Landau theory of charge-density waves in transition-metal dichalcogenides*

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A Landau theory is proposed for charge-density waves (CDW) in transition-metal dichalcogenides with the charge density as an order parameter. The theory predicts the sequence of phases, normal-state–incommensurate-CDW–commensurate-CDW with decreasing temperature, separated by first-order phase transitions. The peaks in charge density lie at "lattice sites" of a hexagonal crystal and for the incommensurate case the theory predicts phononlike distortions of the CDW "lattice" as well as dislocations. Impurities pin the charge density wave, broaden the phase transitions, and stabilize the incommensurate state relative to the commensurate state.

I. INTRODUCTION

Recently the anomalous properties of $TaSe_2$ and similar materials have been attributed to charge-density-wave (CDW) formation.[1–3] In the octahedrally coordinated structure, $1T$-$TaSe_2$ exhibits an incommensurate-charge-density wave (ICDW) above 473 °K and a commensurate-charge-density wave (CCDW) below 473 °K. In the trigonal prismatic coordinated structure, $2H$-$TaSe_2$ is a normal metal above 120 °K and forms a CDW state below 120 °K. These materials are essentially two-dimensional metals with the transition-metal ions on a planar hexagonal lattice. The band structure[4] has sixfold symmetry in the basal plane and the two-dimensional ICDW's form in the ΓM directions. The three possible ICDW's are found to coexist. Electron-diffraction, resistivity, and susceptibility measurements have been made on a number of compounds and binary alloys.

Wilson *et al.*[3] have shown that CDW's in these materials are Fermi-surface-driven instabilities and are therefore related to spin-density waves in chromium,[5,6] to the spiral structures in rare-earth metals,[7] and to long-period ordering in alloys.[8] Overhauser[9] has proposed a CDW ground state for alkali metals but this has not been confirmed. Overhauser[9] and Chan and Heine[10] discuss CDW formation from a microscopic point of view, but the microscopic theory is not well developed.

The purpose of this paper is to write down a phenomenological Landau theory[11] for charge-density waves in the layered compounds and to develop its consequences. We will work with a two-dimensional model of charge-density waves in one layer. The transition temperatures are characteristic of the layer type and are insensitive to the nature of the neighboring layers; this indicates that the dominant interactions are intralayer and that interlayer interactions play only a secondary role. Interlayer interactions do determine the relative phase of CDW's on neighboring layers and provide a three-dimensional stiffness to the structure; the CDW is not two dimensional in the Kosterlitz-Thouless[12] sense. We will choose the electron density as the order parameter and write down the free energy as a power-series expansion in the order parameter and gradients of the order parameter. We include an impurity potential to describe impurity effects. This is accomplished in Sec. II, and the rest of the paper is devoted to calculation of the properties of CDW's using the Landau theory. We first study the phase transitions and show that for the observed triple CDW, the transitions are first order and the phases occur in the order normal–incommensurate–commensurate with decreasing temperature. Impurity effects are then studied, and we find that the impurity potential drives the charge-density wave and smears out the phase transitions. Each impurity is dressed with a cloud of charge-density wave, even in the normal state, and the impurity-impurity interaction is calculated. The incommensurate wave is flexible and can distort in the impurity potential to lower its energy. This stabilizes the incommensurate wave relative to the commensurate wave and depresses that transition temperature. The fluctuation modes are then examined and two hydrodynamic modes (small energy at long wavelength) are found for the ICDW corresponding to the transverse and longitudinal "phonons" of the two-dimensional CDW "lattice." Finally, a "dislocation" in the ICDW "lattice" is discussed, which is the analog of the vortex in superfluid helium and superconductors.

II. LANDAU THEORY

The natural order parameter for charge-density waves is the electronic charge density of the d-band conduction electrons. This charge density is coupled linearly to the longitudinal lattice distortion and the amplitude of the periodic lattice distortion is simply proportional to the amplitude of the charge-density wave. The charge density is a real scalar quantity and one can construct a free-energy functional of the charge density to describe the

triple charge-density wave. With this approach, the gradient terms in the free energy are complicated, as is the fourth-order term. It turns out to be simpler to use three complex order parameters, one for each charge-density wave. We write for the electronic charge density

$$\rho(\vec{r}) = \rho_0(\vec{r})[1 + \alpha(\vec{r})] , \tag{1}$$

where $\alpha(\vec{r})$ is the real order parameter and $\rho_0(\vec{r})$ is the d-electron conduction-band charge density in the normal state. Then we write $\alpha(\vec{r})$ in terms of three complex order parameters $\psi_i(\vec{r})$.

$$\alpha(\vec{r}) = \mathrm{Re}[\psi_1(\vec{r}) + \psi_2(\vec{r}) + \psi_3(\vec{r})] . \tag{2}$$

The next step is to write down an expansion of the free energy in powers of α (or ψ_i) and gradients of α (or ψ_i). We will discuss the various terms individually. For the free energy of one layer, we write the expansion in powers of the order parameter as

$$F_1 = \int d^2r [a(\vec{r})\alpha^2 - b(\vec{r})\alpha^3 + c(\vec{r})\alpha^4 + d(\vec{r})(|\psi_1\psi_2|^2 + |\psi_2\psi_3|^2 + |\psi_3\psi_1|^2)] , \tag{3}$$

where $a(\vec{r})$, $b(\vec{r})$, $c(\vec{r})$, and $d(\vec{r})$ exhibit the periodicity of the crystal lattice. We will write, for example,

$$c(\vec{r}) = c_0 + c_1 \sum_i e^{i\vec{K}_i \cdot \vec{r}} , \tag{4}$$

where the six $\vec{K}_i$ are the six shortest reciprocal-lattice vectors characteristic of the planar hexagonal transition-metal lattice. The constant terms such as c_0 are sufficient to discuss ICDW's, but the umklapp terms such as c_1 are necessary to discuss CCDW's. The unusual form of the fourth-order term in Eq. (3) is chosen to permit description of both single and triple CDW's (see Sec. III).

We next include the random potential $U(r)$, due to impurities for the alloy case. $U(r)$ could also be an external potential.

$$F_2 = \int d^2r\, U(\vec{r})\rho_0(\vec{r})\alpha(\vec{r}) . \tag{5}$$

The gradient terms are chosen so that the free energy of the three charge-density waves is at a minimum when they lie in the right direction and have the right wavelength,

$$F_3 = \int d^2r \left[e(\vec{r}) \sum_i |(\vec{q}_i \cdot \vec{\nabla} - iq_i^2)\psi_i|^2 + f(\vec{r}) \sum_i |\vec{q}_i \times \vec{\nabla}\psi_i|^2 \right] , \tag{6}$$

where

$$|\vec{q}_1| = |\vec{q}_2| = |\vec{q}_3| = 2\pi/\lambda ,$$

and λ is the wavelength of the ICDW, and the three $\vec{q}_i$ vectors lie in ΓM directions 120° apart (Fig. 1). e_0 and f_0 are the elastic constants for the CDW. The total free energy is the sum of three terms

$$F = F_1 + F_2 + F_3 . \tag{7}$$

We make the usual Landau theory assumption that the parameters a_0, b_0, etc., are smooth functions of temperature and can be expanded in powers of $T - T_{NI}$ near the onset temperature. Since a_0 must change sign near T_{NI}, we assume that

$$a_0 = a'(T - T^*) , \tag{8}$$

and that the other parameters are temperature independent. In doing this, we have assumed that the transition is mean-field-like and that critical fluctuations are unimportant.

