PHYSICAL REVIEW B VOLUME 21, NUMBER 9 1 MAY 1980

Phenomenological theory of charge-density-wave states in trigonal-prismatic, transition-metal dichalcogenides

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(Received 21 November 1979)

A free-energy expression (differing in its symmetry from that of McMillan) is proposed for describing charge-density-wave (CDW) states in transition-metal dichalcogenides having trigonal-prismatically coordinated layers (e.g., 2H-TaSe$_2$). An analysis of the single CDW state is given. In disagreement with previous work, we find that, close to the triple point where the normal, commensurate, and incommensurate phases coexist, the incommensurate-commensurate transition is first order; the transition becomes second order only beyond a multicritical point which is located relatively far from the triple point. We obtain analytical solutions for the order parameter in the single CDW state at the triple point.

I. INTRODUCTION

Many layered transition-metal dichalcogenides exhibit phase transitions to charge-density-wave (CDW) states.[1,2] As the temperature is lowered in 2H-TaSe$_2$, for example, there is an apparently second-order phase transition to an incommensurate charge-density-wave phase at $T_0 = 122$ K followed by a first-order phase transition to a commensurate CDW state at $T_d \sim 90$ K[3]. A Landau theory developed by Moncton, Axe, and DiSalvo[3] accounts not only for the existence of the two successive phase transitions, but also for the experimentally observed, second-harmonic distortion of the fundamental CDW.

Independently, McMillan[4,5] developed a somewhat different form of Landau theory. It too allowed for successive phase transitions from the normal to incommensurate and incommensurate to commensurate phases. Furthermore, McMillan's expression for the free energy turns out to be a particularly convenient starting point for an analysis of the incommensurate-to-commensurate transition where a large number of harmonics must be taken into account in a Fourier-series representation of the incommensurate CDW. The consequences of McMillan's free energy have been explored in a number of papers, including Refs. 4–13.

In this paper, materials having the 2H-TaSe$_2$ structure are studied. Section II sets forth a free energy which is appropriate for a description of charge-density-wave formation in such materials. This free energy is different from that of McMillan[4] and takes account of the fact that a given layer of the 2H-TaSe$_2$ structure does not have a center of symmetry.

In attacking the problem of finding the CDW state which minimizes the free energy, we restrict our attention to the single charge-density-wave case where the excess charge density in the CDW is a function of a single Cartesian coordinate; in this case, our free energy can be written in a form identical to that of McMillan (although the relation between the order parameter and the charge density is different). This problem has been studied by a number of other authors.[5,8–13] The possible equilibrium states are the normal state (the absence of a CDW), the commensurate CDW state, and the incommensurate CDW state, and one problem addressed below is that of finding the phase diagram, i.e., the problem of finding which phase is stable at a given temperature and for a given set of material parameters. Since the determination of the phase boundaries defining the normal-to-commensurate and the normal-to-incommensurate phase transitions is a relatively simple matter and well understood, subsequent discussion will focus on the commensurate-to-incommensurate transition.

McMillan[5] and Bak and Emery[10] found, in an approximation where only the phase (and not the amplitude) of the charge-density wave is allowed to vary spatially, that the incommensurate phase near the incommensurate-to-commensurate phase boundary consists of a sequence of commensurate domains separated by relatively well-defined domain walls (called discommensurations by McMillan[5]). They also found that, as the transition temperature was approached, the spacing between the discommensurations tended to infinity, so that the transition was a continuous (i.e., second-order) one. Sufficiently close to the triple point (where the three phases coexist), however, the amplitude variation of the CDW becomes important. The spatial variation of the amplitude (as well as the phase) was studied in Refs. 8, 9, and 12. The conclusion was that the above qualitative description of the incommensurate phase, in particular the finding that the transition to the commensurate phase is continuous, remained correct.

Our work comes to a different conclusion, namely, that the incommensurate-to-commensurate transition is first order near the triple point and that, as one proceeds away from the triple point along the line of equilibrium of the two phases, a multicritical point is encountered past which the phase transition is second order.

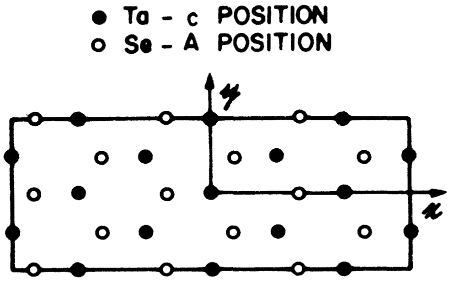
In Sec. III below, we derive the coupled, nonlinear, differential equations which the amplitude and phase of the order parameter must satisfy if they are such as to make the free energy a minimum. Our method is to solve these equations and then to calculate the free energy using the solutions. This differs from the approach of previous authors[8, 9, 12] who determined the order parameter variationally using a truncated, Fourier-series expansion. Section IV presents the results of numerical solutions of the differential equations for the amplitude and the phase of the order parameter; near the triple point, both functions display damped oscillations as one moves away from the center of a discommensuration. In Sec. V, we derive analytical solutions of the differential equations for the amplitude and the phase at the triple point; these new results explain the observation (made in Refs. 8 and 9) that the free energy at the triple point is independent of the spacing between the discommensurations. We use the analytical solutions in Sec. VI to calculate the free energy and the incommensurate-to-commensurate phase boundary near the triple point. In Sec. VII, we determine analytically the asymptotic behavior of the amplitude and the phase, and verify the damped, oscillatory behavior found numerically in Sec. IV. The interaction between discommensurations is calculated in Sec. VIII and the results are used to determine the order of the transition. We show that the damped oscillations in the amplitude and the phase give rise to damped oscillations in the free energy as a function of the spacing between discommensurations, with the consequence that the incommensurate-to-commensurate transition is first order near the triple point. We also show why our conclusions differ from those of previous workers; note that the difference between McMillan's free energy and ours is not the source, for the two can be made identical for the single CDW case. Finally, in the Appendix, we show how we were led to guesses for the two first integrals of the differential equations; these first integrals were the basis for the analytical solutions of Sec. V.

II. SYMMETRY CONSIDERATIONS AND THE FREE ENERGY

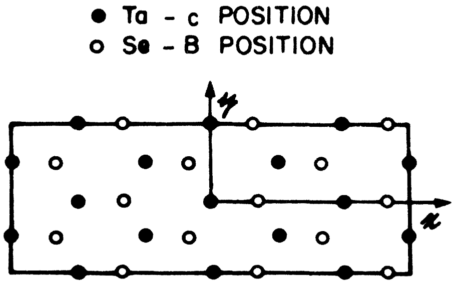
In layered transition-metal dichalcogenide compounds having the 2H-TaSe$_2$ structure (other examples are 2H-NbSe$_2$ and 2H-NbS$_2$), hexagonal sheets of ions are stacked in the sequence $|AcA\ BcB|$; the c sheets are formed from transition-metal ions while the A and B sheets are made up of chalcogen ions.[1-3] The positions of the ions in the AcA layer (called layer 1) and BcB layer (called layer 2) are shown projected onto a plane in Figs. 1(a) and 1(b), respectively. Since the layers are bound together only by relatively weak Van der Waals forces,[1] it has become customary[4] to neglect the interaction between layers as a first approximation when discussing charge-density-wave formation. The two-dimensional space-group symmetry of the layers shown in Figs. 1(a) and 1(b) is $P3m1$. The free energy of a layer should be invariant with respect to all the operations of the space group, and to ensure this, it is sufficient to test for invariance with respect to the generators of the space group; these are the elements of the translation group, together with C_3 (a rotation of $\frac{2}{3}\pi$ about the z axis in Fig. 1) and m (a reflection in the xz plane in Fig. 1).

Let the electronic charge density per unit area in layer 1 be denoted by $\rho(\vec{x}) = \rho_0(\vec{x}) + \delta\rho(\vec{x})$, where ρ_0 is the charge density of the undistorted lattice and $\delta\rho$ is the additional charge density associated with the charge-density wave. Electron-diffraction experiments,[2] for example, allow the detection of the Fourier components $\delta\tilde{\rho}(\vec{k})$ of the charge density defined by

$$\delta\tilde{\rho}(\vec{k}) = (2\pi)^{-2} \int d^2x\, e^{-i\vec{k}\cdot\vec{x}} \delta\rho(\vec{x}) \ . \tag{2.1}$$



(a) LAYER I



(b) LAYER 2

FIG. 1. Atomic positions in the two layers of the unit cell of 2H-TaSe$_2$ projected onto a plane; layers 1 and 2, with stackings AcA and BcB, respectively, are shown in (a) and (b).

The wave vectors in the first Brillouin zone characterizing the charge-density wave in 2H-TaSe$_2$ lie close to the wave vectors $\pm\frac{1}{3}\vec{G}_j$, $j=1,2,3$, where the $\vec{G}_j$ are three of the six shortest reciprocal-lattice vectors as shown in Fig. 2.

The order parameters $\psi_j(\vec{x})$, $j=1,2,3$, are defined by

$$\psi_j(\vec{x})=\int d^2k' e^{i\vec{k}'\cdot\vec{x}}\delta\tilde{\rho}(\tfrac{1}{3}\vec{G}_j+\vec{k}') \quad . \tag{2.2}$$

For this definition of the order parameter to be useful, it is essential that the only Fourier components of the charge density lying in the first Brillouin zone which have an appreciable magnitude are the components $\delta\tilde{\rho}(\pm\frac{1}{3}\vec{G}_j+\vec{k}')$ which have $|\vec{k}'| << |\frac{1}{3}\vec{G}_j|$; the range of integration over $\vec{k}'$ in Eq. (2.2) is thus over all $\vec{k}'$ such that $|\vec{k}'| < k_c$ where the cutoff $k_c << |\frac{1}{3}\vec{G}_j|$. Under these circumstances, the order parameter is a relatively slowly varying function of $\vec{x}$ and the free-energy density in a Landau theory can be expanded in powers of $\psi_j(\vec{x})$ and its spatial derivatives. The charge density $\delta\rho(\vec{x})$ is given in terms of the order parameter $\psi_j(\vec{x})$ by

$$\delta\rho(\vec{x})=\sum_j[\exp(i\tfrac{1}{3}\vec{G}_j\cdot\vec{x})\psi_j(\vec{x})+\text{c.c.}] \quad . \tag{2.3}$$

From Eqs. (2.1) and (2.2), the behavior of the order parameter under the symmetry transformations associated with the generators of the space group $P3m1$ can be deduced. Under a translation by a Bravais-lattice translation vector $\vec{l}$,

$$\psi_j(\vec{x})\rightarrow\exp(-i\tfrac{1}{3}\vec{G}_j\cdot\vec{l})\psi_j(\vec{x}-\vec{l}) \quad . \tag{2.4}$$

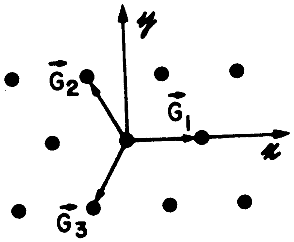


FIG. 2. Portion of the two-dimensional reciprocal lattice of a layer; $\vec{G}_1$, $\vec{G}_2$, and $\vec{G}_3$ are three of the shortest reciprocal-lattice vectors.

