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Long-wavelength excitations in incommensurate intergrowth compounds with application to $Hg_{3-\delta}AsF_6$

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There exists a variety of compounds consisting of two (or more) interpenetrating incommensurate lattices, e.g., $Hg_{3-\delta}AsF_6$, tetrathiafulvalene iodide (TTF-I_x), Nowotny phases. In such materials one expects new hydrodynamic modes associated with a broken translational symmetry. We examine a continuum model of these excitations which appear as "extra" acoustic modes. We consider the case of $Hg_{3-\delta}AsF_6$ explicitly and find a set of "generalized" elastic constants which violate conventional rotational symmetry relations in agreement with existing experiments. At high temperatures there are five acoustic modes; at low temperatures there are four in this material. Owing to the liquidlike properties of this material certain modes become purely dissipative in some propagation directions.

I. INTRODUCTION

Among the various types of incommensurate systems[1] one of the conceptually simplest is that which we will term intergrowth compounds. In their simplest form they consist of two or more regular interpenetrating sublattices with lattice periods which coincide (or are commensurate) in some direction(s) and not in others. It is often helpful to think of one sublattice as the host or receptor lattice into which the second grows. If the host sublattice has linear channels they can be filled with atoms or molecules which can be accommodated into the channels. We call these linear intergrowth compounds and the two sublattices may be incommensurate along the channel direction (Fig. 1). $Hg_{3-\delta}AsF_6$,[2] many salts of planar organic cations with iodine [e.g., tetrathiafulvalene iodide (TTF-I_x)],[3] and various binary alloys with the so-called Nowotny structure[4] are examples. If the host lattice has a layered aspect, they may form regularly staged "sandwich" compounds with appropriate intercalants. We call these planar intergrowth compounds and the two sublattices may be incommensurate along both or only one of the planar directions. For example, graphite[5] forms planar intergrowth compounds with a variety of intercalants.

The purpose of this paper is to investigate the nature of the long-wavelength excitations in such systems. In general there may be more than three acoustic modes. Consider for instance the simple intergrowth compound made up of two sublattices (Fig. 1), with average periods a and b, respectively. Because of the interactions the two lattices A and B modulate each other and the equilibrium positions of the atoms in the incommensurate z direction may be written generally in the form,[6,7]

$$z_n^A = na + u_z^A + f(na + u_z^A - u_z^B) ,$$
$$z_m^B = mb + u_z^B + g(mb + u_z^B - u_z^A) , \tag{1.1}$$

with $f(x+b)=f(x)$; $g(x+a)=g(x)$. For weak enough interactions,[6] and far enough away from commensurability,[8] f and g are continuous analytic functions and the energy of the system remains unchanged when the "phase" $v_z = u_z^A - u_z^B$ is varied. There is thus a continuous symmetry associated with v_z and we therefore expect a gapless mode associated with periodic modulations of this variable. Note that a uniform shift of $u_z^A - u_z^B$ does not indicate a uniform shift of the atoms since the functions f and g generally are not constants; on the other hand, the simultaneous shift $u_z^A = u_z^B = u_z$ gives a uniform displacement of all atoms in both systems. The gapless mode associated with this global translational symmetry is the usual longitudinal-acoustic phonon. If the lattices are charged the situation is more complicated. When

u_z^A is shifted relative to u_z^B there will be a restoring electric force and the mode will acquire a gap as has already been pointed out by Theodorou.[9] There is no continuous symmetry associated with relative displacements of chains in the perpendicular directions, and the corresponding modes will have a gap (normal optic modes).

The plan of the paper is as follows. In Sec. II a general formalism will be outlined. Expressions for equations of motion and the resulting dynamical matrix will be derived. The general effects of long-range Coulomb interactions in screened metals and insulators will be investigated. In Sec. III a simple uniaxial example is studied. The theory developed here may apply to Nowotny phases as found in Mn_xSi_y.[4] Since this compound has low conductivity there may effectively be a gap at long (but not too long) wavelengths. Acoustic and optical experiments are suggested.

In Sec. IV the theory is applied to the mercury chain compound $Hg_{3-\delta}AsF_6$. Several experiments have been performed on this material.[2,10,11] Above a critical temperature $T=120$ K the mercury chains form a liquid and the theory must be slightly modified. Propagating acoustic modes become diffusive along certain symmetry directions. There are in general *five* acoustic modes. A simple relation, involving atomic masses only, is derived for the relative velocities of some transverse modes. The relation replaces the conventional rotational invariance condition and is in good agreement with neutron scattering results of Heilmann *et al.*[10] Below T_c there are four acoustic modes; the fifth mode obtains a gap which develops as $\sqrt{T_c-T}$ within Landau theory. Optical measurements (Brillouin scattering) and further neutron scattering experiments are suggested to check our predictions.

II. LONG-WAVE LATTICE DYNAMICS

In order to discuss the long-wavelength, low-frequency excitations it is sufficient to consider two interpenetrating elastic continua.[12] (The extension to three or more components, when the need arises, is obvious.) We begin by specifying the energy required to elastically deform the material in terms of the vector displacement fields $u_\alpha^i(\vec{r})$ of the two media and their spatial gradients,

$$\partial_\beta u_\alpha^i \equiv (\partial u_\alpha^i/\partial r_\beta) .$$

[$i=(A,B)$ denotes the sublattice, $\alpha=(x,y,z)$.] In this section we consider explicitly only those additional constraints that follow from global translational and rotational invariance, since additional point-symmetry restrictions must be analyzed separately for every case. For convenience we separate the potential,

$$U^{ij}=U_D^{ij}+U_E^{ij}+U_C^{ij} , \tag{2.1}$$

and discuss each separately. U_C^{ij} is due to (possibly screened) Coulomb interaction. U_D^{ij} (U_E^{ij}) is that part of the remaining interaction associated with uniform (spatially varying) displacements.

A. U_D^{ij}

This can depend only upon relative sublattice displacements so we can write at once,

$$U_D^{ij}=\tfrac{1}{2}\int d\vec{r}\sum_{\alpha\beta} D_{\alpha\beta}^{ij}u_\alpha^i u_\beta^j$$

$$=\tfrac{1}{2}\int d\vec{r}\sum_{\alpha\beta}\bar{D}_{\alpha\beta}(u_\alpha^i-u_\alpha^j)(u_\beta^i-u_\beta^j) , \tag{2.2}$$

so that $\underline{D}^{AA}=\underline{D}^{BB}=-\underline{D}^{AB}=-\underline{D}^{BA}=\underline{\bar{D}}$. $\underline{\bar{D}}$ is a symmetric (3×3) matrix.