III. PHASE TRANSITIONS

The Landau theory is capable of describing a variety of situations depending on the magnitudes of the parameters. Here we investigate several phases of the clean metal with $U = 0$. We proceed by solving for the order parameters $\psi_i(\vec{r})$, which minimize the free energy. When there are several

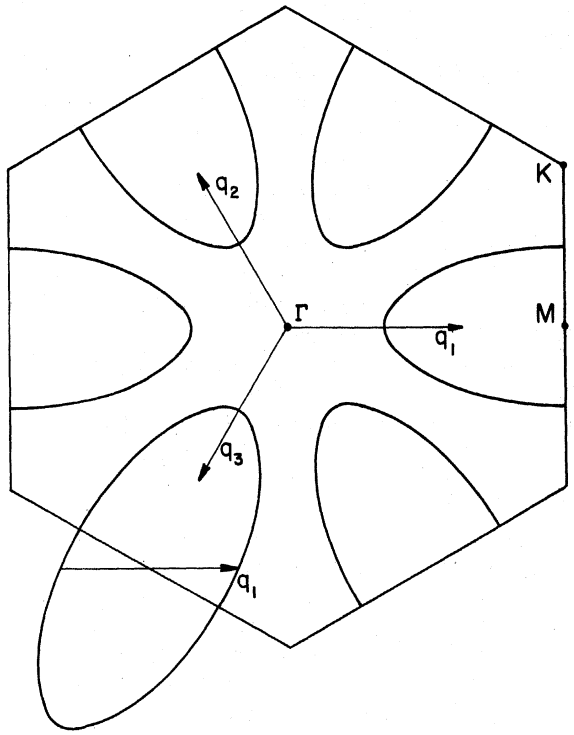

FIG. 1. Sketch of the Fermi surface of $1T$-TaS_2 (Ref. 4) in the basal plane of the first Brillouin zone. The q vectors of the three charge-density waves in the incommensurate state are shown; q_1 is shown as a spanning vector of the Fermi surface. The vector from Γ to M is one half the first reciprocal-lattice vector.

minima of the free energy, that is several possible states of the system, the state with the lowest free energy is thermodynamically stable. Throughout the paper, we will compute the free energy per unit area for one layer.

A. Single ICDW

For the single incommensurate CDW, we write

$$\psi_1(\vec{r}) = \phi_0 e^{i\vec{q}_1\cdot\vec{r}}, \quad \psi_2 = \psi_3 = 0 . \tag{9}$$

After integrating over a plane of unit area, we find for the free energy per unit area for one layer

$$F = \tfrac{1}{2}a_0\phi_0^2 + \tfrac{3}{8}c_0\phi_0^4 . \tag{10}$$

Minimizing F with respect to ϕ_0, we find

$$\phi_0 = \begin{cases} 0, & T > T^* \\ [2a'(T^* - T)/3c_0]^{1/2}, & T < T^* \end{cases} \tag{11}$$

so that the phase transition from the incommensurate to the normal phase is second order with transition temperature $T_{IN} = T^*$. The free energy in the incommensurate phase is

$$F_{1I} = -a_0^2/6c_0 . \tag{12}$$

B. Single CDW

If the wave number of the incommensurate wave is near one-third of a reciprocal-lattice vector, the commensurate phase may be stable. For the single commensurate CDW, we write

$$\psi_1(r) = \phi_0 e^{i\vec{K}_1\cdot\vec{r}/3}, \quad \psi_2 = \psi_3 = 0 , \tag{13}$$

and find

$$F = [\tfrac{1}{2}a_0 + e_0q_1^2(q_1 - \tfrac{1}{3}K_1)^2]\phi_0^2 - \tfrac{1}{4}b_1\phi_0^3 + \tfrac{3}{8}c_0\phi_0^4 . \tag{14}$$

Forcing the wave to be commensurate has cost elastic energy from the gradient terms in the free energy but has gained umklapp energy or "lock-in" energy from the cubic term. The free energy gained is approximately

$$F_{1C} - F_{1I} \approx e_0q_1^2(q_1 - \tfrac{1}{3}K_1)^2\phi_{0I}^2 - \tfrac{1}{4}b_1\phi_{0I}^3 , \tag{15}$$

where ϕ_{0I} is the amplitude of the CDW in the incommensurate phase

$$\phi_{0I} = [2a'(T_{IN} - T)/3c_0]^{1/2} . \tag{16}$$

If $F_{1C} - F_{1I}$ is positive, the incommensurate phase is stable, whereas if $F_{1C} - F_{1I}$ is negative, the commensurate phase is stable. At the phase transition from the incommensurate phase to the commensurate phase $F_{1C} - F_{1I} = 0$ and this condition determines the transition temperature

$$T_{CI} = T_{IN} - \frac{3c_0}{2a'}\left(\frac{4e_0q_1^2(q_1 - \tfrac{1}{3}K_1)^2}{b_1}\right)^2 . \tag{17}$$

The transition energy is given by

$$\Delta S_{CI} = \left.\frac{dF_{1C}}{dT} - \frac{dF_{1I}}{dT}\right|_{T=T_{CI}} = a'e_0q_1^2(q_1 - \tfrac{1}{3}K_1)^2/3c_0 , \tag{18}$$

and the phase transition is first order. The order parameter is larger in the commensurate phase by

$$\Delta\phi_0 = e_0q_1^2(q_1 - \tfrac{1}{3}K_1)^2/3c_0\phi_0 . \tag{19}$$

In the presence of a periodic lattice distortion and charge-density wave, there is an energy gap in the band structure at the Fermi energy over the nested portion of the Fermi surface. Since the energy gap is proportional to the order parameter, the energy gap is larger in the commensurate phase and the susceptibility smaller. The single CDW is a simple example of a commensurate-incommensurate phase transition driven by umklapp terms in the free energy. This case is not observed in practice, and we turn now to the triple CDW.

C. Triple ICDW

We give the three CDW's identical amplitudes

$$\psi_i(\vec{r}) = \phi_0 e^{i\vec{q}_i\cdot\vec{r}} , \tag{20}$$

and compute the free energy

$$F = \tfrac{3}{2}a_0\phi_0^2 - \tfrac{3}{2}b_0\phi_0^3 + \tfrac{3}{8}(15c_0 - 8d_0)\phi_0^4 . \tag{21}$$

Note the presence of a new cubic term (proportional to b_0) and a fourth-order cross term, which were absent for the single CDW case. In order to take advantage of the cubic term in reducing the free energy, we choose the relative phases of the three waves so that the cubic term is attractive. Thus the cubic term acts as a "phasing energy." With b_0 positive, as assumed here, the three CDW's add, as shown in Fig. 2, to give peaks in electron density at lattice sites of a two-dimensional hexagonal lattice with CDW "lattice spacing" equal to K_1/q_1 times the crystal-lattice spacing. We will show below that the triple ICDW exhibits other properties of a two-dimensional "lattice," namely CDW "phonons" and CDW "dislocations." With b_0 negative, the signs of ψ_i are reversed and the CDW "lattice" is a hole lattice rather than an electron lattice; henceforth, we assume $b_0 > 0$.

