition necessitates the introduction of a higher-order treatment of the anharmonicity in a self-consistent fashion.

ACKNOWLEDGMENT

One of the authors (N. S. G.) wishes to thank W. J. Camp for an illuminating discussion.

tric phase was chosen to be as small as possible within the limits of numerical accuracy of the calculation.

¹¹Graphically, T_0 is the temperature at which the line (10b) becomes tangent to one of the temperature-parametrized curves of $\tilde{\varphi}_L$ vs F_{11} in Fig. 1. ¹²The second variation of the free energy for the or-

The second variation of the free energy for the ordered phase solutions is given by $(\delta^2 F / \delta \tilde{\varphi}_L^2) = -3 (\delta F_{11} / \delta \tilde{\varphi}_L) \times [1 + 24\Phi_{11} (\delta F_{11} / \delta \tilde{\varphi}_L)]$. It is straightforward to show that for $0 \le T < T_0$, $0 > (\delta F_{11} / \delta \tilde{\varphi}_L) > - (24\Phi_{11})^{-1}$ for the stable ordered solution, and $(\delta F_{11} / \delta \tilde{\varphi}_L) < - (24\Phi_{11})^{-1}$ for the unstable solution. For $T = T_0$, $(\delta F_{11} / \delta \tilde{\varphi}_L) = - (24\Phi_{11})^{-1}$ for both solutions.

¹³The zero-temperature unstable ordered solutions appear to coincide with the zero-temperature paraelectric solutions on the scale of Fig. 1. This is, in fact, not the case. The difference between the two solutions at zero temperature approaches zero in the limit that the zero-temperature paraelectric frequency approaches zero. Since this frequency is small for the cases considered, the difference between the two solutions is also small.

¹⁴L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading, Mass., 1958), Chap. 14.

¹⁵G. S. Pawley, W. Cochran, R. A. Cowley, and G. Dolling, Phys. Rev. Letters <u>17</u>, 753 (1966).

¹⁶V. V. Goldman, G. K. Horton, and M. L. Klein, Phys. Rev. Letters <u>21</u>, 1527 (1968); <u>24</u>, 1424 (1970).

1932