By hypothesis the two sublattices are incommensurate in at least one direction, which we choose to be z. By arguments of the preceding section U_D must also be form invariant with respect to the relative displacements $u_z^A=-u_z^B=v'$, i.e.,

$$U_D(u_\alpha^A+v'\delta_{\alpha,z'}u_\beta^B-v'\delta_{\beta,z})=U_D(u_\alpha^A,u_\beta^B) .$$

This leads to the requirement $\sum\bar{D}_{z\beta}(u_\beta^A-u_\beta^B)=0$ which can only be satisfied for arbitrary $(\vec{u}^A-\vec{u}^B)$ if $\bar{D}_{z\beta}=\bar{D}_{\beta z}=0$ for all β. If the media are incommensurate along two crystallographic directions it will be possible to freely translate the sublattices relatively in a plane (for example, $y-z$) containing the two incommensurate crystallographic directions. By exactly similar arguments we find in addition $\bar{D}_{y\beta}=\bar{D}_{\beta y}=0$. Finally if the structures are triply incommensurate, if indeed such structures exist, the one remaining element $\bar{D}_{xx}$ vanishes. To summarize, the energies associated with rigid translations are specified by a (3×3) symmetric matrix $\bar{D}_{\alpha\beta}$ which (aside from requirements imposed by point-group symmetry) has one null row and column for every degree of incommensurability.

B. U_E^{ij}

This contribution has the general form,

$$U_E^{ij}=\tfrac{1}{2}\int d\vec{r}\sum_{\alpha\beta}\lambda_{\alpha\gamma\beta\lambda}^{ij}\partial_\gamma u_\alpha^i\partial_\lambda u_\beta^j , \tag{2.3}$$

which is the same as for conventional elasticity, but the constraints imposed by global rotational invariance are relaxed due to the presence of two sublattices. To investigate this decompose $\partial_\gamma u_\alpha^i$ into strain and rotation matrices, which are, respectively, symmetric and antisymmetric,

$$\partial_\gamma u_\alpha^i = \epsilon_{\alpha\gamma}^i + \omega_{\alpha\gamma}^i \ , \tag{2.4}$$

where

$$\underline{\omega} = \begin{bmatrix} 0 & -\omega_z & \omega_y \\ \omega_z & 0 & -\omega_x \\ -\omega_y & \omega_x & 0 \ , \end{bmatrix} \tag{2.5}$$

and $(\omega_x,\omega_y,\omega_z)$ is the axial rotation vector $\delta\vec{r}=\vec{\omega}\times\vec{r}$. Equation (2.4) can be immediately rewritten as follows:

$$U_E^{ij} = \tfrac{1}{2}\int d\vec{r}\sum_{ij}[\,\underline{\epsilon}^i\cdot\underline{c}^{ij}\cdot\underline{\epsilon}^j + \underline{\epsilon}^i\cdot\underline{d}^{ij}\cdot\underline{\epsilon}^j + \underline{\omega}^i\cdot\underline{f}^{ij}\cdot\underline{\omega}^j\,] \ , \tag{2.6}$$

with

$$\lambda_{\alpha\gamma\beta\lambda}^{ij} = (c^{ij}+d^{ij}+f^{ij})_{\alpha\gamma\beta\lambda} \ . \tag{2.7}$$

Since U_E^{ij} can depend only upon relative rotations of the two media we also have

$$U_E^{ij} = \tfrac{1}{2}\int d\vec{r}\sum_{ij}[\,\underline{\epsilon}^i\cdot\underline{c}^{ij}\cdot\underline{\epsilon}^j + \underline{\epsilon}^i\cdot\bar{\underline{d}}^i\cdot(\underline{\omega}^i-\underline{\omega}^j) + (\underline{\omega}^i-\underline{\omega}^j)\cdot\bar{\underline{f}}\cdot(\underline{\omega}^i-\underline{\omega}^j)\,] \ , \tag{2.8}$$

and on comparing Eqs. (2.7) and (2.8) the general symmetry properties are as follows:

(a) For $\underline{c}^{ij}$, $\underline{d}^{ij}$, and $\underline{f}^{ij}$ (and thus for $\underline{\lambda}^{ij}$),

$$\lambda_{\alpha\gamma\beta\lambda}^{ij} = \lambda_{\beta\lambda\alpha\gamma}^{ji} \ . \tag{2.9}$$

(b) $c_{\alpha\gamma\beta\lambda}^{ij} = c_{\gamma\alpha\beta\lambda}^{ij} = c_{\alpha\gamma\lambda\beta}^{ij} = c_{\gamma\alpha\lambda\beta}^{ij}$.

(c) $\underline{d}^{AA} = -\underline{d}^{AB} = \bar{\underline{d}}^A$, $\underline{d}^{BB} = -\underline{d}^{BA} = \bar{\underline{d}}^B$,

$d_{\alpha\gamma\beta\lambda}^{ij} = d_{\gamma\alpha\beta\lambda}^{ij} = -d_{\alpha\gamma\lambda\beta}^{ij} = -d_{\gamma\alpha\lambda\beta}^{ij}$,

$\bar{d}_{\alpha\gamma\beta\beta}^{i} = 0$.

(d) $\underline{f}^{AA} = -\underline{f}^{AB} = -\underline{f}^{BA} = \underline{f}^{BB} = \bar{\underline{f}}$,

$f_{\alpha\gamma\beta\lambda}^{ij} = -f_{\gamma\alpha\beta\lambda}^{ij} = -f_{\alpha\gamma\lambda\beta}^{ij} = f_{\gamma\alpha\lambda\beta}^{ij}$,

$\bar{f}_{\alpha\alpha\beta\lambda} = \bar{f}_{\alpha\gamma\beta\beta} = 0$.

These conditions restrict the number of independent constants as follows: For $\underline{c}^{AA}$ and $\underline{c}^{BB}$ (21), for $\underline{c}^{AB}$ (36), for $\bar{\underline{d}}^A$ and $\bar{\underline{d}}^B$ (18), for $\bar{f}$ (6). Of course the number of constants may be further reduced by point-group symmetry. It is only necessary to note that $\epsilon_{\alpha\gamma}$ and $\omega_{\alpha\gamma}$ transform differently under proper and improper rotations.

