It is a pleasure to thank Professor J. Bok for stimulating discussions.

[1]R. Kubo, J. Phys. Soc. Japan 12, 570 (1957).
[2]H. B. Callen and T. A. Welton, Phys. Rev. 83, 34 (1952).
[3]H. F. Budd, Phys. Rev. 175, 241 (1968).
[4]R. Kubo, S. Miyake, and N. Hashitsume, Solid State Phys. 17, 269 (1965).
[5]E. N. Adams and T. D. Holstein, J. Phys. Chem. Solids 10, 254 (1958).
[6]P. N. Argyres and L. M. Roth, J. Phys. Chem. Solids 12, 89 (1959).
[7]This is unimportant in the present context since we only work to first order in E. To this order then, aside from the usual exclusion factors in the definition of $\hat{C}$, Eq. (6), terms like $\hat{C}\Phi$ would be replaced by $\hat{C}(f_0+\Phi)$, but the integrands in Eqs. (8)-(10) would contain the same $e^{\eta t}$ factors. In place of Eq. (11) one then obtains Eq. (23) of Ref. 3.
[8]G. V. Chester and A. Thellung, Proc. Phys. Soc. (London) 73, 745 (1959).

SOFT PHONON MODE IN SnTe †

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The self-consistent phonon formalism, successful in the description of the quantum crystals He^3 and He^4, is here applied to a discussion of the soft $k=0$ TO mode in SnTe. Straightforward considerations allow us to arrive at a simple expression for $\omega_{TO}^2(k=0)$ in the low-temperature regime. The analysis permits a quantitative fit to the temperature dependence of $\omega_{TO}^2(k=0)$ over a rather wide range of temperature.

It has been established that GeTe undergoes a second-order phase transition from a cubic phase of the NaCl-type structure to a face-centered rhombohedral structure, the transition occurring at about 700°K.[1] Furthermore, GeTe forms with SnTe a continuous range of solid solutions with the transition temperature varying linearly with concentration.[1] Extrapolation to pure SnTe indicates a transition temperature of about 0°K. A tendency toward a structural instability of this type should manifest itself through an abnormally low frequency for the corresponding normal mode. The difficulty of obtaining single crystals of GeTe has prevented a direct measurement of the phonon spectrum by the method of neutron diffraction. Recently, however, this technique has been applied to single crystals of SnTe with the result that a soft TO mode has been observed with a strong temperature dependence.[2] The neutron measurements suggest that SnTe is just barely stable at $T=0$°K. In this Letter we consider the temperature dependence of the $k=0$ TO mode within the context of the self-consistent phonon theory. It should be emphasized that we begin from a microscopic theory for the interatomic potential. The effective potential yielded by this model is incorporated into the self-consistent phonon theory and the temperature dependence of the $k=0$ TO mode is calculated. Simple approximations then allow us to obtain a quantitative fit to the temperature dependence from $T=0$°K to $T\sim\Theta_D$. The theory predicts a definite nonlinear temperature dependence near $T=0$°K. Specifically, we find for the $k=0$ TO mode a temperature dependence of the form

$$\omega_{TO}^2(T)\sim\omega_{TO}^2(0)+A\exp[-\hbar\omega_{TO}(0)/k_BT] \quad (1)$$

in the temperature range $0<T\lesssim\hbar\omega_{TO}(0)/k_B\sim 25$°K.

The mechanism governing ferroelectric-type transitions has been qualitatively understood for some time.[3] A characteristic feature of these displacive transitions is the large-amplitude motion of a group of optic modes near $k=0$. A natural candidate for the description of such a system would be the self-consistent phonon theory,[4] which has proven to be successful in the description of the quantum crystals He^3 and He^4. Anderson[3] has emphasized that when the restoring forces of the optical vibrations are small, the even anharmonic (in particular, the quartic) terms dominate the temperature dependence. Thus, the self-consistent phonon theory, which incorporates all even anharmonic terms in a self-consistent manner, should provide a good description of the lattice dynamics of a crystal

exhibiting a soft optical-phonon mode. In a very elegant paper Boccara and Sarma[5] first emphasized the utility of employing a self-consistent treatment of the lattice dynamics of crystals exhibiting a displacive transition. Their considerations were formal, however, and did not apply to any particular system. More recently, Nettleton[6] has applied the self-consistent phonon theory to the study of $SrTiO_3$. He does not, however, begin from a microscopic viewpoint.