There are two types of fourth-order terms in the theory, a direct term $\frac{1}{8}(3c_0)(|\psi_1|^4 + |\psi_2|^4 + |\psi_3|^4)$ and a cross term $\frac{1}{8}(12c_0 - 8d_0)(|\psi_1\psi_2|^2 + |\psi_2\psi_3|^2 + |\psi_2\psi_3|^2)$. With $d_0 = \frac{3}{2}c_0$, the cross term vanishes and there is no (fourth-order) interaction energy among the three CDW's; the free energy is 3 times that of the single CDW case. For $d_0 < \frac{3}{2}c_0$, the cross term is repulsive and the free energy of the triple CDW state is increased relative to the single CDW state.

To compute the free energy of the triple CDW state, we minimize F with respect to ϕ_0 and find

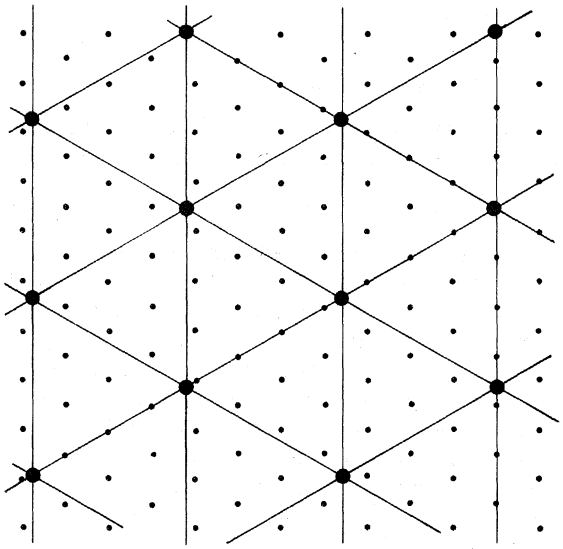

FIG. 2. Dots represent transition-metal atoms on the hexagonal crystal lattice, and the lines represent maxima in the charge density of each of the three CDW's. At the intersection of the lines, the charge densities of each of the three CDW's add up, and there is a peak in electron density represented by the filled circles. These peaks in electron density occur at lattice sites of the CDW "lattice."

$$\phi_0 = \frac{3b_0}{2(15c_0 - 8d_0)} + \left[\left(\frac{3b_0}{2(15c_0 - 8d_0)}\right)^2 - \frac{2a_0}{15c_0 - 8d_0}\right]^{1/2}, \tag{22}$$

and a phase transition which is first order with transition temperature

$$T_{IN} = T^* + b_0^2/a'(15c_0 - 8d_0), \tag{23}$$

and transition entropy

$$\Delta S = 3a'b_0/(15c_0 - 8d_0). \tag{24}$$

With b_0 small, the phase transition is only weakly first order. We now want to compare the free energy of the triple ICDW with the single ICDW to find out which is stable. We temporarily neglect b_0 and find

$$F_{3I} = -3a_0^2/2(15c_0 - 8d_0), \tag{25}$$

which is below F_{1I} provided $d_0 > \frac{3}{4}3c_0$. The amplitudes of the three CDW's are independent if $d_0 = \frac{3}{2}3c_0$; this would be the case if the part of the Fermi surface utilized by one CDW was not affected by the energy gaps of the other two CDW's. One expects a repulsive interaction of CDW's so that $d_0 < \frac{3}{2}3c_0$; since one observes the triple CDW, not the single CDW, we must have $\frac{3}{4}3c_0 < d_0 < \frac{3}{2}3c_0$.

D. Triple CDW in trigonal primatic layers

In $2H$-$TaSe_2$ and related materials, $\vec{q}_1$ is very close to $\frac{1}{3}\vec{K}_1$, and the CDW locks in with $\vec{q} = \frac{1}{3}\vec{K}_1$. To treat this commensurate case, we choose

$$\psi_i(r) = \phi_0 e^{i\vec{K}_i \cdot \vec{r}/3}. \tag{26}$$

The free energy per unit area for one layer is

$$F = (\tfrac{3}{2}a_0 + 3e_0q_1^2(q_1 - \tfrac{1}{3}K_1)^2)\phi_0^2 - (\tfrac{3}{2}b_0 + \tfrac{3}{4}b_1)\phi_0^3 + \tfrac{3}{8}(15c_0 - 8d_0)\phi_0^4. \tag{27}$$

To first order in e_0 and b_1 the free energy difference between the commensurate and incommensurate phases is

$$F_{3C} - F_{3I} \approx 3e_0q_1^2(q_1 - \tfrac{1}{3}K_1)^2\phi_{0I}^2 - \tfrac{3}{4}b_1\phi_{0I}^3, \tag{28}$$

with ϕ_{0I} given by Eq. (22). Forcing the wave to be commensurate has lost elastic energy from the gradient terms in the free energy but has gained umklapp energy from the cubic term. Proceeding as in Sec. III B, we find (neglecting b_0 for simplicity)

$$T_{CI} = T_{IN} - \frac{15c_0 - 8d_0}{2a'}\left(\frac{4e_0q_1^2(q_1 - \tfrac{1}{3}K_1)^2}{b_1}\right)^2, \tag{29}$$

$$\Delta S_{CI} = \frac{3a'e_0q_1^2(q_1 - \tfrac{1}{3}K_1)^2}{15c_0 - 8d_0}, \tag{30}$$

$$\Delta\phi_0 = \frac{e_0q_1^2(q_1 - \tfrac{1}{3}K_1)^2}{(15c_0 - 8d_0)\phi_0}. \tag{31}$$

E. Triple CCDW in octahedral layers

In $1T$-$TaSe_2$, $\vec{q}_1$ is not close enough to $\frac{1}{3}\vec{K}_1$, and it costs too much elastic energy to lock in with $\vec{q} = \frac{1}{3}\vec{K}_1$. Instead, the CDW rotates 13°54' away from the ΓM direction so that $3\vec{p}_1 - \vec{p}_2 = \vec{K}_1$, and $\vec{p}_1$, $\vec{p}_2$ and $\vec{p}_3$ are 120° apart and $|p_1| = |p_2| = |p_3| \approx |q_1|$. The wavelength of the charge-density wave is almost unchanged, and it costs little longitudinal elastic energy (proportional to e_0); however, the large angle of rotation costs transverse elastic energy (proportional to f_0), and for this rotation to occur, f_0 must be small. The umklapp energy now comes from the fourth-order term. We write

$$\psi_i(\vec{r}) = \phi_0 e^{i\vec{p}_i \cdot \vec{r}}, \tag{32}$$

and find

$$F = [\tfrac{3}{2}a_0 + 3e_0(\vec{q}_1 \cdot \vec{p}_1 - q_1^2)^2 + 3f_0(\vec{q}_1 \times \vec{p}_1)^2]\phi_0^2 - \tfrac{3}{2}b_0\phi_0^3 + \tfrac{3}{8}(15c_0 + 4c_1 - 8d_0)\phi_0^4. \tag{33}$$