Under C_3

$$\psi_j(\vec{x})\rightarrow\psi_{j+1}(C_3^{-1}\vec{x}) \quad , \tag{2.5}$$

where $\psi_4(\vec{x})\equiv\psi_1(\vec{x})$, while under m

$$\begin{aligned}\psi_1(x,y)&\rightarrow\psi_1(x,-y) \quad ,\\ \psi_2(x,y)&\rightarrow\psi_3(x,-y) \quad ,\\ \psi_3(x,y)&\rightarrow\psi_2(x,-y) \quad .\end{aligned} \tag{2.6}$$

It is customary to express the free energy as an integral over a local free-energy density and to expand the free-energy density in powers of the order parameter and its spatial derivatives. Thus, for layer 1, the free energy is

$$F_1=F_N+\int\mathfrak{F}_1\,d^2x \quad , \tag{2.7}$$

where

$$\begin{aligned}\mathfrak{F}_1(\vec{x})=A\sum_j|\psi_j|^2+B\sum_j\left|\left(i\frac{\partial}{\partial x_{\parallel j}}+\delta\right)\psi_j\right|^2+C\sum_j\left|\frac{\partial\psi_j}{\partial x_{\perp j}}\right|^2-D\psi_1\psi_2\psi_3-D^*\psi_1^*\psi_2^*\psi_3^*\\ -\sum_j(E\psi_j^3+E^*\psi_j^{*3})+G\sum_j|\psi_j|^4+\tfrac{1}{2}K\sum_{i\neq j}|\psi_i\psi_j|^2+\sum_j(M\psi_j^2\psi_{j+1}^*\psi_{j+2}^*+M^*\psi_j^{*2}\psi_{j+1}\psi_{j+2})\end{aligned} \tag{2.8}$$

and F_N is the free energy of the normal state. Since the free energy is real, A, B, C, G, and K must be real; δ may be assumed real. The variables $x_{\parallel j}$ and $x_{\perp j}$ are the components of $\vec{x}$ parallel and perpendicular to $\vec{G}_j$, respectively. The free energy F_1 given by Eqs. (2.7) and (2.8) is invariant with respect to the symmetry transformations (2.4)–(2.6) associated with the generators of the space group $P3m1$, as it must be.

It should be noted that there is no symmetry argument which requires the parameters D, E, and M to be purely real, so that in general they must be assumed to be complex numbers. Furthermore, it should be noted that Eq. (2.7) is not invariant with respect to an inversion of coordinates, although if D, E, and M were real, it would be; this lack of inversion symmetry is to be expected since a given layer of the 2H-TaSe$_2$ structure does not have a center of symmetry. [Under an inversion of coordinates $\delta\rho(\vec{x})\rightarrow\delta\rho(-\vec{x})$ and $\psi_j(\vec{x})\rightarrow\psi_j^*(-\vec{x})$.] McMillan's free energy [e.g., Eq. (3) of Ref. (4)] is invariant with respect to an inversion of coordinates and therefore does not fully reflect the symmetry properties of the 2H-TaSe$_2$ structure. The reason for this is that the parameters analogous to D, E, and M in Ref. 4 are real.

Another difference between McMillan's work[4] and ours is the choice of the order parameters of the problem. In Ref. 4, it is assumed that a part of the free energy can be written as a functional of the function $\alpha(\vec{r})$ $\{\alpha(\vec{r})=\text{Re}[\psi_1(\vec{r})+\psi_2(\vec{r})+\psi_3(\vec{r})]$ in the notation of Ref. 4$\}$; this appears to us to be unnecessarily restrictive since $\alpha(\vec{r})$ is only one of several different independent linear combinations of the order parameter which one might choose. The free energy is assumed to be a functional of each of the ψ_j's independently in our approach.

Allowing the parameters D, E, and M to be complex is important because this distinguishes between the two different layers in the unit cell of 2H-TaSe$_2$. Noting that, under an inversion of coordinates, the lattice of layer 1 transforms into that of layer 2 (see Fig. 1), and the order parameter $\psi_j(\vec{x})$ transforms to $\psi_j^*(-\vec{x})$, one can show that the free energy of layer 2 is obtained from that for layer 1 [Eqs. (2.7) and (2.8)] by replacing the parameters D, E, and M by their complex conjugates.

The significance of allowing the parameter E to be complex $[E=|E|\exp(i\phi_E)]$ is further illustrated by considering a single-plane-wave commensurate structure defined by $\psi_2=\psi_3=0$, $\psi_1=\text{const}$. The charge density giving the minimum free energy then has the form

$$\delta\rho(\vec{x})=2|\psi_1|\cos[\tfrac{1}{3}(Gx-\phi_E)] \tag{2.9}$$

for layer 1, and

$$\delta\rho(\vec{x})=2|\psi_1|\cos[\tfrac{1}{3}(Gx+\phi_E)] \tag{2.10}$$

for layer 2. The nonzero value of ϕ_E clearly represents the effects of the different locations of the chalcogens in the two different layers.

Finally, we note that there appears to be a logical inconsistency in the assumption that any given thermodynamic potential can be written as a local function of the ψ_j's having the form of Eq. (2.8). For example, let us begin by making the assumption that the thermodynamic grand potential has the form

$$\Omega(T,V,\mu;\psi_j)=\Omega_N(T,V,\mu)+\delta\Omega(T,V,\mu;\psi_j)\ , \tag{2.11}$$

where $\delta\Omega$ may, for example, be assumed to have the form of $F-F_N$ given by Eqs. (2.7) and (2.8). The Helmholtz free energy F can be derived if the grand potential is known by using the formula $F=\Omega+\mu N$ and determining the chemical potential from the solution of the equation $N=-(\partial\Omega/\partial\mu)$. This gives

$$F(T,V,N;\psi_j)=F_N(T,V,N)+\delta\Omega(T,V,\mu_0;\psi_j)+\frac{1}{2}\left(\frac{\partial\mu}{\partial N}\right)\left(\frac{\partial\delta\Omega(T,V,\mu;\psi_j)}{\partial\mu}\right)^2_{\mu=\mu_0} \tag{2.12}$$

correct to fourth order in the ψ_j's, where μ_0 is the chemical potential for $\psi_j=0$, $j=1,2,3$. It is now apparent that if $\delta\Omega$ contains a term of the form

$$\delta\Omega=A\sum_j\int|\psi_j|^2d^2x+\cdots \tag{2.13}$$

then F will contain terms of the form

$$F=\frac{1}{2}\left(\frac{\partial\mu}{\partial N}\right)\left(\frac{\partial A}{\partial\mu}\right)^2\sum_{i,j}\int d^2x\,d^2x'\,|\psi_i(x)|^2\,|\psi_j(x')|^2\ , \tag{2.14}$$

which have a highly nonlocal structure, and cannot be written in the form of an integral of a local function of the ψ_j's having the form of Eq. (2.8). This point is worthy of further discussion, but we do not attempt such a discussion in this paper. A similar problem has been considered previously[14] in connection with a phenomenological theory of the spin-density-wave state of chromium, where it is shown that the conventional form of the theory, in which the free energy is written as a local functional of the order parameter only, cannot account for the linear polarization of the spin-density-wave state.

In this paper, the expansion of the free energy in powers of the order parameter is terminated at terms of fourth order, neglecting terms such as the terms in $|\psi_j|$ raised to the sixth power considered by Jackson *et al.*[9] They conclude that such terms can have a significant effect on the nature of the phase diagram.

III. FREE ENERGY, DIFFERENTIAL EQUATIONS, AND PHASE DIAGRAM FOR THE SINGLE CHARGE-DENSITY-WAVE STATE

The single charge-density-wave state is the state with $\psi_1\neq0$, $\psi_2=\psi_3=0$, and ψ_1 a function of the coordinate x alone. From Eqs. (2.7) and (2.8), the free energy of the state is

$$F=F_N+L_y\int\left[A|\psi_1|^2+B\left|\left(i\frac{d}{dx}+\delta\right)\psi_1\right|^2-(E\psi_1^3+\text{c.c.})+G|\psi_1|^4\right]dx\ , \tag{3.1}$$

where L_y is the length of the sample in the y direction and the integral is over the length L of the sample in the x direction. To obtain an expression which is more convenient for analysis, we write E as $|E|\exp(i\phi_E)$ and define

$$\psi=G\psi_1|E|^{-1}\exp(\tfrac{1}{3}i\phi_E)\ ,\quad v=\tfrac{1}{2}AG/|E|^2\ ,$$

$$\gamma=\tfrac{1}{2}B\delta^2G/|E|^2\ ,\quad F_0=2L_y|E|^4/(\delta G^3)\ .$$

Further, we take the unit of length to be δ^{-1} by replacing x by $x\delta$ and so obtain the expression

$$F=F_N+F_0\int f(x)\,dx\ , \tag{3.2}$$

where the free-energy density $f(x)$ is the dimensionless function

$$f(x) = v|\psi|^2 + \gamma \left| \left(i\frac{d}{dx} + 1 \right) \psi \right|^2 - \mathrm{Re}(\psi^3) + \tfrac{1}{2}|\psi|^4 \ . \tag{3.3}$$

Our result [Eq. (3.2) plus Eq. (3.3)] for the free energy of the single charge-density-wave state is identical to that of McMillian[5]; our order parameter ψ is related to his ϕ by $\psi = (-v)^{1/2}\phi$ and our parameters γ and v to his β and Y by $\gamma = (\beta Y^2)^{-1}$ and $v = -(\beta Y)^{-2}$. We note, however, the presence of the phase factor $\exp(\frac{1}{3} i\phi_E)$ in the above transformation from ψ_1 to ψ; although the free energies can be made equivalent, this factor has the consequence that different charge densities are predicted by the two theories. In the case of the triple charge-density-wave state, it is not possible to make the two free energies equivalent.

The parameters v and γ of the model depend on the material and on the experimental conditions. We make the usual assumptions of a Landau theory: the coefficient v is proportional to $T - T_0$ for temperature T near T_0 (the temperature of the transition between the normal and incommensurate phases) and the coefficient γ is greater than or equal to zero.

In the commensurate phase, the order parameter is a complex constant $\psi_c = a_c \exp(i\phi_c)$; the free energy is

$$F_c = F_N + F_0 L\,\delta f_c \ , \tag{3.4}$$

$$f_c = (v+\gamma)a_c^2 - a_c^3 + \tfrac{1}{2}a_c^4 \ . \tag{3.5}$$

The optimal value of the amplitude is

$$a_c = \tfrac{3}{4} + \tfrac{1}{4}[1 - 16(v + \gamma - \tfrac{1}{2})]^{1/2} \ ; \tag{3.6}$$

the optimal value of the phase is threefold degenerate:

$$\phi_c = 0,\ \tfrac{2}{3}\pi,\ \tfrac{4}{3}\pi,\ (\mathrm{mod}\, 2\pi) \ . \tag{3.7}$$

Setting $f_c = 0$ gives the normal-commensurate phase boundary as the line

$$v + \gamma - \tfrac{1}{2} = 0 \ . \tag{3.8}$$

The normal state ($a = 0$, ϕ indeterminate) is favored for $v + \gamma - \frac{1}{2} > 0$ and the commensurate state is favored for $v + \gamma - \frac{1}{2} < 0$; the transition is first order and the value of a_c at $v + \gamma - \frac{1}{2} = 0^-$ is $a_c = 1$. The boundary is shown in Fig. 3.