The system of interatomic forces at work in SnTe is quite complicated. This is evidenced by the fact that 16 adjustable parameters are needed to fit the phonon dispersion curves within the context of the traditional shell model.[7] Furthermore, covalent bonding almost certainly plays an important role in the IV-VI compounds and V semimetals.[8] Since a proper treatment of lattice anharmonicity requires a knowledge of the functional form of the effective interionic potential, one needs a microscopic approach to the problem quite apart from the parametrized force-constant approach of the shell model. We emphasize again that in the present treatment we begin with a microscopic model for the interatomic potential. To the author's knowledge this is the first such treatment of a displacive transition to begin from such a microscopic basis. The model chosen for the effective ionic interaction is the microscopic dielectric bond-charge model[9] appropriate to octahedrally coordinated lattices. The interaction energy consists of a Coulombic part composed of ion-ion, ion-bond, and bond-bond contributions plus an indirect ion-electron-ion part derived from bare pseudopotential form factors[10] and a nonmetallic screening function. The splitting of the longitudinal and transverse optic modes at $k = 0$ is determined by an effective charge q^* which depends upon the dynamic charges of the ion cores in the two sublattices and upon the departure of the bond-charge position from a point midway between nearest neighbors. The value of q^* was fitted to the splitting of the LO and TO modes in the effectively harmonic region of the spectrum $25°K \ll T < \Theta_D$. The fit in this temperature region yielded $q^* = (1.2 \pm 0.1)e$.

The simplest model for the nonmetallic screening function $\epsilon(k)$ is that given by Penn[11] for an isotropic semiconductor. This model depends on only one parameter which is fixed by the $k = 0$ value of $\epsilon(k)$. The Penn model, however, was found to be inadequate for giving the correct qualitative behavior of the phonon spectrum for $k \neq 0$ along (100). This inadequacy was to be expected, however, since one anticipates that contributions from d core electrons will significantly alter the curvature of $\epsilon(k)$ in the intermediate-k region. For this reason it was necessary to introduce a further parameter which altered the behavior of $\epsilon(k)$ in the region near the first reciprocal lattice vector. The range of variation of the two parameters in $\epsilon(k)$ was determined by fitting the harmonic expression for $\omega_{TO}(k = 0)$ to the observed value in the effectively harmonic region $25°K \ll T < \Theta_D$. With the range of variation of the parameters thus fixed, the temperature dependence of ω_{TO} at $k = 0$ was found to be a rather general result of the model and was quite insensitive to the detailed features of the screening function. Indeed, one of the more significant aspects of the calculation was that the correct temperature dependence was retained over an extremely wide range of variation of the two parameters in $\epsilon(k)$. For this reason we feel that the results of the calculation of the temperature dependence of $\omega_{TO}(0)$ merit presentation here, independent of the calculation of the full spectrum which will be published separately.

The details of the self-consistent phonon theory have been covered extensively elsewhere.[12] Therefore, we limit ourselves here to those aspects of the theory relevant to the present calculation. In lowest order, the self-consistent force constants Φ are derived according to the prescription

$$\Phi_{ij,\sigma\sigma'}(\vec{\tau}_{\sigma\sigma'}) = 4\frac{\delta}{\delta d_{ij,\sigma\sigma'}(\vec{\tau})}(\langle E_c\rangle + \langle E_e\rangle), \quad (2)$$

where

$$\vec{\tau}_{\sigma\sigma'} \equiv \vec{\tau} + \vec{R}_\sigma - \vec{R}_{\sigma'};\ \sigma, \sigma' = 1, 2.$$

Here, $\vec{\tau}$ is a vector of the space lattice and $\vec{R}_\sigma$ is the position vector of each atom within the unit cell. $\langle E_c\rangle$, $\langle E_e\rangle$ represent the thermal averages with respect to the self-consistent density matrix of the Coulombic and electronic contributions to the energy, respectively. Finally,

$$d_{ij,\sigma\sigma'}(\vec{\tau}) \equiv \langle(\vec{u}_{\vec{\tau},\sigma} - u_{0,\sigma'})_i(\vec{u}_{\vec{\tau},\sigma} - \vec{u}_{0,\sigma'})_j\rangle. \quad (3)$$

where $\vec{u}$ represents the atomic displacement operator, is the equal-time displacement-displacement correlation function. $d_{ij,\sigma\sigma'}$ can be diagonalized in the appropriate normal mode representation. The optic modes near $k = 0$ contribute only to $d_{ij,\sigma\sigma'}$ for $\sigma \neq \sigma'$ as expected. With this

in mind we explicitly separate out the contribution to $d_{ij,12}$ of the group of anomalous optic modes near $k=0$:

$$d_{ij,12}(\bar{\tau}) \sim \alpha_0 \delta_{ij} + \Delta_{ij}(\bar{\tau}). \tag{4}$$