Forcing the wave to be commensurate has cost elastic energy to change the wavelength ($\propto e_0$) and elastic energy to rotate the direction of the wave ($\propto f_0$), but has gained fourth-order umklapp energy ($\propto c_1$). We assume $c_1 < 0$ and neglect b_0 for simplicity. The free energy in the commensurate phase is

$$F_{3C} = -\frac{3}{2}\frac{[a_0 + 2e_0(\vec{q}_1 \cdot \vec{p}_1 - q_1^2)^2 + 2f_0(\vec{q}_1 \times \vec{p}_1)^2]^2}{15c_0 - 8d_0 + 4c_1}. \tag{34}$$

The transition temperature is

$$T_{CI} = T_{IN} - \frac{15c_0 - 8d_0}{a'|c_1|}[e_0(\vec{q}_1 \cdot \vec{p}_1 - q_1^2)^2 + f_0(\vec{q}_1 \times \vec{p}_1)^2] \tag{35}$$

and we find

$$\Delta S_{CI} = \frac{4a'[e_0(\vec{q}_1 \cdot \vec{p}_1 - q_1^2)^2 + f_0(\vec{q}_1 \times \vec{p}_1)^2]}{15c_0 - 8d_0}, \tag{36}$$

$$\Delta\phi = \frac{2[e_0(\vec{q}_1 \cdot \vec{p}_1 - q_1^2)^2 + f_0(\vec{q}_1 \times \vec{p}_1)^2]}{(15c_0 - 8d_0)\phi_0}. \tag{37}$$

This theory should describe the phase transition at 473 °K in $1T$-$TaSe_2$. The incommensurate-normal metal transition is not observed in these materials because the crystal structure converts to trigonal prismatic at ≈600 °K. $1T$-TaS_2 undergoes a phase transition at 350 °K from an ICDW state to a complex phase which has not been characterized yet. The experimental situation on the $2H$ phases, to which the theory of Sec. III D should apply, is not yet clear.

The theory predicts that the onset transition from normal metal to ICDW state is at least weakly first order and that the ICDW-CCDW transition is first order with an increased energy gap. The normal order of the phases with decreasing temperature is normal-ICDW-CCDW.

IV. ALLOYS

In this section, we calculate the effects of the impurity potential $U(r)$ on the charge-density wave. The other parameters of the Landau theory will change in a continuous way with impurity concentration, and we are not interested in this effect. The random impurity potential couples directly to the charge-density wave and qualitatively changes the nature of the phase transitions and the fluctuation modes; it is these effects that we wish to describe.

To treat the impurity potential correctly, we should take an ensemble of systems, each with a particular distribution of impurities and a particular impurity potential $U_i(\vec{r})$. We should compute the physical quantity of interest for each system and then take an ensemble average. It is often impossible to carry out a calculation in this order, and one must ensemble average at an intermediate step in the calculation. This introduces an approximation which one should then discuss.

We will discuss impurity effects (i) in the normal phase, (ii) on the incommensurate-normal phase transition, and (iii) on the commensurate-incommensurate phase transition. We will carry out the calculations for the single CDW case; the physics of the impurity effects is clear from this calculation, and the algebra is simpler than that for the triple CDW. We will indicate, where possible, the extensions to the triple CDW case. We will also discuss the charge density near one impurity, as well as impurity-impurity interactions.

A. Normal phase

We consider only one CDW and write the order parameter as the product of a plane wave times a smoothly varying part $\phi(\vec{r})$.

$$\psi_1(\vec{r}) = \phi(\vec{r})\, e^{i\vec{q}_1\cdot\vec{r}}, \quad \psi_2 = \psi_3 = 0 \tag{38}$$

$$\phi(\vec{r}) = \sum_{\vec{q}} \phi_{\vec{q}}\, e^{i\vec{q}\cdot\vec{r}}. \tag{39}$$

In the normal phase, there are only thermal fluctuations and impurity driven fluctuations of $\phi(r)$, and $\phi(r)$ is small. We also Fourier transform the impurity potential in the same way,

$$U(\vec{r})\rho_0(\vec{r}) = \sum_{\vec{q}} U_{\vec{q}}\, e^{i(\vec{q}+\vec{q}_1)\cdot\vec{r}} + \text{c. c.} \tag{40}$$

Since each of the ϕ_q is small, we can expand the free energy to second order in ϕ_q.

$$F = \sum_{\vec{q}} [\tfrac{1}{2}a_0 + e_0(\vec{q}_1 \cdot \vec{q})^2 + f_0(\vec{q}_1 \times \vec{q})^2]\phi_{\vec{q}}^*\phi_{\vec{q}} + \frac{1}{2}\sum_{\vec{q}} (U_{\vec{q}}^*\phi_{\vec{q}} + U_{\vec{q}}\phi_{\vec{q}}^*). \tag{41}$$

Minimizing F with respect to ϕ_q^*, we find

$$\phi_{\vec{q}} = -U_q/2\epsilon_{\vec{q}}^0, \tag{42}$$

$$\epsilon_{\vec{q}}^0 = \tfrac{1}{2}a_0 + e_0(\vec{q}_1 \cdot \vec{q})^2 + f_0(\vec{q}_1 \times \vec{q})^2. \tag{43}$$

Since the impurity potential has random phase, the ensemble average of U_q vanishes,

$$\langle U_{\vec{q}} \rangle = 0, \quad \langle \phi_{\vec{q}} \rangle = 0. \tag{44}$$

However, the structure factor average S_q is nonvanishing.

$$S_{\vec{q}} \alpha \langle \phi_{\vec{q}}^* \phi_{\vec{q}} \rangle = \frac{\langle U_{\vec{q}}^* U_{\vec{q}} \rangle}{4(\epsilon_{\vec{q}}^0)^2} = \frac{Nu_0^2}{4(\epsilon_{\vec{q}}^0)^2}, \tag{45}$$

where u_0 is the space integral of the potential of one impurity, and N is the impurity density. We see that the impurity potential drives the charge-density wave. The effect on the structure factor can be stronger than thermal fluctuations and can produce a visible pretransition effect in electron diffraction well above the phase transition; this effect has been observed in $2H$-$TaSe_2$.[3]

For one impurity at the origin $U_q = u_0$, and we have

$$\phi(\vec{r}) = -\tfrac{1}{2}u_0 \sum_{\vec{q}} \frac{e^{i(\vec{q}+\vec{q}_1)\cdot\vec{r}}}{\epsilon_{\vec{q}}^0}. \tag{46}$$

We find for the charge density (using $e_0 = f_0$ to simplify the integral),

$$\rho(r) = \rho_0(r)\left(1 - \frac{u_0 \cos(\vec{q}_1 \cdot \vec{r}) f(r/\xi)}{4\pi e_0 q_1^2}\right), \tag{47}$$

where $\xi = (2e_0q_1^2/|a_0|)^{1/2}$ is the correlation length, and

$$f(r/\xi) \equiv \int_1^\infty dy\, e^{-yr/\xi}(y^2-1)^{-1/2} . \tag{48}$$

This function is asymptotically

$$f(r/\xi) \sim \begin{cases} \ln(1.12\xi/r), & r/\xi \ll 1 \\ (\pi\xi/2r)^{1/2} e^{-r/\xi}, & r/\xi \gg 1 . \end{cases} \tag{49}$$

Thus, in the normal state, there is a charge-density wave localized on the impurity whose amplitude falls off as $\ln(\xi/r)$ for $r<\xi$ and exponentially for $r>\xi$. Expression (47) is only valid for $rq_1>1$. For the triple CDW, one merely replaces $\cos(\vec{q}_1\cdot\vec{r})$ by $\sum_i \cos(\vec{q}_i\cdot\vec{r})$.