To examine the transition between the normal and incommensurate states, we assume that the order parameter has the form

$$\psi(x) = u_1 e^{i\delta' x} + u_2 e^{-2i\delta' x} \ ; \tag{3.9}$$

the importance of including the second harmonic has been stressed by Moncton, Axe, and DiSalvo.[3] To find the order parameter and the free energy near the phase boundary, we assume that $|u_2|$ is of order $|u_1|^2$ and we keep terms in the free energy only to order $|u_1|^4$. The result is

$$\begin{aligned} \int f(x)\,dx = L\,\delta\{ & [v + \gamma(1-\delta')^2]|u_1|^2 \\ & + [v + \gamma(1+2\delta')^2]|u_2|^2 \\ & - 3\,\mathrm{Re}(u_1^2 u_2) + \tfrac{1}{2}|u_1|^4\} \ . \end{aligned} \tag{3.10}$$

Minimization of this expression with respect to u_1, u_2, and δ' gives,[3] in our notation,

$$\begin{aligned} u_1 &= [\gamma(T_0 - T)/(\gamma - \tfrac{1}{2})]^{1/2} \ , \\ u_2 &= \tfrac{1}{6}(T_0 - T)/(\gamma - \tfrac{1}{2}) \ , \\ \delta' &= 1 - \tfrac{1}{6}(T_0 - T)/(\gamma - \tfrac{1}{2}) \ , \\ \int f(x)\,dx &= -L\,\delta\gamma(T_0 - T)^2/(\gamma - \tfrac{1}{2}) \ , \end{aligned} \tag{3.11}$$

where we have written v as $T - T_0$. Thus, for $\gamma > \frac{1}{2}$, there is a second-order transition at

$$v = 0 \ . \tag{3.12}$$

Note that approximations made here are valid only for $\gamma > \frac{1}{2}$ and for $|(T_0 - T)/(\gamma - \frac{1}{2})| \ll 1$. For $\gamma < \frac{1}{2}$, the assumptions that $|u_2|$ is of order $|u_1|^2$ and that $|u_1|^2$ is small are not valid; in this case, the transition out of the normal state is first order.

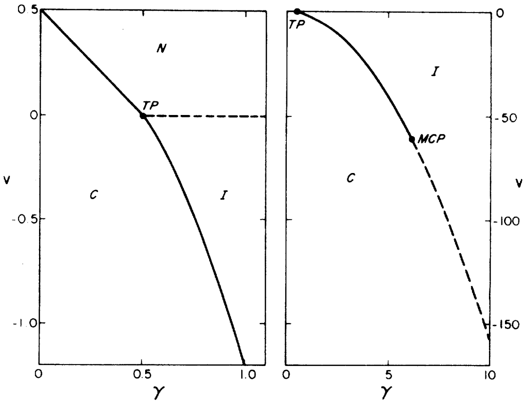


FIG. 3. Phase diagram as determined in this work. The lines are the boundaries between the normal (N), commensurate (C), and incommensurate (I) phases; first-order transitions are shown as solid lines and second-order transitions as dashed lines. The lines meet at the triple point (TP). The C-I transition is first order near the triple point and second order far from it; the changeover occurs at the multicritical point (MCP).

The phase boundaries given by Eqs. (3.8) and (3.12) intersect at the point $\gamma = \frac{1}{2}$, $v = 0$. In Sec. VI, we obtain the previously unknown, analytical expression $v+\frac{3}{2}(\gamma-\frac{1}{2})=0$ for the commensurate-incommensurate phase boundary near this point (which is a triple point).

To treat the incommensurate phase in the general case, we write the order parameter as $\psi(x)=a(x)e^{i\phi(x)}$; the free-energy density $f(x)$ in terms of the amplitude a and the phase ϕ is, from Eq. (3.3),

$$f(x)=\gamma(a')^2+\gamma a^2(\phi'-1)^2+va^2-a^3\cos 3\phi+\tfrac{1}{2}a^4 \ . \tag{3.13}$$

From the results of the two-harmonic approximation [Eq. (3.9)], the incommensurate phase just below the normal-incommensurate boundary has a linear phase $[\phi(x)=\phi(0)+x]$ and a constant amplitude; this form for $\psi(x)$ minimizes the contributions to the free energy from the first two terms in $f(x)$ but also results in a vanishing contribution from the $-a^3\cos 3\phi$ term. With decreasing temperature, it is energetically favorable for both the amplitude and the phase to deform to take advantage of the $-a^3\cos 3\phi$ term in $f(x)$ at the expense of increased contributions from the first two.[5] First, the regions where $\cos 3\phi\approx 1$ expand relative to those where $\cos 3\phi\approx -1$ and second, the amplitude in the former regions is larger than in the latter. The successive passages of $\phi(x)$ through favorable ($\cos 3\phi\approx 1$) and unfavorable ($\cos 3\phi\approx -1$) regions are the basic characteristic of the incommensurate state and we use McMillan's term "discommensuration" for the homogeneity associated with a change of $\frac{2}{3}\pi$ in the phase.

In the absence of perturbations due to impurities, etc., the discommensurations will form a periodic array, and we can focus attention on one discommensuration which we take to be centered at $x=0$; by this we mean that $\phi(0)=\frac{1}{3}\pi$ (the values π or $\frac{5}{3}\pi$ could also have been chosen). The discommensuration extends from $x=-X_1$, where $\phi=0$, to $x=X_2$, where $\phi=\frac{2}{3}\pi$. In common with all previous workers,[5,8,9,12] we assume that the discommensuration is "symmetric" about $x=0$ and therefore that $X_1=X_2$; we denote the common value by X. More precisely, we assume that $\phi(x)-\frac{1}{3}\pi$ is antisymmetric about $x=0$; consequently $\phi''(0)=0$ and, from Eq. (3.17) below, $a'(0)=0$. Conditions at $x=\pm X$ are obtained in a similar fashion; in summary, the conditions on a and ϕ are taken to be

$$\begin{gathered} a'(-X)=0,\quad a'(0)=0,\quad a'(X)=0\ ,\\ \phi(-X)=0,\quad \phi(0)=\tfrac{1}{3}\pi,\quad \phi(X)=\tfrac{2}{3}\pi\ . \end{gathered} \tag{3.14}$$

In the special case of a single discommensuration ($X=\infty$), the conditions are

$$\begin{gathered} a(-\infty)=a_c,\quad a'(0)=0,\quad a(\infty)=a_c\ ,\\ \phi(-\infty)=0,\quad \phi(0)=\tfrac{1}{3}\pi,\quad \phi(\infty)=\tfrac{2}{3}\pi\ . \end{gathered} \tag{3.15}$$

To determine the optimal amplitude and phase, we demand that the free energy be stationary with respect to perturbations in these optimal functions and so obtain the differential equations

$$-2\gamma a''+2\gamma a(\phi'-1)^2+2va-3a^2\cos 3\phi+2a^3=0\ , \tag{3.16}$$

$$-2\gamma a^2\phi''-4\gamma aa'(\phi'-1)+3a^3\sin 3\phi=0\ . \tag{3.17}$$

These equations possess the first integral

$$-\gamma[(a')^2+(a\phi')^2]+(\gamma+v)a^2-a^3\cos 3\phi+\tfrac{1}{2}a^4=\mathcal{G}\ , \tag{3.18}$$

where $\mathcal{G}$ is independent of x, but no further progress in solving them can be made in the general case. Apart from the trivial solutions $a=0$ for the normal state and $a=a_c$, $\phi=0\bmod(\frac{2}{3}\pi)$ for the commensurate state, analytical solutions can be found in only three cases:

i. In the limit $v\to 0$, *near the normal-incommensurate boundary.* See the discussion of the two-harmonic approximation in Sec. II.

ii. In the limit $v\to -\infty$. This is the region of validity of the phase-only approximation of McMillan,[5] Bak and Emery,[10] and Ohmi and Yamamoto.[13] The amplitude has the constant value a_c and the phase satisfies the sine-Gordon equation

$$2\gamma\phi''=3a_c\sin 3\phi\ , \tag{3.19}$$

which has analytical solutions in the form of Jacobian elliptic functions.

iii. At the triple point. The solutions for this case are new with this work and are given in Sec. V below. Note that these solutions cannot be obtained from those of case *i* because the two-harmonic approximation breaks down at the triple point.

In general, the equations must be solved numerically; results of such calculations are given in Sec. IV.

Results for the phase diagram associated with the free-energy expression of Eqs. (3.2) and (3.3) have been obtained by Nakanishi and Shiba,[8] by Jackson, Lee, and Rice[9] and by Yamamoto, Nakayama, and Ohmi.[12] Our results, obtained in the following sections, are shown in Fig. 3. They are in agreement with previous work[8,9,12] for the order and location of the normal-commensurate and normal-incommensurate transitions and for the location of the triple point; also, our result for the location of the incommensurate-commensurate transition differs little (by at most five parts in 10^4) from previous results. Our result for the order of the latter transition is, however, different. In contrast with previous results that this transition is second order for all values of the parameters, our conclusion is that it is first order near the triple point and for a large range beyond; the transition becomes second order only beyond the multicritical point at $(\gamma, v) \approx (6.155, -60.81)$.

IV. NUMERICAL RESULTS

We have solved the differential Eqs. (3.16) and (3.17) by a fourth-order, finite-difference method (with a step size $h = \frac{1}{64}$ in most cases). The equations were linearized about trial solutions and then solved iteratively in the region $0 \leq x \leq X$ with the boundary conditions $a'(0) = 0$, $\phi(0) = \frac{1}{3}\pi$, $a'(X) = 0$, $\phi(X) = \frac{2}{3}\pi$. In the case of a single discommensuration, we applied the latter pair of conditions at $x = 12.5$. The numerical errors were small; the root-mean-square-average values of the left-hand sides of the equations were of order $10^{-12} a_c^3$. The systematic error introduced by the use of a finite-difference approximation for the derivatives was checked in several cases by using a step size of $h = \frac{1}{128}$ and found to be negligible (a few parts in 10^8).

In one series of calculations, we investigated the single discommensuration ($X = \infty$). The parameters γ and v were chosen, the differential equations were solved and the free energy was evaluated from the solutions. For fixed γ, the parameter v was adjusted until the free energy of the state containing a single discommensuration equaled the free energy of the commensurate state; that is, we demanded

$$\int_{-\infty}^{\infty} [f(x;\gamma, v) - f_c(\gamma, v)]\, dx = 0 \ , \qquad (4.1)$$

where the free-energy densities f and f_c of the incommensurate and commensurate states are defined by Eqs. (3.13) and (3.5). The accuracy of the calculations can be judged from the fact that, for $\gamma = \frac{1}{2}$, we obtained the value $v = -1 \times 10^{-8}$ instead of the correct value $v = 0$.