C. U_C^{ij}

At long wavelengths and low frequencies it is sufficient to treat the Coulomb interaction in the electrostatic approximation. Suppose the two submedia have charge densities $\sigma_i = z_i\rho_i$ where z_i is the charge per unit mass and ρ_i is the mass density. For the perturbed medium we have

$$\rho_i(\vec{r}) = \bar{\rho}_i(1+\nabla\cdot\vec{u}^i(\vec{r})) \ , \tag{2.10}$$

or in terms of Fourier-transformed variables,

$$\left[\rho_i(\vec{r}) = V^{-1/2}\sum_q \rho_i(\vec{q})e^{i\vec{q}\cdot\vec{r}},\ \cdots\right] \ ,$$
$$\rho_i(\vec{q}) = \bar{\rho}_i[\delta_{q,0} + i\vec{q}\cdot\vec{u}(\vec{q})] \ . \tag{2.11}$$

The Coulomb interaction is

$$\begin{aligned} U_C^{ij} &= \frac{z_i z_j}{2}\int d\vec{r}\,\rho_i(\vec{r})\phi_j(\vec{r}) \\ &= \tfrac{1}{2}\sum_q v_{ij}(\vec{q})\rho_i(\vec{q})\rho_j(-\vec{q}) \\ &= \tfrac{1}{2}\sum_{q\neq 0} v_{ij}(\vec{q})\sum_{\alpha\beta} q_\alpha q_\beta u_\alpha^i(\vec{q})u_\beta^j(-\vec{q}) \ , \end{aligned} \tag{2.12}$$

where ϕ_j is the electrostatic potential of the jth sublattice. For v_{ij} we will take a simple isotropic form,

$$v_{ij}(\vec{q}) = \frac{4\pi\sigma_i\sigma_j}{\epsilon_0(q^2+\lambda_s^2)} \ , \tag{2.13}$$

with a Thomas-Fermi screening length,

$$\lambda_s = (4\pi e^2\epsilon_0^{-1}n_e/k_BT)^{1/2}$$

for a nondegenerate electron gas,

$$\lambda_s = (6\pi e^2\epsilon_0^{-1}n_e/E_F)^{1/2}$$

for a degenerate electron gas. λ_s goes to zero as $n_e\to 0$ and Eq. (2.13) is thus qualitatively correct for both free- and bound-electron response. (ϵ_0 is the "bare" response of the composite medium.) In Eq. (2.12) $q=0$ is excluded because of charge neutrality. The form of Eq. (2.12) reflects the well-known fact that only longitudinal fluctuations are electrostatically coupled.

The equations of motion are easily derived given the potential $U=\sum U^{ij}$. In terms of Fourier-transformed "density-weighted" variables,

$$w_\alpha^i(\vec{q})=\sqrt{\rho_i}u_\alpha^i(\vec{q}) , \tag{2.14}$$

they take the form

$$\omega^2 w_\alpha^i(\vec{q})=\sum_{j\beta}(\rho_i\rho_j)^{-1/2}M_{\alpha\beta}^{ij}(\vec{q})w_\beta^j(\vec{q}) . \tag{2.15}$$

The $\vec{q}$ dependence of $\vec{M}(\vec{q})$ is quite different depending upon the presence or absence of free electrons. For bound-electron systems ($n_e=0$),

$$M_{\alpha\beta}^{ij}(\vec{q})=\left[D_{\alpha\beta}^{ij}+\Lambda_b^{ij}\left[\frac{q_\alpha q_\beta}{q^2}\right]\right]+q^2\left[\sum_{\gamma\lambda}\lambda_{\alpha\gamma\beta\lambda}^{ij}\left[\frac{q_\gamma q_\lambda}{q^2}\right]\right] , \tag{2.16}$$

where $\Lambda_b^{ij}=4\pi\sigma_i\sigma_j\epsilon_0^{-1}$, while for $n_e\neq 0$,

$$M_{\alpha\beta}^{ij}(\vec{q})=(D_{\alpha\beta}^{ij})+q^2\left[\sum_{\gamma\lambda}(\lambda_{\alpha\gamma\beta\lambda}^{ij}+\Lambda_f^{ij}\delta_{\alpha\gamma}\delta_{\beta\lambda})\left[\frac{q_\gamma q_\lambda}{q^2}\right]\right] , \tag{2.17}$$

where $\Lambda_f^{ij}=4\pi\sigma_i\sigma_j\epsilon_0^{-1}/(q^2+\lambda_s^2)$.

The rigid displacement matrix $\underline{D}$ can always be diagonalized by choosing optic and acoustic modes,

$$u_\alpha=\tfrac{1}{2}(u_\alpha^A+u_\alpha^B),\quad v_\alpha=\tfrac{1}{2}(u_\alpha^A-u_\alpha^B) . \tag{2.18}$$

Suppose there are p directions along which the sublattices are incommensurate (a p-fold incommensurate structure). Diagonalizing $\underline{D}$ shows that there will be a $q=0$ energy gap for all the optic modes with displacements perpendicular to the incommensurate directions. These $(3-p)$ modes can be omitted from further discussion. (Through elastic interactions they produce corrections to the remaining mode velocities of order

$$[1-(cq^2/\omega_{\text{gap}}^2)]^{1/2}\to 0$$

as $q\to 0$. Here c is a typical elastic stiffness.) The three acoustic modes and remaining $\underline{p}$ optic modes constitute the (in general coupled) "slow" or hydrodynamic degrees of freedom.[13] Note, however, that the optic-acoustic mode transformation does not diagonalize the Coulomb interaction, which for insulators contributes an additional $\vec{q}=0$ longitudinal stiffness [Eq. (2.16)]. As a result additional $\vec{q}=0$ gaps open in the p optic branches except for transverse propagation. By contrast for a good conductor where $q\ll\lambda\sim d_0^{-1}$ (d_0 being a typical atomic spacing) the Coulomb term serves only to renormalize the short-range elastic constants $\underline{\lambda}^{ij}$. As is familiar in conventional elasticity both $q<\lambda_s$ and $q>\lambda_s$ regimes may be valid for lightly doped materials in which case additional dispersion occurs as the elastic behavior passes from metallic to insulating.

III. A UNIAXIAL EXAMPLE

Consider the case where both sublattices have uniaxial symmetry with the unique axis coinciding with the common ($p=1$) incommensurate z axis (as in Fig. 1). To further simplify the expressions we assume elastic isotropy in the x-y plane (hexagonal D_{6h} symmetry). There are two invariants bilinear in the displacements u_α^A:

$$\tfrac{1}{2}D_{xx}^{AA}[(u_x^A)^2+(u_y^A)^2] \text{ and } \tfrac{1}{2}D_{zz}^{AA}[(u_z^A)^2] ,$$

and similar terms involving $D_{\alpha\alpha}^{AB}$ and $D_{\alpha\alpha}^{BB}$. There are five invariants bilinear in the strains $\epsilon_{\alpha\gamma}^{AA}$ (analogous to the bulk elastic constants):

$$\tfrac{1}{2}c_1^{AA}[(\epsilon_{xx}^A+\epsilon_{yy}^A)^2],\ c_{13}^{AA}[(\epsilon_{xx}^A+\epsilon_{yy}^A)\epsilon_{zz}^A] ,$$
$$\tfrac{1}{2}c_2^{AA}[(\epsilon_{xx}^A-\epsilon_{yy}^A)^2+4(\epsilon_{xy}^A)^2],\ \tfrac{1}{2}c_{33}^{AA}[(\epsilon_{zz}^A)^2] ,$$

and

$$\tfrac{1}{2}c_3^{AA}[(\epsilon_{xz}^A)^2+(\epsilon_{yz}^A)^2] .$$

There is one invariant linear in $\epsilon^A\omega^A$,

$$d_{44}^{AA}(\epsilon_{xz}^A\omega_{xz}^A+\epsilon_{yz}^A\omega_{yz}^A) ,$$

and two invariants bilinear in ω^A,

$$\tfrac{1}{2}f_3^{AA}[(\omega_{xz}^A)^2+(\omega_{yz}^A)^2] ,$$
$$\tfrac{1}{2}f_{66}^{AA}[(\omega_{xy}^A)^2] ,$$