A second impurity a distance $\vec{R}$ from the first is attracted to the charge density of the first, and the impurity-impurity interaction energy is

$$U_{I\text{-}I} = -\frac{u_0^2}{4\pi e_0 q_1^2} f\left(\frac{R}{\xi}\right)\sum_i \cos(\vec{q}_i\cdot\vec{R}) . \tag{50}$$

Thus, even in the normal state, impurities feel a strong potential attracting them to the "lattice sites" of the triple CDW. The impurity interaction is nothing new; it has been invoked to explain ordering in alloys where one does not observe a CDW but where Fermi-surface effects are believed to be important.

B. Commensurate-incommensurate phase transition

We consider now the ordered phases where the higher-order terms in the free energy are important. We write

$$\psi_1(\vec{r}) = \phi(\vec{r})\, e^{i\vec{p}_1\cdot\vec{r}} , \tag{51}$$

$$\phi(\vec{r}) = \phi_0 + \sum_{\vec{q}} \phi_{\vec{q}}\, e^{i\vec{q}\cdot\vec{r}} , \tag{52}$$

where $\vec{p}_1 = \frac{1}{3}\vec{K}_1$ for the commensurate phase ($\vec{K}_1$ is a reciprocal-lattice vector), and $\vec{p}_1 = \vec{q}_1$ for the incommensurate phase; ϕ_0 is real. ϕ_0 is the uniform charge-density wave amplitude and the ϕ_q are the amplitudes of the thermal or impurity driven fluctuations.

Then, the free energy is

$$F = \epsilon_0^0\phi_0^2 + \tfrac{1}{8}3c_0\phi_0^4 + \frac{1}{2}\sum_q (U_q^*\phi_q + U_q\phi_q^*) + \sum_q \epsilon_q^0\phi_q^*\phi_q + \tfrac{1}{8}3c_0\phi_0^2\sum_q (\phi_q\phi_{-q} + \phi_q^*\phi_{-q}^* + 4\phi_q^*\phi_q)$$
$$+ \tfrac{1}{8}3c_0\left[\sum_p \phi_p^*\phi_{-p}^*\sum_q \phi_q\phi_{-q} + 2\left(\sum_q \phi_q^*\phi_q\right)^2\right] - \tfrac{1}{4}b_1\left(\phi_0^3 + \tfrac{1}{2}3\phi_0\sum_q (\phi_q\phi_{-q} + \phi_q^*\phi_{-q}^*)\right)\delta_{\vec{p}_1,\vec{q}_1} , \tag{53}$$

where

$$\epsilon_q^0 = \tfrac{1}{2}a_0 + e_0[\vec{q}_1\cdot\vec{q} - \vec{q}_1\cdot(\vec{q}_1-\vec{p}_1)]^2 + f_0(\vec{q}_1\times\vec{q})^2 . \tag{54}$$

The last term in (53) is the umklapp term, which is present only for the commensurate phase. Minimizing F with respect to ϕ_0, we find

$$0 = 2\epsilon_0^0\phi_0 + \tfrac{1}{2}3c_0\phi_0^3 + \tfrac{1}{2}3c_0\phi_0(2\lambda_1+\lambda_2) - \tfrac{1}{4}3b_1(\phi_0^2-\lambda_2)\delta_{\vec{p}_1,\vec{q}_1} , \tag{55}$$

where

$$\lambda_1 = \sum_q \phi_q^*\phi_q , \tag{56}$$

$$\lambda_2 = \sum_q \phi_q\phi_{-q} . \tag{57}$$

Minimizing F with respect to ϕ_q^*, we find

$$0 = \tfrac{1}{2}U_q + (\epsilon_q^0 + \tfrac{1}{2}3c_0(\phi_0^2+\lambda_1))\phi_q + (\tfrac{1}{4}3c_0(\phi_0^2+\lambda_2) - \tfrac{1}{4}3b_1\phi_0\delta_{\vec{p}_1,\vec{q}_1})\phi_{-q}^* . \tag{58}$$

We find that ϕ_q and ϕ_{-q}^* are coupled in the ordered phases. Then, changing variables

$$\alpha_{q+-} = (1/\sqrt{2})(\phi_q \pm \phi_{-q}^*) , \tag{59}$$

we find

$$\alpha_{q+-} = -(U_q \pm U_{-q}^*)/2\sqrt{2}\,\epsilon_{q+-} , \tag{60}$$

where

$$\epsilon_{q+-} = \epsilon_q^0 + \tfrac{1}{2}3c_0(\phi_0^2+\lambda_1) \pm (\tfrac{1}{4}3c_0(\phi_0^2+\lambda_2) - \tfrac{1}{4}3b_1\phi_0\delta_{\vec{p}_1,\vec{q}_1}) , \tag{61}$$

which is the energy of magnitude (+) and phase (−) fluctuations. We must now determine the three constants ϕ_0, λ_1, and λ_2 self-consistently. At this point in the calculation, we must ensemble average expressions (56) and (57) for λ_1 and λ_2. This yields

$$\lambda_1 = \sum_q \langle\phi_q^*\phi_q\rangle = \frac{NU_0^2}{8}\sum_q \left(\frac{1}{\epsilon_{q+}^2} + \frac{1}{\epsilon_{q-}^2}\right) , \tag{62}$$

$$\lambda_2 = \sum_q \langle\phi_q\phi_{-q}\rangle = \sum_q \langle\phi_q^*\phi_{-q}^*\rangle = \frac{NU_0^2}{8}\sum_q \left(\frac{1}{\epsilon_{q+}^2} - \frac{1}{\epsilon_{q-}^2}\right) . \tag{63}$$

