tal help of J. A. Ditzenberger is gratefully acknowledged.

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<sup>7</sup>J. Crowell and R. H. Ritchie, J. Opt. Soc. Amer. <u>60</u>, 794 (1970).

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 ${}^{9}k_{\rm F}$  is the Fermi wave vector. In the case of surface

phonons k must be much less than the reciprocal of the lattice spacing.

<sup>10</sup>Strictly speaking Eq. (2) holds only as long as  $Im(\epsilon) = 0$ . For finite  $Im(\epsilon)$  the modes are damped with line shapes determined by  $Im[1/(-\epsilon - 1)]$ .

<sup>11</sup>CaMoO<sub>4</sub> is an insulator with four optical phonons.  $\epsilon(\omega)$  passes through -1 four times at four different frequencies. A. S. Barker, Jr., Phys. Rev. <u>135</u>, A742 (1964).

<sup>12</sup>O. S. Heavens, Optical Properties of Thin Solid Films (Academic, New York, 1955), Chap. 4.

<sup>13</sup>W. E. Anderson, R. W. Alexander, Jr., and R. J. Bell, Phys. Rev. Lett. 27, 1057 (1971).

<sup>14</sup>M. Cardona, Amer. J. Phys. <u>39</u>, 1277 (1971), has also noted this behavior of  $r_p$ .

<sup>15</sup>For the case of antiferromagnetic  $\text{FeF}_2$  with its *c* axis aligned as in Fig. 2, a weak surface-magnon dip should be observable at 53 cm<sup>-1</sup> for an *s*-polarized infrared beam in the coupler.

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## Spurious First-Order Phase Transitions in the Self-Consistent Phonon Approximation

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It is shown that when the self-consistent phonon approximation is applied to displacive phase transitions, it leads to inconsistent results near the transition point, and that this may give rise to spurious first-order transitions.

Until recently, microscopic theories of displacive phase transitions have been based on a perturbation expansion about a harmonic basis. Since the harmonic soft-mode frequencies are imaginary, the contribution of these modes in the anharmonic terms was neglected. A self-consistent treatment of the soft-mode frequencies was first given by Boccara and Sarma<sup>1</sup> by employing at the onset a renormalized phonon basis. Their formal treatment represented (the lowest order of) what is now called the self-consistent phonon approximation<sup>2</sup> (SPA). This approximation has been very successful in describing the anharmonic rare-gas solids, including the quantum crystals of solid helium.

Recent numerical calculations have shown that the SPA gives a first-order transition for a model ferroelectric containing only fourth-order anharmonic interactions.<sup>3</sup> This result is surprising because the phenomenological Landau (Devonshire) theory predicts the transition to be second order when only terms up to fourth order in the polarization are included.<sup>4,5</sup> To illustrate the essential features of the SPA and to understand why a first-order transition is obtained, it is instructive to consider a simple model with a single degree of freedom,

$$H = \frac{1}{2} \sum P_{l}^{2} + \frac{1}{2} \Omega_{0}^{2} \sum_{l} Q_{l}^{2}$$
$$- \frac{1}{2} \sum_{ll'} v(ll') Q_{l} Q_{l'} + \frac{1}{4} \gamma \sum Q_{l}^{4}.$$
(1)

Here  $Q_l$  is a localized normal-mode coordinate describing the ion displacements in cell l, and  $P_l$  is the canonical conjugate momentum,

$$[Q_{i}, P_{i'}] = i\delta_{ii'}.$$

We set  $Q_I = Q_0 + u_I$ , where the thermal average  $Q_0 \equiv \langle Q_I \rangle$  measures the distortion from the hightemperature structure, while  $u_I$  describes the fluctuations about the average value. In the SPA the free energy  $F = \langle H \rangle - TS$  is obtained by using a harmonic trial density matrix.<sup>2</sup> The distortion  $Q_0$  and the effective harmonic force constants are determined by minimizing the free energy. For the Hamiltonian given by Eq. (1) the extremum