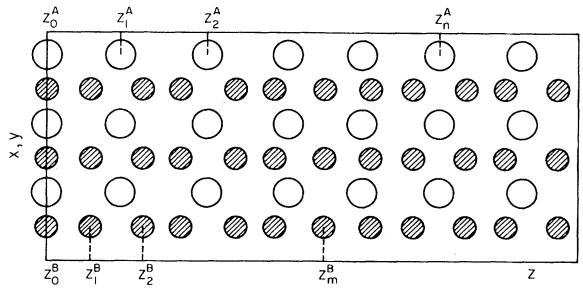

FIG. 1. Uniaxial intergrowth compound. The positions z_n^A and z_m^B for the two sublattices are given by (1.1) with $u_z^A=u_z^B=0$. Sine functions were chosen for f and g.

and

$$f_3^{AA}=c_3^{AA} .$$

There are again similar terms in c^{AB},d^{AB},f^{AB} and c^{BB},d^{BB},f^{BB}. The corresponding Coulomb terms with the same symmetry exist and can be written by inspection.

First consider the $q\to 0$ modes. When Eq. (2.15) is diagonalized by the $(\vec{u}^A,\vec{u}^B)\to(\vec{u},\vec{v})$ transformation the acoustic-mode frequencies vanish and the optic modes are given by

$$\begin{vmatrix} D_1+\Lambda\hat{q}_\perp^2-\bar{\rho}\omega^2 & 0 & \Lambda\hat{q}_{||}\hat{q}_\perp \\ 0 & D_1-\bar{\rho}\omega^2 & 0 \\ \Lambda\hat{q}_{||}\hat{q}_\perp & 0 & \Lambda\hat{q}_{||}^2-\bar{\rho}\omega^2 \end{vmatrix}=0 , \quad (3.1)$$

where $\vec{q}_\perp=\hat{q}_\perp|q|$ and $\hat{q}_{||}=\hat{q}_{||}|q|$ are the components of q parallel and perpendicular to z, and

$$\bar{\rho}=\rho_A\rho_B(\rho_A+\rho_B)^{-1}$$

is the reduced mass density. We assume the two sublattices are polar and insulating ($\sigma_A=-\sigma_B=\sigma$), in which case $\Lambda=4\pi\sigma^2\epsilon_0^{-1}$; otherwise $\Lambda=0$. If $\Lambda\neq 0$ the behavior of the $\vec{q}=0$ modes depends upon the direction along which $\vec{q}\to 0$ as shown schematically in Fig. 2. There is a mode with displacements v_y perpendicular to the scattering plane, with a frequency ω_y independent of $\hat{q}$. The remaining two modes are linear combinations of $v_{||},v_\perp$ and there are two distinct cases [Figs. 2(a) and 2(b)] depending upon whether $D_\perp>\Lambda$ or not. One of these additional modes is gapless only when q is perpendicular to the incommensurate axis.[14] For nonpolar or conducting media the behavior at $q\to 0$ is not singular, and the v_z mode is gapless for all propagation directions.

Now let us investigate the nature of the four slow variables u_x, u_y, u_z, and v_z at finite q. u_y is decoupled and has a frequency given by

$$\omega_y^2=aq_\perp^2+fq_{||}^2 . \quad (3.2)$$

The remaining variables are coupled for a general propagation direction and are solutions of the following secular equation:

$$\begin{array}{c} \begin{matrix} u_x & \qquad u_z & \qquad\qquad v_z \end{matrix} \\ \begin{vmatrix} (a+b)q_\perp^2+fq_{||}^2-\omega^2 & dq_{||}q_\perp & d'q_{||}q_\perp \\ dq_{||}q_\perp & eq_{||}^2+fq_\perp^2-\omega^2 & e'q_{||}^2+f'q_\perp^2 \\ d'q_{||}q_\perp & e'q_{||}^2+f'q_\perp^2 & e''q_{||}^2+f''q_\perp^2+\Lambda(q)q_{||}^2-\omega^2 \end{vmatrix}=0 . \end{array} \quad (3.3)$$

The constants (a,b,d,e,f) can be evaluated from the invariant forms in a straightforward manner. These are the bulk elastic constants [divided by $\rho_T\equiv(\rho_A+\rho_B)$] and involve only the sums of the strain couplings, $\vec{c}^{ij}$. In fact only the term diagonal in v_z contain the rotational couplings, $\underline{d}^{ij}$ and $\underline{f}^{ij}$.

$$\Lambda(q)=[4\pi\sigma^2/\epsilon_0(q^2+\lambda_s^2)]$$

is the Coulomb term described in the preceding paragraph.

The equations of motion given in (3.3) are further simplified for propagation along and perpendicular to the z axis, in which case the u_x mode decouples. The phonon dispersion is shown schematically in Fig. 3, for the polar insulating case $\Lambda(0)\neq 0$. Note that the Cauchy relation which would require that the transverse-mode frequencies of Figs. 3(a) and 3(b) be the same fails trivially in the sense that there are two modes with valid claims to be transverse-acoustic modes when $\vec{q}\perp z$. Furthermore neither of these velocities,

$$v_\pm^2=\frac{(f+f'')\pm[(f-f'')^2+4f'^2]^{1/2}}{2} , \quad (3.4)$$

equals that of the transverse mode with $\vec{q}||z$, for which $v^2=f$.

It should be possible to look for the existence of

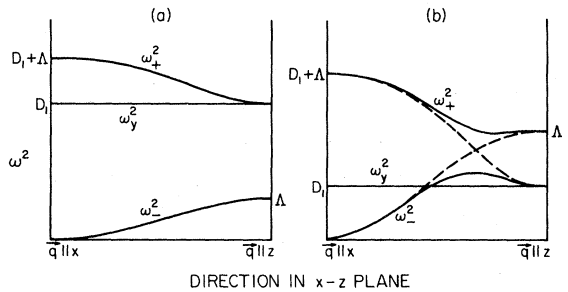

FIG. 2. $\vec{q}=0$ mode frequencies off a uniaxial polar incommensurate insulator. The gap vanishes only for the transverse propagation direction. There are two cases: (a) large mechanical forces, $D_1>\Lambda$, and (b) large Coulomb forces, $\Lambda>D_1$.