The contribution from the acoustic modes near $k=0$ is $O(k^2)$ smaller than α_0. The remainder Δ contains contributions from all modes except the group of anomalous modes near $k=0$. Δ contributes a small and relatively temperature-independent contribution in the region $0 < T < 25^\circ$K. At higher temperatures Δ is approximated by $\Delta \sim \langle u_{01}^2 \rangle + \langle u_{02}^2 \rangle$, which is evaluated in the harmonic approximation. Neglecting the $\bar{\tau}$ dependence in Δ allows us to evaluate the dynamical matrix in a straightforward manner. The long-range Coulomb forces arising from the charges at lattice and bond sites are treated using the usual Ewald techniques. The resulting expression for ω_{TO}^2 $(k=0)$ is

$$\omega_{TO}^2 = [(M_1/M_2)^{\frac{1}{2}} + (M_2/M_1)^{\frac{1}{2}}] \sum_K{}' \tilde{\Phi}(\vec{K}) \cos\vec{K}\cdot(\vec{R}_1 - \vec{R}_2) e^{-\frac{1}{2}K^2(\alpha_0+\Delta)}, \tag{5}$$

where $\vec{K}$ denotes a reciprocal lattice vector and

$$\tilde{\Phi}(K) = \frac{4\pi}{3r_0}\left[(q^*)^2 + Z_1 Z_2\left(\frac{1}{\epsilon_0} - 1\right)\right] - \frac{1}{12\pi r_0} K^4 v_1(K) v_2(K)\left(\frac{1-\epsilon(K)}{\epsilon(K)}\right). \tag{6}$$

The effect of Δ in (5) is to modulate the kernel of the sum by factors of the Debye-Waller type. M_1, M_2 are the masses and Z_1, Z_2 the valences of the Sn and Te ion cores, respectively. ω^2 is given in units of $(me^4/2\hbar^2) r_0^{-2} a_B^{-2} (M_1 M_2)^{-1/2}$. r_0 is the nearest-neighbor distance in a.u., and a_B is the Bohr radius. Finally, $v_\sigma(K) = \frac{1}{2} r_0 v_\sigma^{(b)}(K)$, where $v_\sigma^{(b)}$ represents the usual bare pseudopotential form factor in rydbergs. This last was obtained as the product of the tabulated screened model potential[10] and the free-electron dielectric constant.

In effect, (5) represents a closed self-consistent equation for ω_{TO}, since Δ is treated harmonically and

$$\alpha_0 = (N_0/\omega_{TO}) \coth(\omega_{TO}/2T). \tag{7}$$

N_0 is proportional to the number of modes included in our sampling of the Brillouin zone in the vicinity of $k=0$. In the present calculation N_0 was treated as temperature independent in the low-temperature regime. The value used corresponded to a sampling ~0.01 of the volume of the Brillouin zone.

Equation (5) was solved self-consistently at a number of temperatures. The results for ω_{TO} vs T are shown in Fig. 1. For convenience we have introduced the scale factors

$$\bar{\omega}^2 = (me^4/2\hbar^2)/r_0^2 a_B^2 (M_1 M_2)^{1/2}$$
$$= 2.132 \times 10^{26} \text{ (rad/sec)}^2,$$
$$\bar{T} = \hbar\bar{\omega}/k_B = 7.008 \times 10^2 \,^\circ\text{K}.$$

The first significant deviations from the experimental curve do not begin to appear until above 200°K, which is ~Θ_D. At very low temperatures Eq. (5) yields the limiting form indicated in Eq. (1).

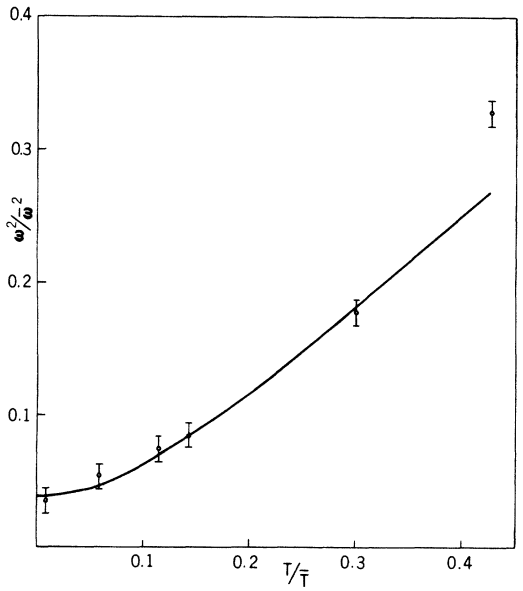

FIG. 1. ω_{TO}^2 vs T for SnTe with data from Pawley et al., Ref. 2.