Solutions for a and ϕ, as functions of x, are given in Figs. 4 and 5. It is a feature of the numerical solutions that in all cases with $\gamma > \frac{1}{2}$, the amplitude a "overshoots" the asymptotic value a_c (the value of a in the commensurate phase for the same values of γ and v). The origin of this unexpected behavior is apparently the $-a^3 \cos 3\phi$ in the free energy; when $\cos 3\phi$ is positive, energy is gained if a is increased, subject, of course, to other terms in the free energy. The overshooting of a is apparent in Fig. 4; the

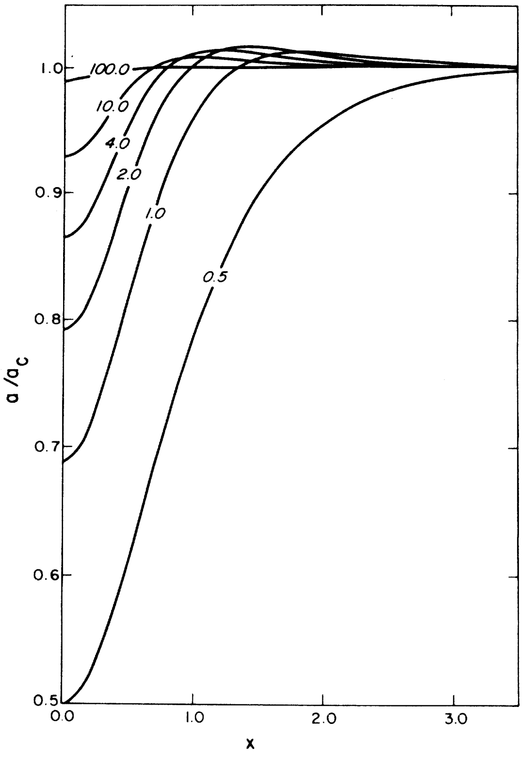


FIG. 4. Reduced amplitude $a(x)/a_c$ as a function of x for a single discommensuration with free energy equal to that of the commensurate state; the numbers associated with the curves are the values of γ.

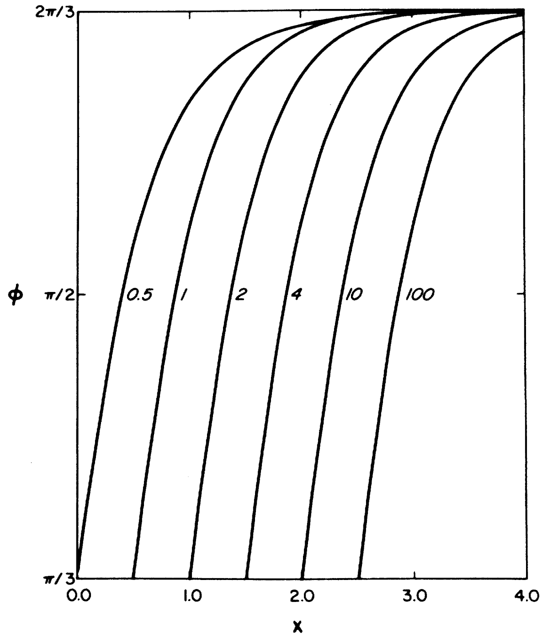


FIG. 5. Phase ϕ as a function of x for a single discommensuration with free energy equal to that of the commensurate state. For clarity, the curves for $\gamma = 1, 2, 4, 10$, and 100 are shifted successively to the right.

phenomenon was also noted by Nakanishi and Shiba[8]—see their Fig. 3.

The amplitude is strongly dependent on position near the triple point, varying there by a factor of 2 [see Eq. (5.6)], and weakly dependent on position far from the triple point. On the other hand, $\phi(x)$ is relatively insensitive to the value of γ; the slope of ϕ at $x=0$ is 1.5 at $\gamma=\frac{1}{2}$, increases to a maximum of ~ 1.63 at $\gamma \approx 2.2$ and then decreases to $\frac{1}{2}\pi = 1.57 \cdots$ at $\gamma=\infty$.

Perhaps the most surprising result is that, for a large range of parameter values, not only the amplitude but also the phase overshoots the asymptotic value; in fact, for this range of values, a and ϕ oscillate about their asymptotic values. In Fig. 6, we have plotted ϕ as a function of x with the scale of the ordinate expanded by roughly a factor of 100 from that of Fig. 5. The overshooting for $\gamma=1$ and 2 is obvious, but the oscillations are revealed only by a further expansion of the scale. This behavior was not pointed out before; perhaps it was obscured by the use, in all previous calculations, of Fourier series expansions. Because of numerical errors, it is not possible to place very good bounds on the range of parameters for which the solutions are oscillatory. In Sec. VII, we examine the asymptotic behavior of a and ϕ, and find that both functions oscillate for γ in the range $\frac{1}{2} < \gamma \lesssim 6.155$ [provided, of course, that v is chosen so that Eq. (4.1) is satisfied].

For γ larger than ~ 6.155, ϕ increases monotonically from its value $\frac{1}{3}\pi$ at the center of the discommensuration to its value $\frac{2}{3}\pi$ at $x=\infty$, but a overshoots the value a_c, so that the two functions approach their limiting values from different sides.

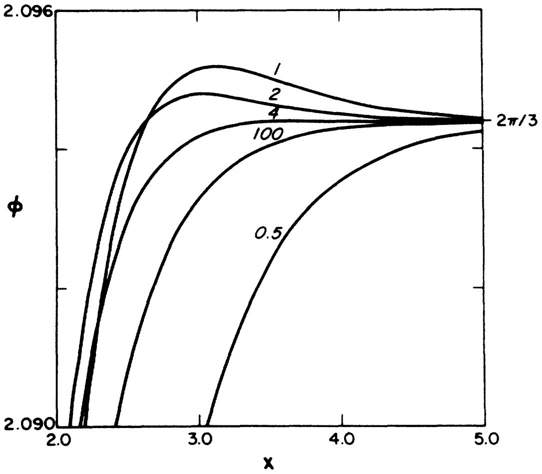


FIG. 6. Curves of Fig. 5 expanded to show the behavior of $\phi(x)$ for large x.

V. ANALYTICAL SOLUTIONS AT THE TRIPLE POINT

At the triple point ($\gamma=\frac{1}{2}, v=0$), the differential Eqs. (3.16) and (3.17) for the amplitude a and the phase ϕ possess analytical solutions, as we shall now show. In the Appendix, the following first integrals of Eqs. (3.16) and (3.17) at the triple point are obtained:

$$\frac{da}{dx} = -a^2 \sin 3\phi \ , \tag{5.1}$$

$$\frac{d\phi}{dx} = 1 - a\cos 3\phi \ . \tag{5.2}$$

Eliminating x from Eqs. (5.1) and (5.2) and solving the resulting differential equation, we find the relation

$$\cos 3\phi = (3Ca^2 - 1)/(2Ca^3) \tag{5.3}$$

between a and ϕ; C is a constant of integration. Using Eq. (5.3) to eliminate ϕ from Eq. (5.1), we obtain the following differential equation for $y=a^2$:

$$\frac{dy}{dx} = 2\left\{ y^3 - \frac{9}{4}y^2 + \frac{3}{2C}y - \frac{1}{4C^2} \right\}^{1/2} \tag{5.4}$$

in the region $0 \le x \le X$ where $\sin 3\phi$ is negative.

We investigate first the single discommensuration characterized by Eqs. (3.15). Since $a_c = 1$ at the triple point, the constant C is seen from Eq. (5.3) to be unity when $X=\infty$. Eq. (5.4) becomes

$$\frac{dy}{(1-y)(y-\frac{1}{4})^{1/2}} = 2dx \ ; \tag{5.5}$$

the solution is

$$a^2(x) = 1 - \frac{3}{4\cosh^2(\frac{1}{2}\sqrt{3}x)} \ . \tag{5.6}$$

Note that the amplitude varies by a factor of 2 over the range $x=0$ to ∞; a and ϕ increase monotonically from their values $\frac{1}{2}$ and $\frac{1}{3}\pi$ at the center of the discommensuration to the values 1 and $\frac{2}{3}\pi$ at $x=\infty$.

For a chain of discommensurations, we write Eq. (5.4) as

$$\frac{dy}{dx} = 2[(y-y_1)(y-y_2)(y-y_3)]^{1/2} \ , \tag{5.7}$$

where $y_1 \le y_2 \le y_3$; the values of these quantities depend on C (and thereby on X) in a fashion to be determined. The solutions $y \equiv y_1$, $y \equiv y_2$, and $y \equiv y_3$ of Eq. (5.7) are inadmissible, for they lead to $\phi = \text{const}$. Solutions with $y \ge y_3$ are likewise inadmissible for they have only one turning point and hence cannot satisfy both $a'(0)=0$ and $a'(X)=0$. We conclude that the desired solutions are bounded by y_1 and y_2; i.e.,

$$y_1 \le y \le y_2 \ . \tag{5.8}$$

The quantities y_1, y_2, and y_3 are found as follows. The condition $\cos 3\phi = -1$ at $x = 0$ gives $y_1 = a_1^2$ where a_1 is the only real and positive zero of

$$f_1(a) = 2a^3 + 3a^2 - 1/C \ . \tag{5.9}$$

From $\cos 3\phi = 1$, $y_2 = a_2^2$ and $y_3 = a_3^2$, where a_2 and a_3 are the two real and positive zeros of

$$f_2(a) = 2a^3 - 3a^2 + 1/C \ ; \tag{5.10}$$

note that we must have $C \geqslant 1$ for these zeros to be real. Explicit results can be obtained in the limit $C \to 1$, where

$$\begin{aligned} y_1 &= \tfrac{1}{4} - \tfrac{2}{3}\epsilon^2 + O(\epsilon^4) \ , \\ y_2 &= 1 - 2\epsilon + \tfrac{1}{3}\epsilon^2 + O(\epsilon^3) \ , \\ y_3 &= 1 + 2\epsilon + \tfrac{1}{3}\epsilon^2 + O(\epsilon^3) \ , \end{aligned} \tag{5.11}$$

and $\epsilon = [\tfrac{1}{3}(C-1)]^{1/2}$, and also in the limit $C \to \infty$, where

$$\begin{aligned} y_1 &= \eta^2 - \tfrac{2}{3}\eta^3 + \tfrac{2}{3}\eta^4 + O(\eta^5) \ , \\ y_2 &= \eta^2 + \tfrac{2}{3}\eta^3 + \tfrac{2}{3}\eta^4 + O(\eta^5) \ , \\ y_3 &= \tfrac{9}{4} - 2\eta^2 - \tfrac{4}{3}\eta^4 + O(\eta^6) \ , \end{aligned} \tag{5.12}$$

and $\eta = (3C)^{-1/2}$.

