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FERROELECTRICITY IN THE IV-VI COMPOUNDS

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Résumé. — Nous donnons ici des résultats préliminaires destinés à l'étude théorique de la transition de phase cubique-rhomboédrique dans le GeTe, le SnTe et les composés GeTe/SnTe. Les calculs actuels sont conduits dans le contexte de l'approximation récemment introduite du phonon self-consistant. L'application de cette théorie aux transitions de déplacement dans les solides a été stimulée par les succès récents de l'approximation du phonon self-consistant qui a pu donner une dépendance en température quantitativement correcte pour ce qui est du coefficient de dilatation thermique des gaz rares solides, néon et argon.

Les deux questions principales qui doivent être discutées à la lumière de ces calculs sont :

1) Est-ce que l'approximation du phonon self-consistant donne une dépendance en température qualitativement correcte pour les phonons de grande longueur d'onde près de la transition dans les modèles ferro-électriques diatomiques cubiques ?

2) Est-ce que la théorie du pseudo-potentiel, modifiée pour inclure les effets de liaison covalents, donnent une interaction indirecte ion-ion qui décrira bien la dynamique de réseau de SnTe et GeTe ?

Abstract. — Preliminary results are reported of calculations aimed at a theoretical study of the cubic-rhombohedral phase transition in GeTe, SnTe and GeTe/SnTe compounds. The present calculations are being carried out within the context of the recently developed self-consistent phonon approximation. The application of this theory to displacive transitions in solids has been stimulated by the recent success of the self-consistent phonon approximation in yielding a qualitatively correct temperature dependence of the thermal expansivity of the rare gas solids neon and argon.

Two major questions to be discussed in the light of the present calculations are :

1) Does the self-consistent phonon approximation yield a qualitatively correct temperature dependence of the long-wavelength phonons near the displacive transition in cubic diatomic ferro-electric models ?

2) Will pseudo-potential theory as modified to include the effects of covalent bonding provide an indirect ion-ion interaction which will adequately describe the lattice dynamics of SnTe and GeTe ?

In view of the renewed experimental effort directed toward an investigation of the IV-VI compounds SnTe and GeTe, it has become imperative that a serious theoretical attempt be made to study the cubic-rhombohedral phase transition in these materials. Optical and ultrasonic experiments aimed at directly measuring the long wavelength phonons near the transition temperature provide a rigorous test of any theory whose goal it is to quantitatively predict the temperature dependence of the long wavelength phonons which characterize these transitions. Furthermore, the relative simplicity of the crystal structure of these substances provide the theorist for the first time with a ferroelectric system amenable to detailed calculations.

In the time that I have at my disposal, I wish to describe briefly the results of some preliminary investigations which have been carried out in an attempt to calculate the phonon dispersion curves of SnTe in the disordered phase. The calculations are being carried out within the context of the recently developed self-consistent phonon theory [1], which has proved to be a successful approximate treatment of lattice anharmonicity in quantum crystals such as solid He³ and solid He⁴.

The basic equations of the self-consistent phonon approximation can be derived using diagrammatic summation techniques [2]. However, the results are most easily arrived at employing a finite temperature variational technique first introduced by Boccara and Sarma [3]. In lowest order the effect of the self-consistent treatment of lattice anharmonicity is to

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modify the force constants in an expression which is otherwise identical to that of the quasi-harmonic approximation. Very briefly, one considers a trial density matrix constructed from a model harmonic Hamiltonian appropriate to the symmetry of the crystal of interest. The internal energy of the crystal is then taken to be the thermal average of the *exact* crystal Hamiltonian using this trial density matrix. Minimizing the free energy with respect to the dynamical matrix of the model harmonic Hamiltonian then results in a self-consistent equation for the phonon frequencies.

Given the effective ionic interaction, application of the formalism of the self-consistent phonon theory becomes relatively straightforward. The approach adopted here in the treatment of SnTe is to employ an effective ionic interaction composed of a direct ion-ion part, which is taken to be coulombic, plus an ion-electron-ion part, derived from a bare pseudopotential and an appropriate screening function. The use of the latter as an indirect ion-ion interaction requires some justification in the present case. It is

well known that the local pseudo potential formalism, although successful in the description of the properties of the simple metals, becomes shrouded in uncertainty when applied to the region of the periodic table occupied by the IV-VI compounds. This is immediately obvious if we note the glaring discrepancies between the semi-empirical form factors of Cohen et al. [4] and the form factors calculated by Animalu and Heine [5] on the assumption of a metallic environment. One of the questions to be examined here is whether or not these discrepancies can be explained on the basis of non-metallic screening alone. The fact that the semi-empirical form factors permit successful calculation of the band structures of these materials motivates us to examine more carefully whether or not the lattice dynamics is also described in a qualitatively correct manner also.