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condition  $\partial F/\partial Q_0 = 0$  takes the form

$$Q_0[\Omega_0^2 - v(0) + \gamma Q_0^2 + 3\gamma \Delta] = 0, \qquad (3)$$

where  $v(0) = \sum_{l} v(ll')$ , and  $\Delta$  is defined below. The effective force constants determine the self-consistent normal-mode frequency. For this model it is given by

$$\omega_q^2 = \omega_0^2 + v(0) - v(q) \sim \omega_0^2 + \alpha^2 q^2, \tag{4}$$

where

$$\omega_0^2 = \Omega_0^2 - v(0) + 3\gamma Q_0^2 + 3\gamma \Delta, \qquad (5)$$

or, in the distorted phase, using Eq. (3)

$$\omega_0^2 = 2\gamma Q_0^2. \tag{6}$$

The correlation function  $\Delta = \langle u_1 u_1 \rangle$  is determined with the help of the fluctuation dissipation theorem,<sup>6</sup>

$$\Delta = N^{-1} \sum_{q^2} \omega_q^{-1} \coth^{\frac{1}{2}} \beta \omega_q \,. \tag{7}$$

If for simplicity we consider the limit  $\omega_q/kT \ll 1$ ,  $\Delta$  may be approximated by the Ornstein-Zernike form,

$$\Delta = k T N^{-1} \sum_{\alpha} (\omega_0^2 + \alpha^2 q^2)^{-1}.$$
 (8)

Evaluating the summation in the Debye approximation we obtain

$$\Delta = \Delta_0 - \Delta_T \tag{9}$$

with

$$\Delta_0 = 3kT/\omega_D^2, \quad \Delta_T = \Delta_0(\omega_0/\omega_D) \tan^{-1}(\omega_D/\omega_0),$$

where  $\omega_D = \alpha q_D$ ,  $q_D$  being the Debye wave vector.  $\Delta_T$  denotes the contribution to  $\Delta$  due to long-wavelength fluctuations. For  $Q_0 \neq 0$ , Eq. (3) may be written

$$a(T - T_0) + \gamma Q_0^2 - 3\gamma \Delta_T = 0, \tag{10}$$

where

$$a = 9\gamma k / \omega_{\rm D}^2$$
,  $T_0 = a^{-1} [v(0) - \Omega_0^2]$ .

Because  $\Delta_T$  is linear in  $\omega_0$  as  $\omega_0 \rightarrow 0$ , it follows from Eqs. (6) and (10) that the transition is first order. However, it is important to note that *the linear term giving rise to the first-order transition is entirely due to the long-wavelength fluctuations.*<sup>7</sup>

In the SPA, correlation functions containing more than two lattice displacement operators are, in effect, factorized into products of pair correlation functions with the latter determined self-consistently. As is well known, any such factorization procedure breaks down sufficiently close to the transition point where the fluctuations are large. Criteria determining the size of the critical region, within which such simple approximations break down, have been given by Ginzburg.<sup>8</sup> For displacive phase transitions the condition for the validity of the simple approximation is precisely the requirement that the last term in Eq. (10) be small compared with the second term,<sup>9</sup>

$$3\gamma \Delta_T \ll \gamma Q_0^2$$
. (11)

Therefore, in the region where the SPA is valid,  $Q_0$  follows the usual square-root behavior characteristic of mean field for a second-order transition. The linear term becomes important only within the critical region where the SPA is no longer applicable.

The SPA for displacive phase transitions is analogous to the BCS theory for superconductivity.<sup>10</sup> The reason this difficulty does not arise in the BCS theory is, at least in part, because of the difference in statistics.

A model somewhat similar to that in Ref. 3 recently was used to describe the structural transitions in the perovskite structures.<sup>11</sup> However, in calculating the thermally averaged quantities  $Q_0$  and  $\Delta$ , the interaction between displacements in different cells was treated in a mean field approximation (MFA). For models with only fourthorder anharmonic interactions the MFA gives a second-order transition.<sup>11,12</sup> When third-order coupling to strain is included, a first- or secondorder transition is obtained depending on the strength of the coupling to the strain.