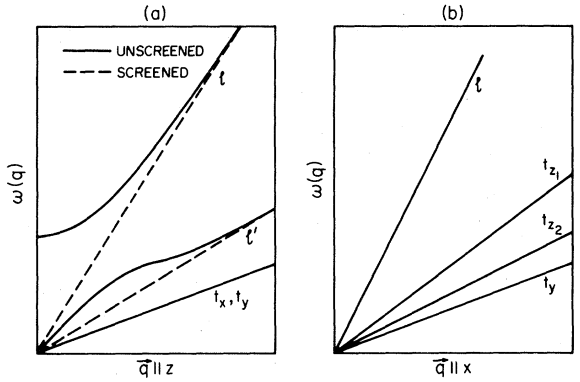

FIG. 3. Phonon dispersion for a uniaxial incommensurate polar material. (a) q along unique axis. (b) q perpendicular to unique axis. Subscripts indicate displacement direction.

these extra acoustic modes in intergrowth compounds by ultrasonic and/or light scattering techniques. Of the materials mentioned in the introduction, the Nowotny phase alloys (e.g., Mn_xSi_y) are attractive both because of the relatively simple tetragonal structure and because the materials are semiconductors and thus offer the possibility of plasmon-related dispersion in the longitudinal modes propagating along the c axis. Another example of such a system with tetragonal symmetry is the organic salt diethyldihydrophenazonium iodide.[15]

IV. AN EXAMPLE WITH NEW FEATURES: $Hg_{3-\delta}AsF_6$

The structure of the mercury chain compound $Hg_{3-\delta}AsF_6$ is formed by a body-centered tetragonal lattice of AsF_6 anions through which pass two nonintersecting orthogonal arrays of mercury cations parallel to the basal plane edges of the AsF_6 host lattice (Fig. 4). At high temperature the mercury atoms form an "incommensurate" liquid with no long-range atomic positional order, but at $T_c = 120$ K there is a phase transition into a structure where the mercury chains form an incommensurate ordered lattice (Fig. 5).

The theory naturally splits into two parts: one which is valid above T_c and one which describes the properties below T_c. Since the formalism derived so far applies to solid phases only it has to be slightly modified above T_c where the mercury system has some liquid properties.

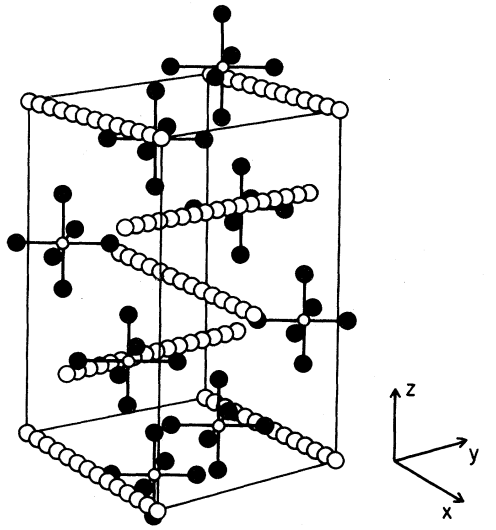

FIG. 4. Structure of $Hg_{3-\delta}AsF_6$. The Hg atoms on the chains are shown schematically. Above 120 K the Hg atoms form a fluid with no long-range order.

A. Acoustic modes in $Hg_{3-\delta}AsF_6$, $T > T_c$

The compound consists of three lattices: one (AsF_6) with three-dimensional positional order and two mercury chain lattices with two-dimensional order of the *chain* positions but no ordering in the third direction. The continuous symmetry of the Hg liquid has thus been broken in the two perpendicular directions for each lattice. In a sense, the structure is similar to a "smectic-A" liquid crystal where the continuous symmetry is broken in one direction but the system remains fluid in the two

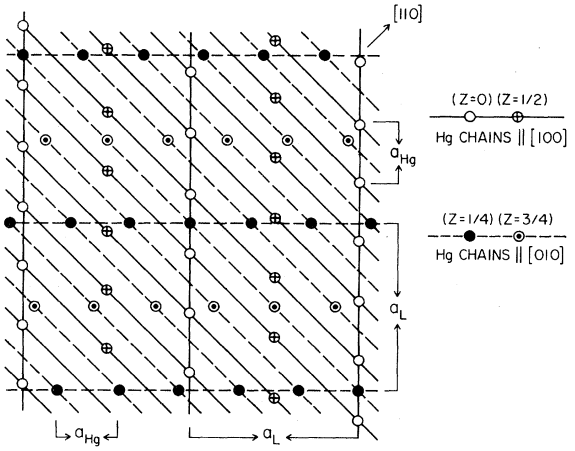

FIG. 5. Ordered structure of $Hg_{3-\delta}AsF_6$ below 120 K.

perpendicular directions.

Now, let u_x^A, u_y^A, and u_z^A denote displacements of the AsF_6 lattice in the x, y, and z directions (defined in Fig. 4), respectively. Similarly, let u_x^x, u_y^x, u_z^x and u_x^y, u_y^y, u_z^y be the displacements of the two mercury lattices. The coordinates (u_y^x, u_z^x), (u_x^y, u_z^y), (u_x^A, u_y^A, u_z^A) are all associated with broken symmetries, but the coordinates u_x^x and u_y^y are of a different nature. They describe translations along chains of Hg mass density, and their gradients describe mass-density fluctuations rather than strains of a mercury lattice. We shall see that this leads to diffusive modes along certain directions.

Following the program defined in Sec. II we first construct the terms U_D in the expansion of the potential energy which depend on uniform sublattice displacements:

$$\begin{aligned} U_D = &\tfrac{1}{2}D_{yy}^{Ax}(u_y^x - u_y^A)^2 + \tfrac{1}{2}D_{xx}^{Ay}(u_x^y - u_x^A)^2 \\ &+ \tfrac{1}{2}D_{zz}^{Ax}(u_z^x - u_z^A)^2 + \tfrac{1}{2}D_{zz}^{Ay}(u_z^y - u_z^A)^2 \\ &+ \tfrac{1}{2}D_{zz}^{xy}(u_z^x - u_z^y)^2 . \end{aligned} \tag{4.1}$$

These terms give the potential energies associated with relative displacements of the three lattices and involve only coordinates associated with broken symmetries. In the 9×9 dynamical matrix, (4.1) determines (together with the appropriate masses) the gaps of four "fast" optic modes. There are thus $9-4=5$ slow acoustic modes. Near $\vec{q}=0$ the terms in (4.1) force the perpendicular displacements of the chains to follow the AsF_6 lattice for the acoustic modes

$$\begin{aligned} &u_y^x = u_y^A , \\ &u_x^y = u_x^A , \\ &u_z^x = u_z^y = u_z^A . \end{aligned} \tag{4.2}$$