With these reservations in mind, let us examine briefly the equations which are necessary for the description of a lattice with two atoms per unit cell within the framework of the self-consistent phonon theory. The phonon frequencies are determined self-consistently from the quasi-harmonic dispersion relation

$$\omega_{k\lambda}^2 \mathbf{e}_{k\lambda} = \sum_{\tau} \sum_{\sigma', \sigma''} \frac{1}{\sqrt{M_{\sigma} M_{\sigma'}}} [\delta_{\sigma, \sigma'} - \delta_{\sigma', \sigma''} \exp(-ik \cdot \tau_{\sigma\sigma'})] \Phi_{\sigma\sigma''}(\tau_{\sigma\sigma'}) \cdot \mathbf{e}_{k\lambda}^{\sigma'} \quad (\text{II.1})$$

where :

$$\tau_{\sigma\sigma'} \equiv \tau + \mathbf{R}_{\sigma} - \mathbf{R}_{\sigma'} \quad (\text{II.2})$$

In the above, τ is a vector ⁽¹⁾ of the space lattice and \mathbf{R}_{σ} represents the position vector of each atom within the unit cell. The effective force constants are derived according to the prescription

$$\Phi_{\sigma\sigma'}(\tau_{\sigma\sigma'}) = 4 \frac{\delta}{\delta d_{\sigma\sigma'}(\tau_{\sigma\sigma'})} [\langle E_{\text{coul}} \rangle + \langle E_{\text{elec}} \rangle] \quad (\text{II.3})$$

where

$$d_{\sigma\sigma'}(\tau_{\sigma\sigma'}) = \langle (\mathbf{u}_{\tau+\sigma} - \mathbf{u}_{\sigma'}) (\mathbf{u}_{\tau+\sigma} - \mathbf{u}_{\sigma'}) \rangle \quad (\text{II.4})$$

is the displacement-displacement correlation function. The equation determining the phonon frequencies is clearly self-consistent in that the effective force constants depend upon d through the thermal average. The displacement-displacement correlation function can, of course, be diagonalized in an appropriate normal mode representation and when this is done it takes the form :

$$d_{\sigma\sigma'}(\tau_{\sigma\sigma'}) = \frac{1}{N} \sum_{k\lambda} \frac{1}{\omega_{k\lambda}} \coth \frac{\beta \omega_{k\lambda}}{2} \left\{ \frac{1}{2} \left[\frac{1}{M_{\sigma}} \mathbf{e}_{k\lambda}^{\sigma} \mathbf{e}_{k\lambda}^{\sigma} + \frac{1}{M_{\sigma'}} \mathbf{e}_{k\lambda}^{\sigma'} \mathbf{e}_{k\lambda}^{\sigma'} \right] - \frac{1}{\sqrt{M_{\sigma} M_{\sigma'}}} \frac{1}{2} (\mathbf{e}_{k\lambda}^{\sigma} \mathbf{e}_{k\lambda}^{\sigma'} + \mathbf{e}_{k\lambda}^{\sigma'} \mathbf{e}_{k\lambda}^{\sigma}) \cos \mathbf{k} \cdot \tau_{\sigma\sigma'} \right\} \quad (\text{II.5})$$

In the particular case of interest here, where the force constants consist of a direct Coulomb part plus an electronic part, there is no difficulty in writing down the explicit functional dependence of the force cons-

tants on d . For simplicity, we write them down for the case of purely metallic screening alone. The more complicated case of non-metallic screening requires modifications which will be discussed shortly. With this in mind, the force constants take the form :

⁽¹⁾ Vectors are represented by roman bold type characters (\mathbf{R}) and matrix by italic bold type characters (\mathbf{d}).

$$\begin{aligned}
\Phi_{\sigma\sigma'}(\tau_{\sigma\sigma'}) = & -\frac{4}{a} \int \frac{d^3g}{(2\pi)^3} \mathbf{g}\mathbf{g} \cos \mathbf{g} \cdot \boldsymbol{\tau}_{\sigma\sigma'} \times \left[\frac{2\pi Z_\sigma Z_{\sigma'}}{g^2} \exp(-g^2/4\eta) + F_{\sigma\sigma'}(g) \right] \exp\left(-\frac{1}{2} \mathbf{g} \cdot \mathbf{d}_{\sigma\sigma'} \cdot \mathbf{g}\right) + \\
& + \frac{2}{a} Z_\sigma Z_{\sigma'} \frac{2}{\sqrt{\pi}} \int_{\eta^{1/2}}^{\infty} d\rho [\det(\mathbf{I} + 2\rho^2 \mathbf{d}_{\sigma\sigma'})]^{-1/2} \\
& \times \{ 4\rho^4 \boldsymbol{\tau}_{\sigma\sigma'} \cdot [\mathbf{I} + 2\rho^2 \mathbf{d}_{\sigma\sigma'}]^{-1} [\mathbf{I} + 2\rho^2 \mathbf{d}_{\sigma\sigma'}]^{-1} \cdot \boldsymbol{\tau}_{\sigma\sigma'} - 2\rho^2 [\mathbf{I} + 2\rho^2 \mathbf{d}_{\sigma\sigma'}]^{-1} \}
\end{aligned} \tag{II.6}$$