Writing

$$\epsilon_{q+-} = \beta_{+-} + e_0[\vec{q}_1\cdot\vec{q} - \vec{q}_1\cdot(\vec{q}_1-\vec{p}_1)]^2 + f_0(\vec{q}_1\times\vec{q})^2 , \tag{64}$$

$$\beta_{+-} = \tfrac{1}{2}a_0 + \tfrac{1}{2}3c_0(\phi_0^2+\lambda_1) \pm (\tfrac{1}{4}3c_0(\phi_0^2+\lambda_2) - \tfrac{1}{4}3b_1\phi_0\delta_{\vec{p}_1,\vec{q}_1}) , \tag{65}$$

we perform the integrals in (62) and (63) and find

$$\lambda_{1,2} = \tfrac{1}{2}C(1/\beta_+ \pm 1/\beta_-)\,, \tag{66}$$

$$C = NU_0^2/(4\pi)^2(e_0 f_0)^{1/2} q_1^2\,. \tag{67}$$

Substituting (66) into (55) and (65), we find three equations for β_+, β_-, and ϕ_0 which must be solved self-consistently:

$$\beta_+ = \tfrac{1}{2}a_0 + \tfrac{1}{4}9c_0\phi_0^2 + \tfrac{1}{4}3c_0C(3/\beta_+ + 1/\beta_-) - \tfrac{1}{4}3b_1\phi_0\delta_{\vec{p}_1,\vec{q}_1}\,, \tag{68}$$

$$\beta_- = \tfrac{1}{2}a_0 + \tfrac{1}{4}3c_0\phi_0^2 + \tfrac{1}{4}3c_0C(1/\beta_+ + 3/\beta_-) + \tfrac{1}{4}3b_1\phi_0\delta_{\vec{p}_1,\vec{q}_1}\,, \tag{69}$$

$$\phi_0^2 = (2/3c_0)\{-2\epsilon_0^0 - \tfrac{1}{4}3c_0C(3/\beta_+ + 1/\beta_-) + [\tfrac{1}{4}3b_1\phi_0 + (3b_1C/8\phi_0)(1/\beta_+ - 1/\beta_-)]\delta_{\vec{p}_1,\vec{q}_1}\}\,. \tag{70}$$

The solution of these three equations will occupy the rest of this section. There are two types of solutions: (i) $\phi_0 = 0$, $\lambda_1 = \lambda_2$, normal state; and (ii) $\phi_0 \neq 0$, ordered state. The phase transition from the normal to the incommensurate phase will be taken up in Sec. IV C. Here we study the commensurate-incommensurate phase transition and assume that it occurs well below the transition to the normal state.

We first examine the solutions for the pure metal ($C = 0$). For the incommensurate phase, we find

$$\phi_0^2 = 2|a_0|/3c_0\,; \quad \beta_+ = |a_0|\,; \quad \beta_- = 0\,. \tag{71}$$

From (64), the energy spectrum for amplitude fluctuations ϵ_{q+} exhibits a gap ($= |a_0|$), whereas the energy spectrum for phase fluctuations ϵ_{q-} vanishes as $q \to 0$. For the commensurate phase, the amplitude fluctuations are essentially unchanged, but the phase fluctuation spectrum has a gap of

$$\beta_- = \tfrac{1}{8}9b_1(2|a_0|/3c_0)^{1/2} - e_0q_1^2(q_1 - \tfrac{1}{3}K_1)^2 > 0\,. \tag{72}$$

In the commensurate phase, the CDW is pinned to the crystal lattice, and this introduces a gap in the phase fluctuation spectrum as well.

We turn now to the dirty material where C is finite. If we try to use straightforward perturbation theory for small C we get into trouble. In zeroth order $\beta_- = 0$ for the incommensurate phase and the integral of $1/\epsilon_{q-}^2$ diverges. We can, however, use a self-consistent perturbation scheme, being careful to treat the long-wavelength phase fluctuations correctly. We first eliminate the ϕ_0^2 term from (68) and (69) using (70). Then using

$$\beta_+ \approx |a_0|\,, \tag{73}$$

we find

$$\beta_- = \tfrac{1}{2}g + (\tfrac{1}{4}g^2 + \tfrac{1}{4}3c_0C)^{1/2}\,, \tag{74}$$

$$g = -3c_0C/4|a_0| + [-e_0q_1^2(q_1 - p_1)^2 + \tfrac{1}{8}9b_1(2|a_0|/3c_0)^{1/2}]\delta_{q_1,p_1} \tag{75}$$

The free-energy difference between the commensurate and incommensurate phases is

$$F_C - F_I = \Delta S^p(T - T_{CI}^p) + \tfrac{33}{32}C^2c_0\left(\frac{1}{\beta_{-C}^2} - \frac{1}{\beta_{-I}^2}\right) + \tfrac{1}{2}C\ln\frac{\beta_{-C}}{\beta_{-I}}\,, \tag{76}$$

where ΔS^p is the transition entropy for the pure metal, and T_{CI}^p is the transition temperature. For small C, we have

$$\beta_{-I} \approx (\tfrac{1}{4}3c_0C)^{1/2}\,, \tag{77}$$

$$\beta_{-C} \approx g_0 = \tfrac{1}{8}9b_1(2|a_0|/3c_0)^{1/2} - e_0^2q_1^2(q_1 - \tfrac{1}{3}K_1)^2\,, \tag{78}$$

and

$$F_C - F_I \approx \tfrac{1}{4}C\left(\ln\frac{4g_0^2}{3c_0C} - \frac{11}{2}\right) + \Delta S^p(T - T_{CI}^p)\,, \tag{79}$$

and the transition temperature of the dirty metal is

$$T_{CI}^d \approx T_{CI}^p - \frac{C}{4\Delta S^p}\left(\ln\frac{4g_0^2}{3c_0C} - \frac{11}{2}\right)\,. \tag{80}$$

The principal effect of the impurities is to pin the long-wavelength phase fluctuations in the incommensurate phase and introduce a gap $(\tfrac{1}{4}3c_0C)^{1/2}$ in the excitation spectrum. The phase fluctuations of the commensurate phase are already pinned to the lattice and are essentially unmodified. Another way of saying this is that the incommensurate CDW is flexible and can adjust itself to take advantage of the impurity potential, whereas the commensurate CDW is inflexible. The expansion parameter used above is $(3c_0C/4g_0^2)^{1/2}$, which is the ratio of the gaps. When this parameter is large, we have

$$F_C - F_I \approx \tfrac{1}{8}9C(4g_0^2/3c_0C)^{1/2} + \Delta S^p(T - T_{CI}^p)\,, \tag{81}$$

$$T_{CI}^d \approx T^p - (9C/8\Delta S^p)(4g_0^2/3c_0C)^{1/2}\,. \tag{82}$$

The free energy is singular at $C = 0$, and this is why straightforward perturbation theory fails. Within the approximations used, the phase transition is first order and sharp. We have, however, performed the ensemble average at an intermediate step in the calculation, and this is physically equivalent to taking into account the average effects of impurities on the excitation spectrum but omitting fluctuations in impurity density. Since the transition temperature is a strong function of impurity concentration, fluctuations in concentration will broaden the phase transition. The correlation length for phase fluctuations is finite in the dirty case and is

$$\xi_{ph} \approx [2e_0q_1^2/(3c_0C)^{1/2}]^{1/2}\,. \tag{83}$$

The sharp reduction in T_{CI} is observed in the isoelectronic alloy $Ta_{1-x}Nb_xSe_2$.[3]

C. Incommensurate-normal-state transition

In the normal state near the phase transition, we must use the full nonlinear Eqs. (68)–(70) but with $\phi_0 = 0$; this implies $\beta_+ = \beta_-$, and we find