At this point we could in principle proceed as in the preceding section, introducing center of mass modes $\vec{u}$ and modes $\vec{v}$ for which the center of mass is at rest. However, for reasons which become clear later we shall choose instead the following coordinates which are orthogonal to the optic modes at $\vec{q}=0$:

$$\begin{aligned} &u_x = \tfrac{1}{2}(u_x^A + u_x^y) , \\ &u_y = \tfrac{1}{2}(u_y^A + u_y^x) , \\ &u_z = \tfrac{1}{3}(u_z^A + u_z^x + u_z^y) , \\ &w_x = u_x^x , \\ &w_y = u_y^y . \end{aligned} \tag{4.3}$$

Here, u_z describes displacement of the whole system in the z direction, u_x describes displacement of the AsF_6 and the y chains in the x direction, and u_y is the displacement of the AsF_6 lattice and the x chains in the y direction.

Our task now is to form the most general biquadratic form in the gradients of the hydrodynamic variables defined above. The potential energy is invariant under the tetragonal point-group operations. We define the symmetric pseudostrains,

$$\epsilon_{\alpha\beta}^A = \tfrac{1}{2}(\partial_\alpha u_\beta^A + \partial_\beta u_\alpha^A) \quad \alpha,\beta = x,y,z , \tag{4.4a}$$

$$\left.\begin{aligned} &\epsilon_{\alpha'\beta'}^B = \tfrac{1}{2}(\partial_{\alpha'} w_{\beta'} + \partial_{\beta'} w_{\alpha'}) \\ &\epsilon_{\alpha' z}^B = \tfrac{1}{2}\partial_z w_{\alpha'} \end{aligned}\right\} \quad \alpha',\beta' = x,y ,$$

and pseudorotations,

$$\begin{aligned} &\omega_{\beta\gamma}^A = \tfrac{1}{2}(\partial_\beta u_\gamma - \partial_\gamma u_\beta) , \\ &\omega_{xy}^B = \tfrac{1}{2}(\partial_x w_y - \partial_y w_x) . \end{aligned} \tag{4.4b}$$

The elastic energy does not depend on the rotations and $\epsilon_{\alpha' z}$ separately, but only on the combinations

$$(\omega_{yz}^A - \epsilon_{yz}^B), \quad (\omega_{xz}^A - \epsilon_{xz}^B), \quad (\omega_{xy}^A - \omega_{xy}^B) .$$

The combinations $\omega_{yz}^A = \epsilon_{yz}^B$, $\omega_{xz}^A = \epsilon_{xz}^B$, and $\omega_{xy}^A = \epsilon_{xy}^B$ describe global rotations around the x, y, and z axis, respectively. Group theoretical considerations based on these symmetries lead to the following invariants in the expansion of the potential energy.

(a) Six invariants in $\epsilon_{\alpha\beta}^A$. They are the usual invariants in tetragonal systems:

$$\begin{aligned} &\tfrac{1}{2}c_{11}^A[(\epsilon_{xx}^A)^2 + (\epsilon_{yy}^A)^2] , \\ &\tfrac{1}{2}c_{33}^A(\epsilon_{zz}^A)^2 , \\ &c_{12}^A\epsilon_{xx}^A\epsilon_{yy}^A , \\ &c_{13}^A(\epsilon_{xx}^A + \epsilon_{yy}^A)\epsilon_{zz}^A , \\ &2c_{66}^A(\epsilon_{xy}^A)^2 , \\ &2c_{44}^A[(\epsilon_{xz}^A)^2 + (\epsilon_{yz}^A)^2] . \end{aligned} \tag{4.5a}$$

(b) Three invariants in ϵ^B:

$$\begin{aligned} &\tfrac{1}{2}c_{11}^B[(\epsilon_{xx}^B)^2 + (\epsilon_{yy}^B)^2] , \\ &c_{12}^B\epsilon_{xx}^B\epsilon_{yy}^B , \\ &2c_{66}^B(\epsilon_{xy}^B)^2 . \end{aligned} \tag{4.5b}$$

(c) Four invariants which couple $\epsilon_{\alpha\beta}^B$ and $\epsilon_{\alpha\beta}^A$:

$$\begin{aligned} &c_{11}^{AB}(\epsilon_{xx}^A\epsilon_{xx}^B + \epsilon_{yy}^A\epsilon_{yy}^B) , \\ &c_{12}^{AB}(\epsilon_{xx}^A\epsilon_{yy}^B + \epsilon_{xx}^B\epsilon_{yy}^B) , \\ &c_{13}^{AB}[\epsilon_{zz}^A(\epsilon_{xx}^B + \epsilon_{yy}^B)] , \\ &4c_{66}^{AB}\epsilon_{xy}^A\epsilon_{xy}^B . \end{aligned} \tag{4.5c}$$

(d) Three invariants coupling rotations with rotations and strains:

$$2c_{44}^{AB}[\epsilon_{xz}^{A}(\omega_{xz}^{A}-\epsilon_{xz}^{B})+\epsilon_{yz}^{A}(\omega_{yz}^{A}-\epsilon_{yz}^{B})]\,,$$
$$2f_{66}^{AB}(\omega_{xy}^{A}-\omega_{xy}^{B})^2\,, \tag{4.5d}$$
$$2f_{44}^{AB}[(\omega_{yz}^{A}-\epsilon_{yz}^{B})^2+(\omega_{xz}^{A}-\epsilon_{xz}^{B})^2]\,.$$

The relevant part of the kinetic energy density T is

$$T=\tfrac{1}{2}(\rho_A+\tfrac{1}{2}\rho_B)\dot{u}_x^2+\tfrac{1}{2}(\rho_A+\tfrac{1}{2}\rho_B)\dot{u}_y^2\,,$$
$$+\tfrac{1}{2}(\rho_A+\rho_B)\dot{u}_z^2+\tfrac{1}{2}(\tfrac{1}{2}\rho_B)\dot{w}_x^2\,,$$
$$+\tfrac{1}{2}(\tfrac{1}{2}\rho_B)\dot{w}_y^2\,, \tag{4.6}$$

where ρ_A is the mass density of the AsF_6 lattice, and ρ_B is the mass density of the Hg system. Note that the mass associated with the w modes is *half* the mercury mass; the mass associated with the u_z mode is the *total* mass, and the mass of the u_x and u_y modes is that of the AsF_6 lattice plus half the mercury mass.