When the MFA is applied to the model given by Eq. (1), Eqs. (2)-(6) remain unchanged. However,  $\Delta$  is then given by

$$\Delta = \frac{1}{2} \Omega^{-1} \coth \frac{1}{2} \beta \Omega, \qquad (12)$$

where  $\Omega^2 = \omega_0^2 + v(0)$ . An expansion of  $\Delta$  in powers of  $\omega_0$  contains only even powers of  $\omega_0$ , and the transition is second order. That is, the MFA effectively cuts off the long-wavelength fluctuations and prevents these from becoming so large as to invalidate the factorization approximation. In this sense the MFA, unlike the SPA, is a consistent approximation. It should be emphasized, however, that the order of the transition can be determined definitely only when a correct description within the critical region is available. For any approximation procedure it is important to check for consistent results for one physical system but not for another, as evidenced by the BCS theory and the SPA.

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 $^{3}$ N. S. Gillis and T. R. Koehler, Phys. Rev. B <u>4</u>, 3971 (1971), and Phys. Rev. B (to be published).

<sup>4</sup>L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading, Mass., 1958), Sect. 135.

<sup>5</sup>A. F. Devonshire, Advan. Phys. <u>3</u>, 85 (1954).

<sup>6</sup>See for example R. Brout, *Phase Transitions* (Benjamin, New York, 1965).

<sup>7</sup>For dipolar forces, the linear term is replaced by  $Q_0^{2} \ln Q_0$ . However, the transition remains first order.

<sup>8</sup>V. L. Ginzburg, Fiz. Tverd. Tela <u>2</u>, 2031 (1960) [Sov. Phys. Solid State <u>2</u>, 1824 (1961)].

<sup>9</sup>This condition applies strictly speaking only for  $T < T_c$ . For  $T > T_c$  the critical region is determined by comparing fluctuations of the second and higher orders. If it is assumed that the critical region is roughly symmetrical about  $T_c$ , then Eq. (11) is also the condition for the validity of the factorization approximation.

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## **Optical Rectification by Impurities in Polar Crystals**

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When illuminated by an optical source, absorbing impurities in polar crystals produce a macroscopic polarization due to both the change in electric dipole moment from ground to optically excited states and a pyroelectric effect in the host lattice following thermalization of the excitation. The relevance of these mechanisms to relaxation processes is demonstrated by a measurement of the dispersion of optical rectification in LiTaO<sub>3</sub>:Cu<sup>++</sup> over the range of rectified frequencies from 0 to  $10^{12}$  Hz.

Previous studies<sup>1-3</sup> of optical rectification have dealt exclusively with the nonlinear properties of transparent electro-optic crystals. In this Letter we report efficient optical rectification in polar crystals due to impurity absorption. The absorbing impurities produce a polarization proportional to optical intensity due to two effects. If the relaxation of the optically excited impurites is largely nonradiative, a pyroelectric polarization results from the heating of the host lattice following thermalization of the excitation. Also, the acentric character of a polar host polarizes an impurity ion, producing an electric dipole moment which may be different in the excited state than in the ground state, and hence results in a macroscopic polarization upon optical excitation. This effect, which does not occur in nonpolar materials has been observed<sup>4</sup> in chromium-doped  $LiTaO_3$  and  $LiNbO_3$ . Although the pyroelectric effect is well known for its detector applicatons,<sup>5</sup> its relevance to fast nonradiative relaxation has not been considered previously.

For a two-level atomic system with a nonradiative relaxation time  $\tau$ , the macroscopic polarization *P*, due to these two effects, is determined by the approximate equation

$$\frac{\partial P}{\partial t} + \frac{1}{\tau} P = \frac{\alpha \Delta \mu I(t)}{\hbar \omega_0} + \frac{\alpha}{C_{\nu}} \left( \frac{\partial P_3}{\partial T} \right) \frac{1}{\tau} \int I(t) dt, \qquad (1)$$

where  $\alpha$  is the optical absorption coefficient for incident light of intensity I(t) and frequency  $\omega_0$ ,  $\Delta \mu$  is the difference in dipole moment of the impurity ions between ground and excited states,  $\partial P_3/\partial T$  is the pyroelectric coefficient of the host lattice, and  $C_v$  is the specific heat. For simplicity we have excluded the effects of saturation and coherent population fluctuations in Eq. (1). Also, the time interval of interest is assumed to be short relative to both thermal and acoustic transients, i.e., the adiabatic, clamped-material properties are used in (1).

Alternatively, these mechanisms can be represented in the frequency domain by second-order nonlinear susceptibilities for difference frequency