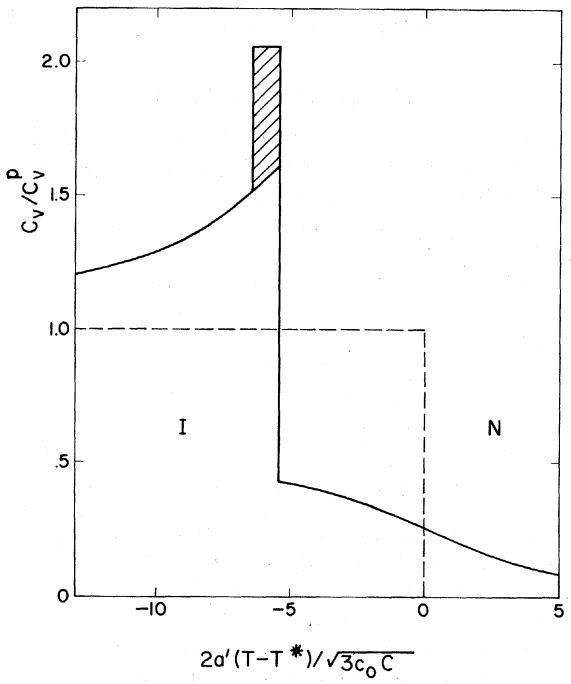

FIG. 3. Detail of the heat capacity near the incommersurate–normal-metal transition according to the approximate theory for the clean (dashed-line) and dirty (solid-line) case. The cross hatched area is the transition entropy for the alloy case which is weakly first order. The approximation used for the alloy neglects fluctuations of impurity concentration and yields a spurious first-order transition; this phase transition should be smeared out.

$$\beta_+ = \tfrac{1}{4}a_0 + [(\tfrac{1}{4}a_0)^2 + 3c_0C]^{1/2} . \tag{84}$$

At the pure-metal transition temperature ($a_0 = 0$), there is an energy gap in the fluctuation spectrum of $(3c_0C)^{1/2}$, and the correlation length is finite.

$$\xi \approx [e_0 q_1^2/(3c_0C)^{1/2}]^{1/2} ; \quad T = T^* . \tag{85}$$

In the incommensurate state near the phase transition, we must solve Eqs. (68)–(70) numerically. We first define dimensionless variables

$$\bar{\beta}_\pm = 2\beta_\pm/(3c_0C)^{1/2} , \tag{86}$$

$$\bar{\phi}_0 = \phi_0/(2|a_0|/3c_0)^{1/2} , \tag{87}$$

and the dimensionless coupling constant

$$\bar{g} = (3c_0C/4a_0^2)^{1/2} . \tag{88}$$

Equations (68)–(70) now read

$$\bar{\beta}_+ = 1/\bar{g} - (3/\bar{\beta}_+ + 1/\bar{\beta}_-) , \tag{89}$$

$$\bar{\beta}_- = 1/\bar{\beta}_+ - 1/\bar{\beta}_- , \tag{90}$$

$$\bar{\phi}_0^2 = 1 - \bar{g}(3/\bar{\beta}_+ + 1/\bar{\beta}_-) , \tag{91}$$

and the free energy is

$$c_0F/a_0^2 = -\tfrac{1}{3}\bar{\phi}_0^2 + \tfrac{1}{6}\bar{\phi}_0^4 + \tfrac{2}{3}\bar{g}^2(\ln\bar{\beta}_+ + \ln\bar{\beta}_-) - \tfrac{1}{3}\bar{g}(1/\bar{\beta}_+ + 1/\bar{\beta}_-)$$
$$+ \tfrac{1}{3}\bar{g}\bar{\phi}_0^2(3/\bar{\beta}_+ + 1/\bar{\beta}_-) + \tfrac{1}{6}\bar{g}^2[(1/\bar{\beta}_+ - 1/\bar{\beta}_-)^2$$
$$+ 2(1/\bar{\beta}_+ + 1/\bar{\beta}_-)^2] . \tag{92}$$

By minimizing F with respect to $\bar{\beta}_+$, $\bar{\beta}_-$, and $\bar{\phi}_0$, one can rederive (89)–(91). To solve the equations, we choose a value for $\bar{\beta}_-$ and solve (90) for $\bar{\beta}_+$, then we solve (89) for $\bar{g}$ and find $\bar{\phi}_0$ from (91); the free energy is then found from (92). We must compare free energies of the normal and incommensurate states to decide which state is stable at a particular temperature. From the free energy, one can compute the heat capacity, and this is shown in Fig. 3. There is a pretransition heat capacity in the normal phase due to the buildup of CDW driven by the impurity potential. The transition temperature is suppressed somewhat, and the transition to a finite ϕ_0 is weakly first order, with ϕ_0 at the phase transition being 0.8 of the pure-metal value. In the ordered phase, the fourth-order interaction suppresses the ϕ_q driven by the impurity potential. The fact that one finds a sharp first-order phase transition is undoubtedly an artifact arising from the way that the impurity averaging is done. Fluctuations in impurity concentration will smear the "phase transition" and remove the sharp details. Thus, one must be cautious in accepting at face value the results of this type of effective-potential method. The mechanism for the depression of the commensurate-incommensurate transition appears to be physically correct. Spatial fluctuations in impurity density will cause spatial fluctuations in the energy gap for phase fluctuations but will not qualitatively affect the free-energy difference.

V. FLUCTUATION MODES

In this section, we study the order-parameter fluctuation modes for the triple ICDW in pure material. In Sec. IV, we found the energies of these modes for single ICDW's and CCDW's. For the commensurate state, we found an amplitude fluctuation mode with an energy gap $|a_0|$ at long wavelength and a phase fluctuation mode with an energy gap given by (72). For the incommensurate state, we found an amplitude fluctuation mode with an energy gap $|a_0|$ and a phase fluctuation mode with no energy gap (a hydrodynamic mode). The energy of the phase fluctuation mode is

$$\epsilon_q^- = e_0(\vec{q}_1 \cdot \vec{q})^2 + f_0(\vec{q}_1 \times \vec{q})^2 \tag{93}$$

for the incommensurate wave. This last mode is Overhauser's phason.[13]

For the triple ICDW case, we omit the impurity potential, while the umklapp terms drop out. We write

$$\psi_i(\vec{r}) = \phi_i(\vec{r})\, e^{i\vec{q}_i\cdot\vec{r}}\,, \tag{94}$$

$$\phi_i(\vec{r}) = \phi_0 + \sum_q \phi_{iq}\, e^{i\vec{q}\cdot\vec{r}}\,, \tag{95}$$

where the $\phi_i(\vec{r})$ is slowly varying. The free energy is then

$$F = \int d^2r \left(\tfrac{1}{2}a_0 \sum_i |\phi_i|^2 - \tfrac{1}{4}3b_0(\phi_1\phi_2\phi_3 + \phi_1^*\phi_2^*\phi_3^*) + \tfrac{1}{8}3c_0 \sum_i |\phi_i|^4 + (\tfrac{1}{2}3c_0 - d_0)(|\phi_1\phi_2|^2 + |\phi_2\phi_3|^2 + |\phi_3\phi_1|^2) + e_0 \sum_i |\vec{q}_i\cdot\vec{\nabla}\phi_i|^2 + f_0 \sum_i |\vec{q}_i\times\vec{\nabla}\phi_i|^2 \right). \tag{96}$$