The dynamical matrix $\underline{D}$ may be derived from (4.5) and (4.6) in the usual way. The general problem of finding the normal mode frequencies, $\underline{D}(\omega)(u_x,u_y,u_z,w_x,w_y)=0$, is prohibitively complicated. However, the problem is greatly simplified by the extra constraint that since the mercury chains form a liquid there can be no elastic energy, or restoring force, from shear strains, $\partial_{y,z}w_x,\partial_{x,z}w_Y$ in the Hg "lattice," hence

$$c_{66}^{B}=c_{66}^{AB}=c_{44}^{AB}=f_{66}^{AB}=f_{44}^{AB}=0\,. \tag{4.7}$$

This is the point where the choice (4.1) simplifies the calculations. Using the standard coordinates defined in Sec. II the simple condition (4.7) would be replaced by much more complicated relations.

The dynamical matrix becomes

u_x	u_y	u_z	w_x	w_y
$c_{11}^{A}q_x^2+c_{66}^{A}q_y^2$ $+c_{44}^{A}q_z^2$ $-(\rho_A+\frac{1}{2}\rho_B)\omega^2$	$(c_{12}^{A}+c_{66}^{A})q_xq_y$	$(c_{13}^{A}+c_{44}^{A})q_xq_z$	$c_{11}^{AB}q_x^2$	$c_{12}^{AB}q_xq_y$
	$c_{11}^{A}q_y^2+c_{66}^{A}q_x^2$ $+c_{44}^{A}q_z^2$ $-(\rho_A+\frac{1}{2}\rho_B)\omega^2$	$(c_{13}^{A}+c_{44}^{A})q_yq_z$	$c_{12}^{AB}q_xq_y$	$c_{11}^{AB}q_y^2$
		$c_{33}^{A}q_z^2+c_{44}^{A}(q_x^2+q_y^2)$ $-(\rho_A+\rho_B)\omega^2$	$c_{13}^{AB}q_xq_z$	$c_{13}^{AB}q_zq_y$
			$c_{11}^{B}q_x^2-\frac{1}{2}\rho_B\omega^2$	$c_{12}^{B}q_xq_y$
				$c_{11}^{B}q_y^2-\frac{1}{2}\rho_B\omega^2$.

The matrix is symmetric and only the upper right triangle is shown. In special directions it is possible to derive explicit expressions for the normal modes. For instance, in the $\Delta(100)$ direction ($q_y=q_z=0$) the dynamical matrix becomes

u_x	u_y	u_z	w_x	w_y
$c_{11}^{A}q_x^2-(\rho_A+\frac{1}{2}\rho_B)\omega^2$	0	0	$c_{11}^{AB}q_x^2$	0
	$c_{66}^{A}q_x^2-(\frac{1}{2}\rho_B+\rho_A)\omega^2$	0	0	0
		$c_{44}^{A}q_x^2-(\rho_A+\rho_B)\omega^2$	0	0
			$c_{11}^{B}q_x^2-\frac{1}{2}\rho_B\omega^2$	0
				$\frac{1}{2}\rho_B\omega^2$.

The normal modes are as follows:

(i) Two longitudinal modes involving u_x and w_x. The modes are mixed because of the c_{11}^{AB} term which couples density fluctuations in the x chains to strains in the AsF_6 lattice plus y-chain system.

Emery and Axe[16] have analyzed the spatial fluctuations of the Hg atoms along the chain as derived from neutron studies[2,10] and showed that they are liquidlike. Good qualitative agreement ($\sim 10\%$) was obtained with the assumption that the mea-

sured modes are purely of the w_x (or w_y) type. However, in principle the Hg fluctuations involve both (coupled) u and w modes. It is possible that this may contribute to the remaining discrepancy between theory and observation.

(ii) Transverse mode polarized in the z direction. Its velocity is

$$v(T_z,\Delta)=[(c_{44}^A/(\rho_A+\rho_B)]^{1/2} . \tag{4.8}$$

(iii) Two transverse modes polarized in the y direction. The u_y mode and the w_y mode are, respectively,

$$\begin{aligned} &v(T_{1y},\Delta)=[c_{66}^A/(\rho_A+\tfrac{1}{2}\rho_B)]^{1/2} , \\ &v(T_{2y},\Delta)\equiv 0 . \end{aligned} \tag{4.9}$$

In the $\Lambda(001)$ direction the five modes can be characterized as follows:

(i) One longitudinal mode,

$$v(L,\Lambda)=[c_{33}^A/(\rho_A+\rho_B)]^{1/2} ,$$

(ii) Two degenerate u_x, u_y modes,

$$v(T_1,\Lambda)=[c_{44}/(\rho_A+\tfrac{1}{2}\rho_B)]^{1/2} , \tag{4.10}$$

(iii) Two degenerate transverse w_x, w_y modes,

$$v(T_2,\Lambda)\equiv 0 . \tag{4.11}$$

Note the relation between the velocity of the transverse mode propagating in the x direction and polarized along the z direction, and the mode propagating in the z direction and polarized in the x direction

$$R=\frac{v(T_x,\Lambda)}{v(T_z,\Delta)}=\left[\frac{\rho_B+\rho_A}{\frac{1}{2}\rho_B+\rho_A}\right]^{1/2}>1 . \tag{4.12}$$

In a conventional elastic medium with tetragonal symmetry $R=1$ since both modes involve the identical strain component ϵ_{zx}. (In the long-wavelength limit the two modes differ only by a rotation about y.) The violation of the conventional $R=1$ rotational symmetry condition was noted in an inelastic neutron scattering study by Heilmann *et al.*[10] The reason for this violation is that for the transverse mode polarized along z, both Hg sublattices are coupled to the AsF_6 whereas for the transverse mode polarized along x, the x-axis Hg chain sublattice is decoupled. In either case the shearing of the Hg sublattices contributes to the inertia but produces no restoring forces due to the liquidlike nature. Thus R depends only upon the masses of the various lattices, not upon the effective elastic constants which are not known *a priori*. It is therefore a simple matter to insert known atomic masses to calculate R:

$$\begin{aligned} &\rho_A\sim M(\mathrm{As})+6M(\mathrm{F})=189 , \\ &\rho_B\sim(3-\delta)M(\mathrm{Hg})=285 , \end{aligned} \tag{4.13}$$

which gives $R=1.27$. Heilmann *et al.* found $R=1.25\pm0.1$, and the value derived here is well within their uncertainty.

The transverse $\omega\equiv 0$ modes arise as a result of the lack of potential energy associated with shear strains in a liquid. We expect the modes to be *diffusive*,

$$\omega=\frac{iq^2\eta}{\frac{1}{2}\rho_B} , \tag{4.14}$$

where η is an appropriate viscosity.