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sion.

[1]J. Goldak, C. S. Barrett, D. Innes, and W. Youdelis, J. Chem. Phys. 44, 3323 (1966); J. N. Bierly, L. Muldawer, and O. Beckman, Acta Met. 11, 447 (1963).

[2]G. S. Pawley, W. Cochran, R. A. Cowley, and G. Dolling, Phys. Rev. Letters 17, 753 (1966).

[3]P. W. Anderson, in Fizika Dielektrikov, edited by G. I. Skanavi (Academy of Sciences of the U.S.S.R., Moscow, 1960); W. Cochran, Phys. Rev. Letters 3, 412 (1959).

[4]D. J. Hooton, Phil. Mag. 3, 49 (1958); J. Ranninger, Phys. Rev. 140, A2031 (1965); T. R. Koehler, Phys. Rev. Letters 17, 89 (1966), and 18, 516 (1967), and Phys. Rev. 165, 942 (1968); P. Choquard, The Anharmonic Crystal (W. A. Benjamin, Inc., New York, 1967).

[5]N. Boccara and G. Sarma, Physics 1, 219 (1965).

[6]R. E. Nettleton, Z. Physik 220, 401 (1969).

[7]E. R. Cowley, J. K. Darby, and G. S. Pawley, to be published.

[8]M. H. Cohen, L. M. Falicov, and S. Golin, IBM J. Res. Develop. 8, 215 (1964); J. Birman, in Proceedings of the International Colloquium in IV-VI Compounds, Paris, 1968 (to be published).

[9]J. C. Phillips, Phys. Rev. Letters 19, 415 (1967), and Phys. Rev. 166, 832 (1968), and 168, 917 (1968); R. M. Martin, Phys. Rev. Letters 21, 536 (1968).

[10]W. A. Harrison, Pseudopotentials in the Theory of Metals (W. A. Benjamin, Inc., New York, 1966).

[11]D. R. Penn, Phys. Rev. 128, 2093 (1962).

[12]N. R. Werthamer, to be published; also, Refs. 4 and 5.

MICROWAVE EMISSION FROM n-TYPE InSb ASSOCIATED WITH HELICAL INSTABILITY

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The microwave emission from n-type InSb in crossed magnetic and low electric fields at nitrogen temperature was investigated experimentally. It was found that the emission was caused by a helical instability of a high-current filament formed at an electrode contact.

Microwave emission from n-type InSb which is subjected to magnetic fields and relatively low electric fields has been observed by several authors.[1-6] Helicon waves interacting with drifting carriers[2] and acoustic phonons interacting with drifting electrons via deformation-potential coupling[6,7] have been proposed as origins of the microwave emission but these explanations have not been successful. We further investigated this type of microwave emission with n-type InSb and n-type Ge crystals and have come to the conclusion that the microwave emission is closely related to a helical instability on a high-current filament formed in the vicinity of the electrode contact.

Experimental setup.—About 120 pieces of n-type InSb single crystal of impurity concentration 1×10^{14} cm^{-3} were investigated. All the specimens had a cross section 1×1 mm^2 but their lengths ranged from 0.2 to 10 mm. The specimen was mounted as part of the inner conductor of a coaxial line and immersed in liquid nitrogen. A dc magnetic field was applied at an angle to the length of the specimen. One end of the coaxial line was connected with heterodyne receivers which covered from 25 kHz to 1.4 GHz and from 1.8 to 7.6 GHz. An electric field was applied across the length of the specimen.

Effects of electrode contact.—Musha, Lindvall, and Hägglund[3] and Eidson and Kino[4] reported that the microwave emission was affected by the polarity of the applied electric field. The observations suggest to us that current oscillations are generated in the vicinity of electrode contacts and give rise to the microwave emission. Three types of electrodes were used in our experiment: (1) a silver wire of diameter 100 μm which was indium soldered, (2) a silver wire of diameter 100 μm which was spot-welded, and (3) a tungsten wire of diameter 120 μm with a very sharp end which made a point contact to the specimen.

In order to see whether the current oscillation is generated near the electrode or deep in the body of semiconductor, a specimen (10 mm long) was made which had a indium-soldered contact at one end and a spot-welded contact at the other. In addition, contact was made to a ring electrode painted with silver paste, 1 mm from the spot-welded end. It was found that the microwave emission was observed when the electric field was applied between the spot-welded electrode and the third electrode which was positively biased, and that the strength and polarity of the electric field applied between the indium-soldered electrode and the third electrode had little effect on the microwave emission.