where :

$$F_{\sigma\sigma'}(g) = \frac{g^2}{8\pi} W_\sigma(g) W_{\sigma'}(g) \left(\frac{1 - \varepsilon(g)}{\varepsilon(g)} \right) \tag{II.7}$$

Here Z_σ represents the valence of an ion core of species σ and $W_\sigma(g)$ represents the bare pseudo-potential form factor associated with this ion core $\varepsilon(g)$ is the usual free electron screening function. The force constants are independent of the value chosen for η , which is a convergence constant of the Ewald type introduced for calculational convenience. Since \mathbf{d} is a positive definite matrix, the integral in wave-vector space will converge for $\eta = \infty$; i. e., we can eliminate the second term in Φ entirely. However, in the true harmonic approximation where \mathbf{d} is identically zero or, in actual practice, where \mathbf{d} may be very small it may be calculationally necessary to keep η finite.

For non-metallic screening the function $(1 - \varepsilon)/\varepsilon$ no longer approaches (-1) for long wavelength, implying that charge has been transferred from the pseudo-atom to the covalent bond. Charge neutrality then requires that additional terms appear in the Coulomb contribution to the effective force constants arising from the electrostatic interaction of the electronic charges localized in the covalent bond.

It is appropriate at this point to take note of some important general features of the present problem. First, let us recall from the usual harmonic approximation that the sum over lattice vectors of the force constants Φ which appears in the dynamical matrix converts the integral over all wave-vectors to a discrete sum in reciprocal space. This is no longer possible in the general self-consistent case because of the additional lattice dependence in \mathbf{d} . As a consequence, it is necessary to know the pseudopotential form factors for arbitrary wave-vector. This introduces a problem not encountered in some of the more recent calculations of the lattice dynamics of the simple metals with only one atom per unit cell. In these calculations the acoustic modes are seen to be relatively insensitive to the long range character of the pseudopotential in wave-vector space. Similarly, in band structure determinations, only the region between 0 and $2k_F$ is

important. This is in direct contrast to the present case where the long-range behaviour of the pseudo-potential is of importance in determining the character of the optical modes. If one adopts the approach of fitting an analytic form to the semi-empirical form factors between 0 and $2k_F$, then one is faced with the uncertainty of how to cut off the pseudopotential for values of the wave-vector greater than $2k_F$.

As was stated previously, the formulae which we have written down for the effective force constants rigorously hold only for the case of purely metallic screening. In spite of the inappropriateness of the metallic model for the description of a semi-conductor such as SnTe, I think it important to examine briefly what consequences metallic screening has on the lattice dynamics of a diatomic material. Two general features of the diatomic metallic model are immediately obvious. First, the direct Coulomb interaction between any pair of ions is exactly cancelled for large inter-ionic separation, leaving a residual interaction which is asymptotically entirely of a screened nature. Secondly, the longitudinal optic mode becomes degenerate with the transverse optic mode at large wavelengths. This results from the fact that the effective ionic charge which would ordinarily split the two branches for small wave-vector is here entirely screened out by the electrons. We can pursue the metallic model somewhat further and ask what would result from using Animalu-Heine form factors in conjunction with metallic screening, ignoring for the moment the fact that the longitudinal optic and transverse optic modes are degenerate for long wavelength. For any lattice constant reasonably appropriate to SnTe, explicit calculation shows that the Animalu-Heine form factors yield an unstable structure, evidenced by the low-lying acoustic modes becoming imaginary along symmetry directions in the irreducible $1/48$ of the Brillouin zone. More relevant to the ferroelectric system is the fact that the metallic form factors cannot produce the cancellation of forces necessary to yield a displacive transition near $T = 0$.

At long wavelengths, at least, one can make a crude analysis of the effects of covalent bonding on the pho-

non spectrum of an otherwise metallic model by starting from the picture of a periodic array of neutral pseudo-atoms. Then, one major effect of bonding in an antisymmetric compound such as SnTe is to superimpose ionic charges of opposite sign on the two atoms in the basic unit cell. This effective charge produces a splitting of the longitudinal and transverse optic modes near zero wave-vector and at the same time lowers the low-lying optic mode. Thus, we are provided with a mechanism by which one can achieve the appropriate cancellation of forces necessary to produce a displacive transition.