Clearly $y_1 = a^2(0)$ and $y_2 = a^2(X)$; x as a function of y is then given by

$$2x = \int_{y_1}^{y} \frac{dy}{[(y-y_1)(y-y_2)(y-y_3)]^{1/2}} \ . \tag{5.13}$$

Following Refs. 15 and 16, we make the substitution

$$w = -(y - y_1 - s)/(y - y_1 + s) \ , \tag{5.14}$$

where $s = [(y_3 - y_1)(y_2 - y_1)]^{1/2}$, which converts this integral into a standard form of the elliptic integral of the first kind:

$$\kappa x = \int_w^1 \frac{dt}{(1-t^2)^{1/2}(t^2 - 1 + m)^{1/2}} = \mathrm{F}(\theta | m) \ , \tag{5.15}$$

where

$$\begin{aligned} m &= 4s/\kappa^2 \ , \\ \sin^2\theta &= (1 - w^2)/m \ , \\ \kappa &= (y_3 - y_1)^{1/2} + (y_2 - y_1)^{1/2} \ . \end{aligned} \tag{5.16}$$

The inversion of Eq. (5.15) gives a in terms of a Jacobian elliptic function

$$a^2(x) = a^2(0) + s\left[\frac{1 - \mathrm{dn}(\kappa x | m)}{1 + \mathrm{dn}(\kappa x | m)}\right] \ . \tag{5.17}$$

Equation (5.15) also gives the half-period X as

$$X = \kappa^{-1} K(m) \ , \tag{5.18}$$

where $K(m) = \mathrm{F}(\tfrac{1}{2}\pi | m)$ is the complete elliptic integral of the first kind, with "parameter" m. The solutions for a and ϕ in the region $0 \leqslant x \leqslant X$ are then given by Eqs. (5.17) and (5.3).

Although the results of the previous paragraph hold for all $X \geqslant \tfrac{1}{3}\pi$, they are not very illuminating. To obtain some insight into the nature of the solutions for closely spaced discommensurations, we examine the case $C \to \infty$. The calculation can be done in a number of ways. The direct method is to expand about the trivial solutions (the atomic displacements are zero) $a = 0$, $\phi = \tfrac{1}{3}\pi + x$ of Eqs. (5.1) and (5.2). The solutions are given parametrically as

$$\begin{aligned} a = \xi &- \tfrac{1}{3}\xi^2 \cos\frac{\pi x}{X} - \tfrac{1}{36}\xi^3 \cos\frac{2\pi x}{X} \\ &- \tfrac{1}{54}\xi^4 \cos\frac{\pi x}{X}\left[\cos^2\frac{\pi x}{X} + 4\right] + \cdots \ , \end{aligned} \tag{5.19}$$

$$\begin{aligned} \phi = \tfrac{1}{3}\pi\left[1 + \frac{x}{X}\right] &+ \tfrac{1}{3}\xi \sin\frac{\pi x}{X} + \tfrac{1}{18}\xi^2 \sin\frac{2\pi x}{X} \\ &+ \tfrac{1}{27}\xi^3 \sin\frac{\pi x}{X}\left[-\tfrac{4}{3}\sin^2\frac{\pi x}{X} + \tfrac{23}{4}\right] + \cdots \ , \end{aligned} \tag{5.20}$$

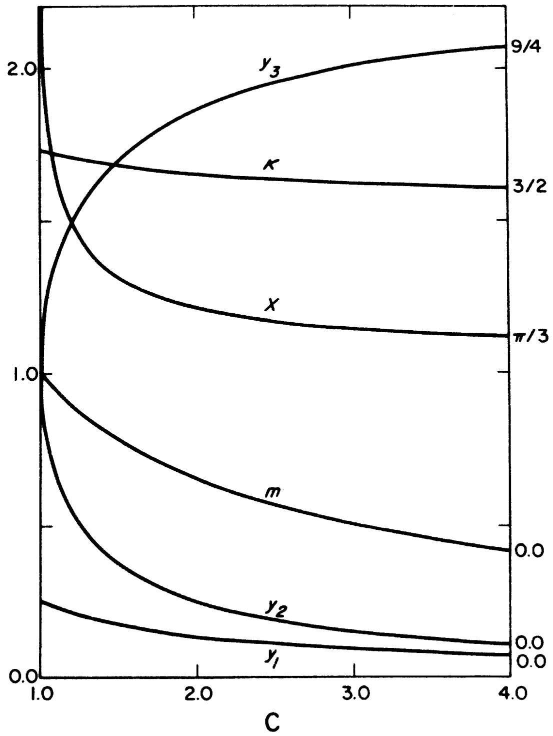


FIG. 7. Quantities y_1, y_2, y_3, m, κ, and X (the half-period) as functions of the parameter C. The values of the various quantities at $C = \infty$ are given at the right-hand side of the figure.

in terms of the quantity ξ defined by

$$X=\tfrac{1}{3}\pi[1+\tfrac{2}{3}\xi^2+O(\xi^4)] \;; \tag{5.21}$$

ξ is related to C by

$$3C\xi^2=1+\tfrac{11}{18}\xi^2+O(\xi^4) \;. \tag{5.22}$$

These results show how the amplitudes of the lower harmonics change as the discommensurations become more widely separated.

The quantities y_1, y_2, y_3, X, κ, and m are given as functions of C by Fig. 7; all vary monotonically as C increases from 1 to ∞. X approaches $\frac{1}{3}\pi$ as $C\rightarrow\infty$; that is, there are no solutions of the differential equations when $X<\frac{1}{3}\pi$. Expressions for y_1, y_2, and y_3 in the limit $C\rightarrow 1$ are given by Eqs. (5.11); for the other quantities we have

$$\begin{aligned} s&=\tfrac{3}{4}[1-\tfrac{20}{9}\epsilon^2+O(\epsilon^4)] \;,\\ \kappa&=\sqrt{3}[1-\tfrac{2}{9}\epsilon^2+O(\epsilon^4)] \;,\\ m&=1-\tfrac{16}{9}\epsilon^2+O(\epsilon^4) \;,\\ K(m)&\rightarrow\tfrac{1}{2}\ln(9/\epsilon^2) \;,\\ C-1&=3\epsilon^2\rightarrow 27e^{-2\sqrt{3}\,X} \;. \end{aligned} \tag{5.23}$$

VI. FREE ENERGY NEAR THE TRIPLE POINT

The analytical results of Sec. V for the amplitude and the phase at the triple point allow us to obtain analytical results for the free energy near the triple point.

We expand a and ϕ as

$$a=a_0+a_1 \;,\quad \phi=\phi_0+\phi_1 \;, \tag{6.1}$$

about the solutions a_0 and ϕ_0 at the triple point. The free energy of a chain of discommensurations is then

$$F=F_c+2NF_0\int_0^X dx\,\{[\tfrac{1}{3}a_0a_0'+a_0'a_1+a_0^2(\phi_0'-1)\phi_1]'+v(a_0^2-1)+(\gamma-\tfrac{1}{2})[a_0^2(\phi_0'-1)^2+(a_0')^2-1]\} \tag{6.2}$$

to first order in v, $\gamma-\frac{1}{2}$, a_1 and ϕ_1; note that a_1 and ϕ_1 are of first order in v and $\gamma-\frac{1}{2}$. The first of the three terms in the integrand vanishes on integration because of the conditions $a_0'=0$ and $\phi_1=0$ at both $x=0$ and $x=X$; the third term can be transformed with the help of Eqs. (5.1) and (5.2) and

$$a_0^4=a_0^3\cos 3\phi_0+\tfrac{1}{3}(a_0a_0')' \;.$$

The expression reduces to

$$F=F_c+2NF_0\int_0^X dx\left\{[v+\tfrac{3}{2}(\gamma-\tfrac{1}{2})](a_0^2-1)+\frac{(\gamma-\frac{1}{2})\frac{1}{2}(C-1)}{C}\right\} . \tag{6.3}$$

To evaluate the free energy, we use Eq. (5.7) to write the only nontrivial integral in Eq. (6.3) as

$$\int_0^X a_0^2\,dx=\frac{1}{2}\int_{y_1}^{y_2}\frac{y\,dy}{[(y-y_1)(y-y_2)(y-y_3)]^{1/2}} \;; \tag{6.4}$$

a direct calculation starting from the result Eq.(5.17) appears intractable. A tedious evaluation using the transformations of Refs. 15 and 16 results in

$$\int_0^x a_0^2\,dx=\tfrac{1}{2}(y_2+y_3)x-\tfrac{1}{2}\kappa\mathrm{E}(\theta|m)+\tfrac{1}{2}(y-y_1+s)^{-1}\frac{dy}{dx} \;, \tag{6.5}$$

where $\mathrm{E}(\theta|m)$ is the elliptic integral of the second kind; the other quantities are defined in Sec. V. The free energy is therefore

$$\begin{aligned} F=F_c+2NF_0\{&[v+\tfrac{3}{2}(\gamma-\tfrac{1}{2})]\\ &\times[(\tfrac{1}{2}y_2+\tfrac{1}{2}y_3-1)X-\tfrac{1}{2}\kappa E(m)]\\ &+(\gamma-\tfrac{1}{2})\tfrac{1}{2}X(C-1)/C\} \;, \end{aligned} \tag{6.6}$$

where $E(m)=\mathrm{E}(\frac{1}{2}\pi|m)$ is the complete elliptic integral of the second kind, with "parameter" m, as defined in Refs. 15 and 16; again, $\kappa X=K(m)$. We emphasize that our result Eq. (6.6) is valid only to first order in v and $(\gamma-\frac{1}{2})$.

Examining first the case of a single discommensuration, we find

$$F=F_c+2NF_0[v+\tfrac{3}{2}(\gamma-\tfrac{1}{2})](-\tfrac{1}{2}\sqrt{3}) \;. \tag{6.7}$$

Hence the commensurate phase is favored if $v+\frac{3}{2}(\gamma-\frac{1}{2})<0$ and the incommensurate phase if $v+\frac{3}{2}(\gamma-\frac{1}{2})>0$, at least for a single discommensuration. In the other limit of maximally packed discommensurations $(X=\frac{1}{3}\pi)$, the free energy is

$$F=F_c-F_0L\,\delta[v+(\gamma-\tfrac{1}{2})] \;. \tag{6.8}$$

Since, to first order in v and $(\gamma-\frac{1}{2})$,

$$F_c=F_N+F_0L\,\delta[v+(\gamma-\tfrac{1}{2})] \;, \tag{6.9}$$

Eq. (6.8) reduces to $F=F_N$; that is, the transition to the normal state takes places when the half-period X of the discommensuration chain reaches the value $\frac{1}{3}\pi$.

To describe the free energy for intermediate spacings of the discommensurations, we define

$$g_1=[\tfrac{1}{2}(y_2+y_3)-1]X-\tfrac{1}{2}\kappa E(m) \ , \tag{6.10}$$

$$g_2=\tfrac{1}{2}X(C-1)/C \ . \tag{6.11}$$

g_1 is negative for all C and increases in magnitude monotonically with C; g_2 vanishes at $C=1$ and increases monotonically with C; values are given in Fig. 8.