The minimum in the free energy is for $\phi_{iq} = 0$ and ϕ_0 given by (22). Near that minimum, we can expand F in powers of ϕ_{iq} and keep only second-order terms. We find

$$F = F(\phi_0) + \sum_{iq} [\tfrac{1}{2}a_0 + \tfrac{1}{2}3c_0\phi_0^2 + (3c_0 - 2d_0)\phi_0^2 + e_0(\vec{q}_i\cdot\vec{q})^2 + f_0(\vec{q}_i\times\vec{q})^2]\phi_{iq}^*\phi_{iq} + \tfrac{1}{8}3c_0\phi_0^2 \sum_{iq} (\phi_{iq}\phi_{i-q} + \phi_{iq}^*\phi_{i-q}^*) - \tfrac{1}{4}3b_0\phi_0(\phi_{1q}\phi_{2-q} + \phi_{1q}^*\phi_{2-q}^* + \text{permutations})\,. \tag{97}$$

In order to find the eigenmodes, we first transform to amplitude (+) and phase (−) variables

$$\alpha_{iq}^{+-} = (1/\sqrt{2})(\phi_{iq} \pm \phi_{i-q}^*)\,, \tag{98}$$

and find

$$F = F(\phi_0) + F^+ + F^-\,, \tag{99}$$

$$F^- = \sum_{iq} [\tfrac{1}{4}3b_0\phi_0 + e_0(\vec{q}_1\cdot\vec{q})^2 + f_0(\vec{q}_1\times\vec{q})^2]\alpha_{iq}^{-*}\alpha_{iq}^- + \tfrac{1}{4}3b_0\phi_0 \sum_q (\alpha_{1q}^{-*}\alpha_{2q}^- + \alpha_{2q}^{-*}\alpha_{1q}^- + \text{permutations})\,, \tag{100}$$

with a similar expression for F^+. The amplitude fluctuations have a large energy gap $3|a_0|c_0/(15c_0 - 8d_0)$ at long wavelength and are uninteresting. We now diagonalize the 3×3 matrix of Eq. (100) and find one phase fluctuation mode with an energy gap $\frac{1}{4}9b_0\phi_0$ involving relative motion of the three CDW's and two hydrodynamic modes (i.e., zero gap), with energies

$$\bar{\epsilon}_q^1 = (\tfrac{1}{4}e_0q_1^2 + \tfrac{3}{4}f_0q_1^2)q^2\,, \tag{101}$$

$$\bar{\epsilon}_q^2 = (\tfrac{3}{4}e_0q_1^2 + \tfrac{1}{4}f_0q_1^2)q^2\,, \tag{102}$$

with $\vec{q}$ along a symmetry axis. These modes involve long-wavelength distortions of the charge-density lattice and are the transverse and longitudinal "phonons" of the ICDW "lattice." These modes are probably overdamped (due to the resistivity of electron motion relative to the crystal lattice), but we do not yet have a dynamical theory to describe the motion. The thermally excited "phonons" will induce diffuse scattering near the CDW Bragg scattering peak, with intensity proportional to

$$\langle|\phi_q|^2\rangle = \sum_i kT/\bar{\epsilon}_q^i\,. \tag{103}$$

VI. DISLOCATIONS

We have seen that the triple ICDW has peaks of electron density at the "lattice" sites of a hexagonal "crystal" and that the long-wavelength distortions of the ICDW are the "phonons." One wonders if there may be other imperfections or distortions analogous to crystalline imperfections or distortions. Vacancies or interstitials are not possible because the units making up the ICDW "lattice" are not discrete. However, "dislocations" are possible, and we will now describe a "dislocation" in the charge-density wave. We emphasize that the host crystal is assumed to be perfectly uniform and that only the charge-density wave is distorted into a "dislocation." It will be apparent that the ICDW "dislocation" is perfectly analogous to the vortex line in superfluid helium and superconductors. Following (94), we write a trial solution for the order parameter with a "dislocation" at the origin.

$$\phi_1(\vec{r}) = f(r)\, e^{-i(\theta-\pi/2)}\,, \tag{104}$$

$$\phi_2(\vec{r}) = f(r)\, e^{i(\theta-\pi/2)}\,, \tag{105}$$

$$\phi_3(\vec{r}) = f(r)\,, \tag{106}$$

$$f(r) = \phi_0(1 - e^{-\alpha r})\,, \tag{107}$$

where θ is the angle between $\vec{r}$ and $\vec{q}_1$. Using (1), one can compute the electron density and show that (104)–(107) represent an edge dislocation with Burger's vector in the $\vec{q}_3$ direction. Substituting (104)–(107) into the free-energy expression, we find

$$F \approx F(\phi_0) + (4\pi/\alpha^2)|F(\phi_0)| + 8\pi e_0q_1^2\phi_0^2\ln(\alpha R)\,, \tag{108}$$

where we have used the isotropic approximation ($e_0 = f_0$), and R is the radius of the crystal or half the distance to the nearest dislocation of opposite sign. The two terms are the condensation energy of the core region (core radius $\approx 1/\alpha$) and the distortion energy of the ICDW outside the core. In the core, ϕ is small and this region is normal. Minimizing F with respect to α, we find

$$\alpha^2 = 3|a_0|/4e_0q_1^2 = 3/2\xi^2\,, \tag{109}$$

so that the core radius is approximately equal to one correlation length. This describes the two-dimensional properties of a "dislocation" in one layer. As regards the three-dimensional structure, it is possible, in principle, to have a "dislocation" pair in one layer with the other layers uniform. It is also possible to have a dislocation proceeding vertically through a number of layers. In order to discuss these possibilities, it is necessary to consider interlayer interactions in some detail, and we will not pursue the matter here.

VII. CONCLUSIONS

We have written down a conventional but rather complicated Landau theory to describe charge-density waves in layered compounds. We have discussed the nature of the phase transitions between the normal incommensurate and commensurate phases and concluded that the phases should appear in this order with decreasing temperature and that the phase transitions should be first order. The peaks of electron density occur at lattice sites of a hexagonal "crystal," and we calculate the behavior of two other crystalline properties, "phonons" and "dislocations." Impurities distort the charge-density wave and pin it. Since the incommensurate wave is more flexible, it can distort more readily and gain more energy from the impurity potential than can the commensurate wave. This reduces the commensurate-incommensurate transition temperature for the alloy.

There are a number of things that we have not done in this paper.

(i) We have not considered interlayer interactions. The transition temperatures in one layer are relatively insensitive to the nature of the neighboring layers, which indicates that the intralayer interactions are dominant. Interlayer interactions are important in establishing the relative phase of the CDW's in different layers and in converting the two-dimensional "phonon" spectrum into a three-dimensional one. We want to emphasize that the long-wavelength behavior is three dimensional, not two dimensional in the Kosterlitz-Thouless sense.

(ii) At this point, the Landau theory is entirely phenomenological, and the parameters must be determined from experiment. It will be of great interest to derive the Landau parameters from a microscopic theory once a quantitative microscopic theory is developed. There is a small parameter in the problem, $kT_c/(d$ bandwidth), and one anticipates that, as in superconductivity, the behavior may be mean-field-like over a wide temperature range.

(iii) We have not considered the dynamic behavior of this system. Perhaps the next step is to develop a dynamical Landau theory.

(iv) The most interesting properties of the CDW's are the transport properties, and one would like to have a microscopic transport theory, as well as accurate measurements of resistivity and thermal conductivity.

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