Now it is well known that the NaCl structure reverts to an unstable simple cubic structure if the two atomic species are allowed to become the same. This presumably explains why the group V semimetals must distort to a face-centered rhombohedral structure in order to maintain stability. It has been conjectured that by making the antisymmetric component of the pseudo-potential large enough, one can stabilize the NaCl structure for all temperatures. Indeed, one of the arguments put forth to explain the difference in transition temperature between GeTe and SnTe is that the antisymmetric component of the pseudopotential for GeTe must be a factor of two or so smaller than that for SnTe [6]. This appears not to be entirely true. If we examine the magnitudes of the antisymmetric components of the semi-empirical form factors for GeTe and SnTe in the region between 0 and $2 k_F$ they agree to within a few per cent. These, in turn, agree reasonably well with the antisymmetric component derived from the Animalu-Heine form factors. Thus, although it appears that it is certainly a necessary condition for the stability of the NaCl structure that the antisymmetric component be non-zero, it does not appear to be sufficient.

Preliminary calculations indicate that firstly, the stability of the NaCl structure in the disordered phase and secondly, the possibility of a displacive transition is partly tied to a broadening of the potential well of the symmetric component of the pseudopotential in the region of intermediate wave-vector. This is supported by the fact that the symmetric component of the semi-empirical form factors for SnTe differ from the Animalu-Heine form factors by as much as 60 % in the region between 0 and $2 k_F$. This is not surprising and one might attempt to explain the difference on the basis of non-metallic screening. Let us recall that according to the recent theory of Phillips [7], the contribution of the semi-empirical form factor may be thought of as consisting of a part due to a modification of the metallic form factor arising from the intro-

duction of non-metallic screening plus a coulombic contribution from the covalent charge.

The simplest description of non-metallic screening is the model dielectric function of Penn [8], which has proved to be successful in the description of the covalent properties of Ge and Si. If we employ data appropriate to SnTe in conjunction with the Penn model we find that the contribution from non-metallic screening is negligible in the wave-vector region of interest. Furthermore, the relatively large value of $\epsilon_\infty(0)$ in SnTe [8] (~ 40) indicates that the direct bond contribution is at least a factor of two less than that in Ge or Si where already it is only $\sim .01$ Ryd. Presumably, the conclusion to be drawn from these considerations is that the simple Penn model is probably inadequate for the description of the narrow gap semiconductor SnTe.

In summary then, it appears that three definite conclusions can be drawn from the present preliminary calculations :

- 1) For simple models of the inter-atomic potential in diatomic materials, the self-consistent phonon theory provides an adequate treatment of the temperature dependence of the anomalous low-lying transverse optic mode which heralds a displacive transition.
- 2) The long-range behavior of the pseudo-potential in wave-vector space must be better known.
- 3) A better determination of the non-metallic screening function must be made.

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DISCUSSION

PAWLEY, G. S. — Our phonon fitting to SnTe (ref [11], previous paper) using a screening model

suggests that a non-ionic model for SnTe is poorer than an ionic model.

SAUNDERS, G. A. — In view of the lack of knowledge of the effective ionicity and the force constants in SnTe and alloys, would ultrasonic experiments to determine the elastic constants as a function of temperature be a useful contribution ?

GILLIS, N. S. — Yes, these experiments would be a definitive contribution, but for a different reason than your question implies. Any determination of the effective ionicity from experiment would depend upon the model assumed for the system. On the other hand, it would be of great interest to observe whether there is an anomalous behavior of the long-wavelength acoustic modes near the transition temperature.

HERMAN, F. — 1) It is generally agreed that there is some degree of arbitrariness in the choice of pseudopotential form factors in empirical band structure and lattice vibrational calculations. To what extent does

this arbitrariness moderate your qualitative conclusions ?

2) Am I correct in assuming that you are trying to construct a pseudopotential that is successful both in the energy band and lattice vibrational contexts ?

GILLIS, N. S. — 1) First, as I tried to emphasize earlier in my talk, there exist great difficulties in trying to justify a priori the use of the local pseudopotential formalism in the region of the periodic table occupied by the IV-VI compounds. Therefore, I would rather call my approach a « model » potential approach in the sense that I would like to employ the semi-empirical form factors of Cohen et al., given an appropriate screening function. I think that some of the arbitrariness in the determination of the form factors could probably be removed by extending the calculations to larger wave vectors. This would certainly be of interest to me since, as I mentioned, the long-range behavior of the pseudopotential in wave-vector space is of importance in determining the character of the optic modes.

2) Yes.