These results show that the incommensurate phase, for any X, is unstable below the line

$$v+\tfrac{3}{2}(\gamma-\tfrac{1}{2})=0 \tag{6.12}$$

for, in this case, the first term inside the curly bracket in Eq. (6.6) is greater than zero whereas the second is non-negative (because $\gamma\geq\frac{1}{2}$). Equation (6.12) therefore gives the commensurate-incommensurate transition line in the neighborhood of the triple point. To demonstrate the result (6.12) explicitly, we set $F=F_c$ in Eq (6.6) and thereby obtain the condition

$$v+g(\gamma-\tfrac{1}{2})=0 \ , \tag{6.13}$$

where

$$g=\tfrac{3}{2}+g_2/g_1 \ ; \tag{6.14}$$

as shown in Fig. 8, g decreases monotonically from $\frac{3}{2}$ at $C=1$ to 1.0 at $C=\infty$, and the lowest line is obtained for a single discommensuration.

Keeping γ and v fixed, we first minimize the free energy with respect to X. This optimal value of X is found to increase monotonically from $\frac{1}{3}\pi$ to ∞ as v decreases from 0 to $-\frac{3}{2}(\gamma-\frac{1}{2})$ with γ fixed. Consequently, both the normal-incommensurate and incommensurate-commensurate transitions are predicted to be continuous: If γ is fixed at some value greater than $\frac{1}{2}$ and v is varied, the normal state is stable for $v>0$; for $v=0-$, the discommensurations are maximally packed, but the normal-incommensurate transition is second order because the amplitude of the charge-density wave is zero; as v decreases further, the discommensurations spread out in a continuous manner until, at $v+\frac{3}{2}(\gamma-\frac{1}{2})=0+$, there is only one discommensuration; for $v+\frac{3}{2}(\gamma-\frac{1}{2})<0$, the commensurate phase is stable.

The prediction of Eq. (6.6) is therefore that the incommensurate-commensurate transition is of second order near the triple point. This prediction is, however, incorrect, for we show in Sec. VIII that the transition is of first order in this region. Equation (6.6) fails in this respect because it neglects higher-order terms which, unfortunately, cannot be calculated with the method of this section but which are crucial for determining the order of the transition; as we shall see, however, the transition becomes more nearly second order as the triple point is approached. These higher-order corrections to Eq. (6.6) will not change the slope of the phase boundary near the triple point, however, and Eq. (6.12) is correct.

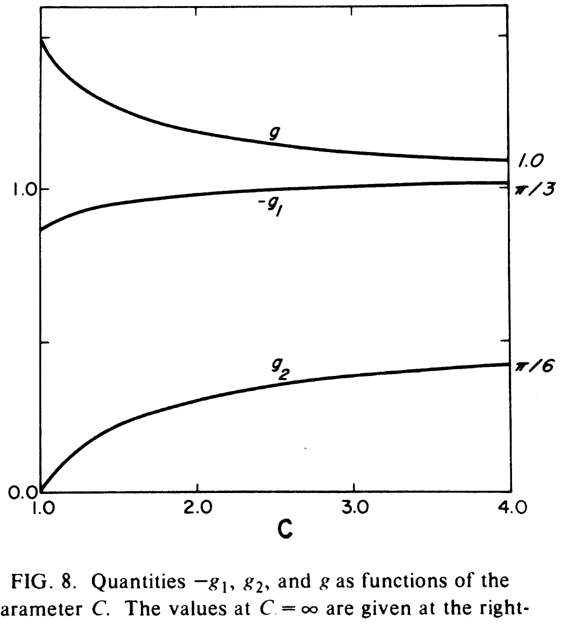


FIG. 8. Quantities $-g_1$, g_2, and g as functions of the parameter C. The values at $C=\infty$ are given at the right-hand side of the figure.

VII. ASYMPTOTIC BEHAVIOR OF a AND ϕ FOR A SINGLE DISCOMMENSURATION

In this section, we determine the manner in which a and ϕ approach their limiting values far from the center of a single discommensuration. The results verify the oscillatory behavior found in the numerical solutions of the differential Eqs. (3.16) and (3.17), and are used in Sec. VIII to determine the asymptotic interaction of discommensurations.

We take the single discommensuration to be centered at $x=0$ and apply the conditions of Eqs. (3.15). On defining

$$a(x)=a_c+\tilde{a}(x) \ ,$$

$$\phi(x)=\begin{cases}\tilde{\phi}(x), & x<<-1 \ , \\ \tilde{\phi}(x)+\frac{2}{3}\pi, & x>>1 \ ,\end{cases} \tag{7.1}$$

we find the linearized equations satisfied by $\tilde{a}$ and $\tilde{\phi}$:

$$-2\gamma\tilde{a}''-4\gamma a_c\tilde{\phi}'+(2\gamma+2v-6a_c+6a_c^2)\tilde{a}=0 \ , \tag{7.2}$$

$$-2\gamma a_c^2\tilde{\phi}''+4\gamma a_c\tilde{a}'+9a_c^3\tilde{\phi}=0 \ . \tag{7.3}$$

These equations are valid for both $x\rightarrow+\infty$ and $x\rightarrow-\infty$; because $a(x)$ is symmetric about $x=0$ whereas $\phi(x)-\frac{1}{3}\pi$ is antisymmetric, we need examine only the former case. Inspection shows that the decay constants of $\tilde{a}$ and $\tilde{\phi}$ must be identical; substitution of

$$\tilde{a}=\mathfrak{a}e^{-\alpha x} \ ,$$
$$\tilde{\phi}=\Phi e^{-\alpha x} \ , \tag{7.4}$$

gives, for the ratio of the amplitudes,

$$\frac{\mathfrak{a}}{\Phi}=\frac{9a_c^2-2\gamma a_c\alpha^2}{4\gamma\alpha} \ , \tag{7.5}$$

and, for the mutual decay constant α, the quartic equation

$$(\gamma\alpha^2)^2+(6\gamma+2v-6a_c)(\gamma\alpha^2)+\tfrac{9}{4}a_c(-4\gamma-4v+3a_c)=0 \ . \tag{7.6}$$

The results Eqs. (7.5) and (7.6) are valid for all values of γ and v but are of interest to us only for those pairs such that the free energy of the state containing a single discommensuration equals the free energy of the commensurate state (and is less than the free energy of the normal state). Near the triple point ($\gamma=\frac{1}{2}$), the discriminant $\mathfrak{D}$ of the above equation (viewed as a quadratic equation in $\gamma\alpha^2$) is negative; to lowest order,

$$\alpha^2=3\pm 2i(-6v)^{1/2} \ . \tag{7.7}$$

The discriminant remains negative until $\gamma=\bar{\gamma}=6.155\pm0.005$, at which point it vanishes; it is positive for $\gamma>\bar{\gamma}$:

$$\mathfrak{D}<0, \ \tfrac{1}{2}<\gamma<\bar{\gamma} \ , \tag{7.8}$$

$$\mathfrak{D}>0, \ \bar{\gamma}<\gamma \ . \tag{7.9}$$

Note that, in agreement with the results of Sec. V, the decay is purely exponential at the triple point.

In the case $\frac{1}{2}<\gamma<\bar{\gamma}$, both values of α^2 are complex and hence a and ϕ display damped oscillations as they approach their limiting values, in agreement with the numerical results. The asymptotic behavior is

$$\tilde{a}=\tfrac{1}{2}\mathfrak{a}e^{-\alpha x}+\text{c.c.}=|\mathfrak{a}|\exp(-\alpha_1 x)\cos(\alpha_2 x-\psi_a) \ , \tag{7.10}$$

$$\tilde{\phi}=\tfrac{1}{2}\Phi e^{-\alpha x}+\text{c.c.}=|\Phi|\exp(-\alpha_1 x)\cos(\alpha_2 x-\psi_\phi) \ , \tag{7.11}$$

where $\alpha=\alpha_1+i\alpha_2$ is the root for Eq. (7.6) with positive real and imaginary parts. The relative amplitude and phase are given by Eq. (7.5) and

$$\mathfrak{a}/\Phi=|\mathfrak{a}|/|\Phi|\exp(i\psi_a-i\psi_\phi) \ ; \tag{7.12}$$

the absolute amplitudes and phases can be determined only from the numerical solutions of the differential equations.

In the case $\bar{\gamma}<\gamma$, both values of α^2 are real and, as must be the case, both are found to be positive; the desired decay constant is the positive root of the smaller value of α^2. The ratio of the amplitudes, as determined from Eq. (7.5), is negative for all $\gamma>\bar{\gamma}$, in agreement with the numerical result that a and ϕ approach their limiting values from opposite sides.

The real and imaginary parts of the decay constant are given as functions of γ in Fig. 9. The absolute value of the imaginary part is zero for $\gamma=\frac{1}{2}$, increases to a maximum of $\sim$1.0 at $\gamma\sim2$ and then decreases to zero at $\gamma\sim6.155$; the "half-period" of the oscillations, $\pi/|\text{Im}\alpha|$, is found to be in good agreement with that estimated from the numerical solutions of Sec. IV—for $\gamma=2$, the values are 3.142 and 3.125 ±0.031, respectively. For $\gamma\gtrsim6.155$, the imaginary part is zero and there are two, real decay constants. The smaller decay constant gradually decreases to the value $\frac{3}{4}\pi$ of the phase-only discommensuration as $\gamma\rightarrow\infty$. The larger decay constant increases without limit as $\gamma\rightarrow\infty$, but no significance can be attached to this result, for the correction to the leading term is proportional to the square of the leading term as soon as the larger decay constant is more than twice the smaller. There is no suggestion of a rapidly varying term in the numerical solutions of the differential equations (see Figs. 4 and 5).

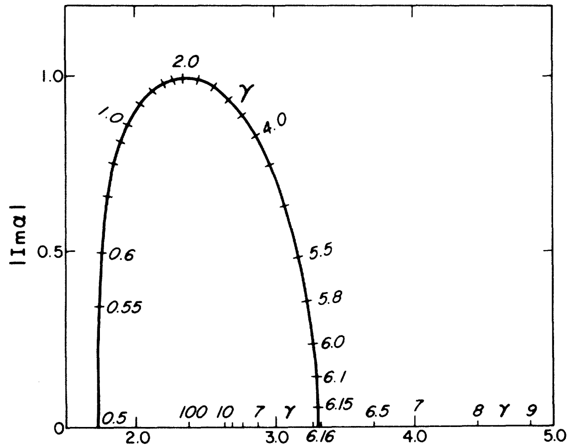


FIG. 9. Real and imaginary parts of the decay constants as functions of γ. For $\frac{1}{2}<\gamma\lesssim6.155$, there are two complex decay constants given by $\text{Re}\alpha\pm i|\text{Im}\alpha|$; for $\gamma\gtrsim6.155$, there are two real decay constants.