In general directions all modes are propagating because of the coupling between $w_{x,y}$ modes and u modes. Near the high-symmetry direction there is a crossover between diffusive and propagating behavior. For a similar situation, see the discussion by Martin *et al.*[13] on diffusive and propagating modes in a smectic-A crystal. The transverse modes propagating perpendicular to the smectic planes are diffusive because the smectics are liquidlike within planes, but generally the modes are all propagating.

The predicted behavior of the mode velocities as a function of propagation direction in the x-z and x-y planes is shown in Figs. 6(a) and 6(b). The internal regions of the figures are schematic, but the

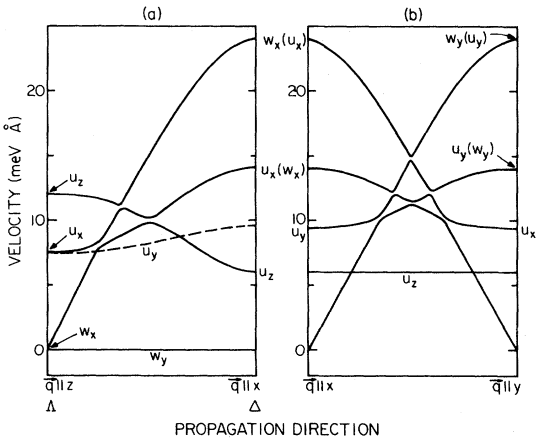

FIG. 6. Phonon velocities vs propagation direction in $Hg_{3-\delta}AsF_6$, $T>T_c$. (a) Propagation in x-z plane. (b) Propagation in x-y plane. The symbols denote the nature of the mode along the symmetry direction (or within the plane, if appropriate).

velocities along the principal directions are fixed at their measured values.[10]

B. Acoustic modes in $Hg_{3-\delta}AsF_6$, $T < T_c$

Below T_c the phases or displacements of the x and y chains lock together (Fig. 5). The densities of the condensed mercury atoms can be written in the form

$$\rho_x = \psi_x \exp(i\vec{q}_1 \cdot \vec{r}) + \text{c.c.} ,$$
$$\rho_y = \psi_y \exp(i\vec{q}_1 \cdot \vec{r}) + \text{c.c.} , \tag{4.15}$$

where $\psi_x = -\psi_y$ and $\vec{q}_1 = (2\pi/a)(\delta,\delta,0)$. It costs energy to slide the x system without sliding the y system in a similar way. The symmetry is lowered (orthorhombic) since the $(\delta,\delta,0)$ direction is singled out relative to the $(-\delta,\delta,0)$ direction. The potential energy associated with the phase locking is of the form[17]

$$U' = \tfrac{1}{2} D_{xy}^{xy} (w_x - w_y)^2 . \tag{4.16}$$

An optical mode with a $q = 0$ gap, given by

$$\omega_0 = (D_{xy}^{xy}/\rho_B)^{1/2} ,$$

develops. Within the Landau theory, $D_{xy}^{xy} \sim (T_c - T)$ so $\omega_0 \sim (T_c - T)^{1/2}$.[17] We are thus left with four slow modes. Three of the hydrodynamic coordinates are associated with the displacements of the whole crystal; $v_x = \frac{1}{2}(u_x + w_x)$, $v_y = \frac{1}{2}(u_y + w_y)$, and u_z. The fourth mode is $w = \frac{1}{2}(w_y + w_x)$. This last mode is unusual in that it involves Hg chains moving in perpendicular directions. Also, there is now a transverse restoring force in the Hg lattice, and the elastic constants (4.7) are nonzero. The kinetic energy associated with the w coordinate is

$$T_w = \tfrac{1}{2} \rho_B \dot{w}^2 . \tag{4.17}$$

The dynamical matrix is 4×4. In the q_x direction there is one mode polarized in the z direction with velocity,

$$v(T_2,\Delta) = [(c_{44}^A + f_{66}^{AB} - c_{44}^{AB})/(\rho_A + \rho_B)]^{1/2} ,$$

and three modes mixing u_x, u_y, and w. There is no mode with zero velocity. In the q_z direction there is a longitudinal mode with velocity

$$v(L,\Lambda) = [c_{33}^A/(\rho_A + \rho_B)]^{1/2} ,$$

as above T_c, and a transverse mode with $u_x = u_y$. In addition there are two more transverse modes mixing $u_x = u_y$ and w. At T_c one of these modes becomes degenerate with the $(1,-1,0)$ transverse mode; the other becomes dissipative. A Landau theory analysis yields a velocity proportional to $(T_c - T)^{1/2}$.[17] The ratios between transverse mode velocities in different directions always depend on effective elastic constants which we do not know.

Existing neutron scattering experiments have established very clearly the existence of the extra acoustic modes in $Hg_{3-\delta}AsF_6$, as well as the remaining qualitative features of this treatment.[10,11] In particular, the lack of propagating shear modes of the Hg lattice above T_c, and the growth of such modes below T_c have been observed at short wavelengths. It would be very interesting to extend such measurements to the long-wavelength regime treated here using acoustic or light scattering methods, although the former may be difficult because of the sensitivity of the material to ambient environments, and the latter difficult because of small light-penetration depths.

ACKNOWLEDGMENT

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$$F=\tfrac{1}{4}r'(|\psi_x|^2+|\psi_y|^2)+r''(\psi_x\psi_y^*+\psi_y\psi_x^*)+\cdots$$
$$=\tfrac{1}{2}r'A^2+r''A^2\cos(\phi_x-\phi_y)\ .$$

The phases ϕ_x and ϕ_y are defined by $\psi_x=A\exp i\phi_x$, $\psi_y=A\exp i\phi_y$. The second term gives the energy associated with shifting the x chains relative to the y chains: $\phi_x=(2\pi/b)w_x$, $\phi_y=(2\pi/b)w_y$. Expanding the cosine term we can identify the coefficient D_{xy}^{xy} defined in (4.16): $D_{xy}^{xy}=r''A^2(2\pi/b)^2\sim(T_c-T)$. The coupling term fixes $\psi_x=-\psi_y=\psi$ in the ordered phase. If gradient terms are included the free energy takes the form,

$$F=\tfrac{1}{2}rA^2+\tfrac{1}{2}c_xA^2\left[\frac{d\phi}{dx}\right]^2$$
$$+\tfrac{1}{2}c_yA^2\left[\frac{d\phi}{dy}\right]^2+\tfrac{1}{2}c_zA^2\left[\frac{d\phi}{dz}\right]^2,$$

with x and y axes chosen along (110) and (−110). Since $\phi=(2\pi/b)w$ the coefficients can be identified with the elastic constants determining the velocity below T_c. The velocity is proportional to $A\sim(T_c-T)^{1/2}$. Near T_c the Landau theory is not applicable. A renormalization-group theory (Ref. 18) suggests that the transition is in fact discontinuous.
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