VIII. ASYMPTOTIC INTERACTION OF DISCOMMENSURATIONS

The calculation of the asymptotic interaction of discommensurations proceeds along lines familiar from the theory of superconductivity[17–20] (where one calculates the interaction of vortices). One first determines pairs of parameters (γ, v) such that $F_{\text{single}}(\gamma, v)$, the free energy of the state containing a single discommensuration, is equal to $F_c(\gamma, v)$, the free energy of the commensurate state. For a given pair of parameter values, one then calculates $F_{\text{chain}}(\gamma, v) - F_c(\gamma, v)$, the free energy of the state containing a chain of discommensurations relative to the free energy of the commensurate state; to obtain analytical results, it is necessary to assume that the discommensurations are widely separated. If the difference is negative, the chain of discommensurations has a lower free energy than a single discommensuration, and the transition from the commensurate state to the incommensurate state is discontinuous (i.e., of first order); the interaction is called attractive. If it is positive, the transition is of second order and the interaction is called repulsive. One can view this procedure as a calculation of the interaction energy $F_{\text{int}}(\gamma, v)$ defined by

$$F_{\text{chain}}(\gamma, v) = F_c(\gamma, v) + N[F_{\text{single}}(\gamma, v) - F_c(\gamma, v)] + F_{\text{int}}(\gamma, v) \ ,$$

for the second term on the right-hand side vanishes.

The free energy of the chain of discommensurations is

$$F_{\text{chain}} = F_c + NF_0 \int_{-X}^{X} [f(x;\gamma, v) - f_c(\gamma, v)]\, dx \ , \tag{8.1}$$

where f and f_c are given by Eqs. (3.13) and (3.5), N is the number of discommensurations in the sample and $2X$ is the length of each; we have focused attention on one discommensuration—the conditions of Eqs. (3.14) apply.

By assumption, the discommensurations of the chain are widely separated (i.e., $X >> 1$) so that, within each, the functions a and ϕ (the latter $\operatorname{mod}\frac{2}{3}\pi$) are very nearly equal to the corresponding functions a_0 and ϕ_0 for a single discommensuration, centered at $x=0$, for which the conditions (3.15) apply. We therefore write

$$\begin{aligned} a(x) &= a_0(x) + a_1(x) \ , \\ \phi(x) &= \phi_0(x) + \phi_1(x) \ , \end{aligned} \tag{8.2}$$

and expand $f(x)$ in the perturbations a_1 and ϕ_1. For a reason to become clear later, it is necessary to go to second order:

$$f(x) = f_0(x) + f_1(x) + f_2(x) + \cdots \ , \tag{8.3}$$

where the subscripts denote the orders of the terms; $f_0(x)$ is $f(x)$ with a and ϕ replaced by a_0 and ϕ_0.

Now, in the general case, we have no analytical results for even the zero-order functions a_0 and ϕ_0, much less the perturbations a_1 and ϕ_1. We therefore go through a sequence of manipulations whose purpose is to express the integral in Eq. (8.1) as a quantity evaluated at the ends ($x = \pm X$) of the discommensuration, so that both sets of functions are required only in a region far from the center of all discommensurations; only in such a region can analytical results be obtained.

The first-order term $f_1(x)$ is easily transformed to

$$f_1(x) = 2\gamma[a_0'a_1 + a_0^2(\phi_0' - 1)\phi_1]' \ , \tag{8.4}$$

with the help of the differential Eqs. (3.16) and (3.17) satisfied by a_0 and ϕ_0. To transform the second-order term $f_2(x)$, the linearized equations for a_1 and ϕ_1

$$-2\gamma a_1'' + [2\gamma(\phi_0' - 1)^2 + 2v - 6a_0\cos 3\phi_0 + 6a_0^2]a_1 + 4\gamma a_0(\phi_0' - 1)\phi_1' + (9a_0^2 \sin 3\phi_0)\phi_1 = 0 \ , \tag{8.5}$$

$$-2\gamma a_0^2\phi_1'' - 4\gamma a_0 a_0'\phi_1' + (9a_0^3\cos 3\phi_0)\phi_1 - 4\gamma a_0(\phi_0' - 1)a_1' + \{-4\gamma[a_0(\phi_0' - 1)]' + 9a_0^2\sin 3\phi_0\}a_1 = 0 \ , \tag{8.6}$$

are sufficient, for the corrections to Eqs. (8.5) and (8.6) contribute only to f_3 and higher-order terms. Multiplying the left-hand sides of Eqs. (8.5) and (8.6) by $-\frac{1}{2}a_1$ and $-\frac{1}{2}\phi_1$ respectively, and adding the results to our expression for f_2, we obtain an expression of the desired form

$$f_2(x) = \gamma[a_1a_1' + a_0^2\phi_1\phi_1' + 2a_0(\phi_0' - 1)a_1\phi_1]' \ . \tag{8.7}$$

It remains to transform the integral

$$\int_{-X}^{X} [f_0(x) - f_c]\, dx \ .$$

Now, by assumption, γ and v are such that

$$\int_{-\infty}^{\infty} [f_0(x) - f_c]\, dx = 0 \ , \tag{8.8}$$

and hence

$$\int_{-X}^{X} [f_0(x) - f_c]\, dx = -\int_{-\infty}^{-X} [f_0(x) - f_c]\, dx - \int_{X}^{\infty} [f_0(x) - f_c]\, dx \ . \tag{8.9}$$

The functions a_0 and ϕ_0 are therefore required only in the asymptotic regions $x < -X$ and $x > X$. We substitute $a_0(x) = a_c + \tilde{a}(x)$ in both integrals, $\phi_0(x) = \tilde{\phi}(x)$ in the first, and $\phi_0(x) = \frac{2}{3}\pi + \tilde{\phi}(x)$ in the second; in this calculation as well, it is necessary to retain second-order terms. The zero-order term cancels against the term f_c, and the first-order term reduces to $-2\gamma a_c^2 \tilde{\phi}'$ because of the differential equation satisfied by a_0. For the reduction of the second-order term, it is sufficient to use the linearized Eqs. (7.2) and (7.3) for $\tilde{a}$ and $\tilde{\phi}$. Multiplying the left-hand sides of Eqs. (7.2) and (7.3) by $-\frac{1}{2}\tilde{a}$ and $-\frac{1}{2}\tilde{\phi}$, respectively, and adding the results to our expression for the second-order term, we find the following expression for $f_0(x) - f_c$ in the asymptotic regions:

$$f_0(x) - f_c = \gamma(-2a_c^2\tilde{\phi} + \tilde{a}\tilde{a}' + a_c^2\tilde{\phi}\tilde{\phi}' - 2a_c\tilde{a}\tilde{\phi})' \ , \tag{8.10}$$

On combining our results and using

$$\tilde{a}(\pm\infty) = 0, \quad \tilde{\phi}(\pm\infty) = 0 \ , \tag{8.11}$$

we arrive at an expression of the desired form

$$\begin{aligned} F_{\text{chain}} - F_c = \gamma N F_0 [\, & 2a_0' a_1 + 2a_0^2(\phi_0' - 1)\phi_1 \\ & + a_1 a_1' + a_0^2 \phi_1 \phi_1' + 2a_0(\phi_0' - 1) a_1 \phi_1 \\ & - 2a_c^2\tilde{\phi} + \tilde{a}\tilde{a}' + a_c^2\tilde{\phi}\tilde{\phi}' - 2a_c\tilde{a}\tilde{\phi}\,]_{-X}^{X} \end{aligned} \tag{8.12}$$

to second order in a_1, ϕ_1, $\tilde{a}$, and $\tilde{\phi}$. This cumbersome expression can be reduced by (i) noting that $\tilde{\phi}(\pm X) = -\phi_1(\pm X)$, (ii) replacing a_0 by $a_c + \tilde{a}$, and (iii) using the fact that a_0, a_1, ϕ_0', and ϕ_1' are even functions of x whereas a_0', a_1', and ϕ_1 are odd; to second order in small quantities,

$$\begin{aligned} F_{\text{chain}} - F_c = 2\gamma N F_0 [\, & (\tilde{a} + a_1)\tilde{a}' + (\tilde{a}' + a_1')a_1 \\ & - 2a_c(\tilde{a} + a_1)\phi_1 + a_c^2(\tilde{\phi}' + \phi_1')\phi_1\,] \ , \end{aligned} \tag{8.13}$$

where all quantities are evaluated at $x = X$. Note that the two first-order terms have combined to yield higher-order terms; this is the reason that it was necessary to carry out the calculations to second order.

To obtain the perturbations, we note that, to lowest order [which is all that is needed in Eq. (8.13)], a and ϕ must be constants plus linear superpositions (with unit coefficients) of the solutions for the two single discommensurations on either side; that is, for $|x - X| << X$,

$$a(x) = a_0(x) + a_0(x - 2X) + B_a \ , \tag{8.14}$$

$$\phi(x) = \phi_0(x) + \phi_0(x - 2X) + B_\phi \ , \tag{8.15}$$

The requirement that $\phi(X) = \frac{2}{3}\pi$ gives $B_\phi = 0$, since $\phi_0(X) + \phi_0(-X) = \frac{2}{3}\pi$. To obtain B_a we note that, in the region of validity of Eqs. (8.14) and (8.15), Eqs. (8.5) and (8.6) become

$$-2\gamma a_1'' - 4\gamma a_c \phi_1' + (2\gamma + 2v - 6a_c + 6a_c^2)a_1 = 0 \ , \tag{8.16}$$

$$-2\gamma a_c^2 \phi_1'' + 4\gamma a_c a_1' + 9a_c^3 \phi_1 = 0 \ , \tag{8.17}$$

which are identical to Eqs. (7.2) and (7.3) for $\tilde{a}$ and $\tilde{\phi}$. Hence $B_a = -a_c$ and the perturbations are

$$a_1(x) = a_0(x - 2X) - a_c \ , \tag{8.18}$$

$$\phi_1(x) = \phi_0(x - 2X) \ . \tag{8.19}$$

These results are nothing but the obvious

$$a(x) - a_c = [a_0(x) - a_c] + [a_0(x - 2X) - a_c] \ ,$$

$$\phi(x) - \tfrac{2}{3}\pi = [\phi_0(x) - \tfrac{2}{3}\pi] + [\phi_0(x - 2X) - 0] \ .$$

Our result Eq. (8.13) then reduces to, since $F_c = F_{\text{single}}$,

$$F_{\text{chain}} - F_{\text{single}} = 4\gamma N F_0(\tilde{a}'\tilde{a} - a_c^2\tilde{\phi}'\tilde{\phi} + 2a_c\tilde{a}\tilde{\phi}) \ . \tag{8.20}$$

In the case $\frac{1}{2} < \gamma < \bar{\gamma}$, where a and ϕ display damped oscillations, the free energy of the chain is obtain by substitution of Eqs. (7.10) and (7.11) into Eq. (8.20):

$$\frac{(F_{\text{chain}} - F_{\text{single}})}{\gamma N F_0} = (-\alpha\mathcal{A}^2 + \alpha a_c^2\Phi^2 + 2a_c\mathcal{A}\Phi)e^{-2\alpha X} + \text{c.c.} \ ; \tag{8.21a}$$

an alternate form is

$$\frac{F_{\text{chain}} - F_{\text{single}}}{2\gamma N F_0 |\Phi|^2} = \exp(-2\alpha_1 X) \left| -\alpha\left(\frac{\mathcal{A}}{\Phi}\right)^2 + a_c^2\alpha + 2a_c\left(\frac{\mathcal{A}}{\Phi}\right) \right| \cos(2\alpha_2 X + \psi) \ , \tag{8.21b}$$

where $\alpha_1 = \text{Re}\,\alpha$, $\alpha_2 = |\text{Im}\,\alpha|$, and ψ is an undetermined phase. The free-energy difference is an exponentially damped, oscillatory function of X, the interaction is attractive (because F_{chain} is less than F_{single} for some finite values of X) and the incommensurate-commensurate transition is of first order.

It is of interest to examine the above results in the vicinity of the triple point where simple results can be obtained. To the order given,

$$\alpha_1=\sqrt{3},\quad \alpha_2=(-2v)^{1/2}\ ,$$
$$\mathcal{A}/\Phi=\sqrt{3}-2i(-2v)^{1/2}\ , \tag{8.22}$$
$$-\alpha(\mathcal{A}/\Phi)^2+a_c^2\alpha+2a_c\mathcal{A}/\Phi=6i(-2v)^{1/2}\ .$$

From the analytical solutions of Eqs. (5.3) and (5.6), we obtain for a single discommensuration ($C=1$) at the triple point the result

$$\tilde{\phi}=-\tfrac{1}{2}\sqrt{3}e^{-\sqrt{3}x}\ , \tag{8.23}$$

which verifies that $\alpha_1=\sqrt{3}$ and gives, to a sufficient approximation, $\Phi=-\frac{1}{2}\sqrt{3}$. From Eq. (8.21a), we obtain

$$F_{\text{chain}}-F_{\text{single}}=\tfrac{1}{2}9NF_0(-2v)^{1/2}e^{-2\sqrt{3}X}\times\sin[2(-2v)^{1/2}X]\ . \tag{8.24}$$

On the other hand, the analytical result Eq. (6.6) reduces to the limit $X \gg 1$ to

$$F_{\text{chain}}-F_{\text{single}}=-18vNF_0Xe^{-2\sqrt{3}X} \tag{8.25}$$

on the line $v+\frac{3}{2}(\gamma-\frac{1}{2})=0$ where $F_{\text{single}}=F_c$ to first order. The results Eqs. (8.24) and (8.25) are identical to leading order; comparison of them provides insight into the nature of the expansion in Sec. VI and shows why the method used there failed to reveal the first-order transition.

To illustrate our results, we have plotted, in Figs. 10–12, the free energy [calculated from Eqs. (3.2) and (3.13) using the solutions of Eqs. (3.16) and (3.17) with the boundary conditions (3.14)] as a function of the half-period X of the discommensuration chain. Because our results differ from those of previous workers, we have chosen to make a direct comparison with some published curves. In Fig. 10, we have plotted the free energy (relative to the normal state) versus $\frac{1}{3}\pi/X$ (this quantity is identical to the quantity δ of Ref. 8) for $\gamma=\frac{125}{81}$ and for three values of v; the parameters were chosen so that Fig. 10 is directly comparable (apart from a one-part-in-80 change in the scale of the ordinate) with Fig. 1 of Ref. 8. There is no evidence for oscillations in the free energy. By plotting the free energy relative to the commensurate state (rather than the normal state), one can achieve a 20-fold change in the scale of ordinate for the same values of v; on this scale, there is evidence for fine structure in the curves. To provide convincing evidence for the structure, we have plotted in Fig. 11 the free energy versus $\frac{1}{3}\pi/X$ for three different values of v; the scale of the ordinate differs by a factor of 200 from that of Fig. 10. Although the oscillations are not visible, there is clearly a local minimum in the curve for $v=-3.48$.

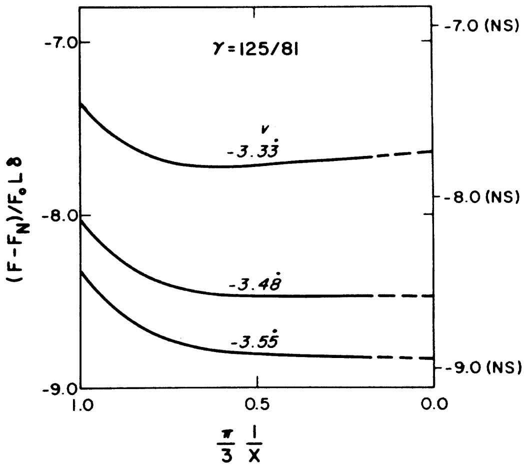


FIG. 10. Free energy relative to the normal state vs $\frac{1}{3}\pi/X$ for $\gamma=\frac{125}{81}$ and three values of v. The ordinates at the right-hand side of the graph are those of Ref. 8.

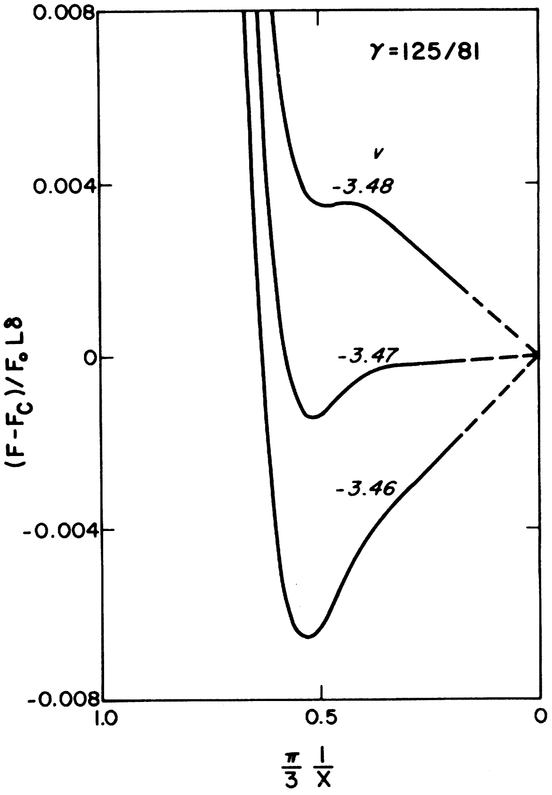


FIG. 11. Free energy relative to the commensurate state versus $\frac{1}{3}\pi/X$ for $\gamma=\frac{125}{81}$ and three values of v more closed space than those of Fig. 10.

Finally, in Fig. 12 we have plotted the free energy for even more closely spaced values of v; the scale of the ordinate differs from that of Fig. 10 by a factor of 10^3. It is clear that the incommensurate-commensurate transition for $\gamma=\frac{125}{81}$ takes place not at $v=-3.47069\cdots$, for which value the free energy of the state containing a single discommensuration equals that of the commensurate state, but rather at $v=-3.47186\pm0.00003$.

We have made calculations similar to those described in the previous paragraph for the additional cases $\gamma=0.55$, 1.0, 2.0, 4.0, and 6.0. Again only small differences between the two critical values of v were found; the relative difference had a maximum value of five parts in 10^4 and decreased toward both the triple point and the multicritical point.

The attractive interaction clearly has a negligible consequence with respect to the location of the incommensurate-to-commensurate phase boundary and one might incorrectly conclude that the transition, though of first order, is "weakly" so. In fact, for $\gamma=2$, the half-period X at the transition is only twice its minimum value of $\frac{1}{3}\pi$. Another indication that the transition should not be viewed as weakly first-order (except near the triple point and near the multicritical point) is that the change in the slope of the free energy at the transition is not small: For $\gamma=2$,

$$\frac{\partial}{\partial v}\left[\frac{F-F_c}{F_0L\delta}\right]=-1.24\ ,$$

which is to be compared with

$$\frac{\partial}{\partial v}\left[\frac{F_c-F_N}{F_0L\delta}\right]=a_c^2=8.53\ ;$$

that is, the discontinuity in the entropy at the transition is not small compared to the entropy in the commensurate state (relative to the normal state) just below the transition.

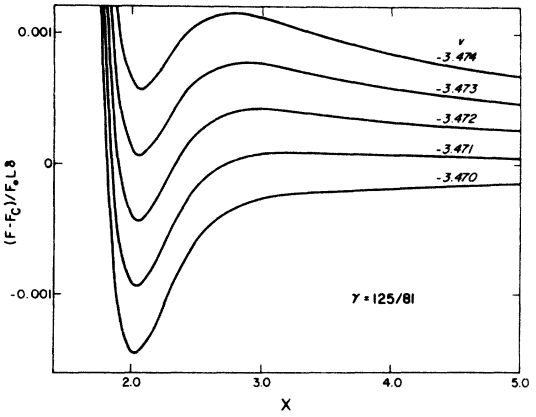


FIG. 12. Free energy relative to the commensurate state vs X for $\gamma=\frac{125}{81}$ and v close to -3.47.

The additional calculations referred to above provide some confirmation for one's expectation that the half-period X at the transition increases to infinity as both the triple point and the multicritical point are approached, so that the transition becomes more nearly second order in these limits. For $\gamma=0.55$, 1.0, $\frac{125}{81}$, 2.0, 4.0, and 6.0, the values of X are 4.59, 2.24, 2.05, 2.04, 2.46, and 5.4, respectively.

We should point out that the attractive interaction found here comes about in a way quite different from that found in the theory of superconductivity (where the interaction is attractive at $T=T_c$ for type-I materials and, for $T<T_c$, for some type-II materials as well[19]). In the latter case, the free-energy expression involves two terms, a positive term involving the superfluid velocity and a negative term involving the order parameter. Near the transition temperature, both terms decay in a purely exponential manner but with different decay lengths; the sign of the free energy therefore depends on relative magnitudes of the decay lengths. In contrast, the attractive interaction found here is due entirely to the oscillatory behavior of the amplitude and the phase.

In the other case $\bar{\gamma}<\gamma$, the decay length α is real and Eq. (8.20) becomes

$$\frac{F_{\text{chain}}-F_{\text{single}}}{4\gamma NF_0|\Phi|^2}=e^{-2\alpha X}\left[-\alpha\left[\frac{\mathcal{A}}{\Phi}\right]^2+2a_c\left[\frac{\mathcal{A}}{\Phi}\right]+a_c^2\alpha\right]\ . \tag{8.26}$$

We find, on evaluating the square bracket in Eq. (8.26) for (γ,v) values such that $F_{\text{single}}=F_c$, that it is positive for all $\gamma>\bar{\gamma}$ (though it approaches zero for $\gamma\to\bar{\gamma}$). Hence $F_{\text{chain}}>F_{\text{single}}$, the interaction is repulsive and the incommensurate-commensurate transition is second order.

These conclusions apply, of course, only to widely separated discommensurations and there is the possibility that the free-energy difference, while positive for large separations, might vanish for small separations. Check calculations made for $\gamma=6.16$ and 100.0 show no such behavior, however, and we conclude that the transition is second order for all $\gamma>\bar{\gamma}$.

ACKNOWLEDGMENTS

This research was supported by the Natural Sciences and Engineering Research Council of Canada.

APPENDIX

The procedure used to obtain the first integrals Eqs.(5.1) and (5.2) of Eqs. (3.16) and (3.17) may be applicable to other problems and so we provide an outline of it.

We assume that the following statements hold at the triple point, whatever the separation between the discommensurations: (i) there exist first integrals of the form

$$a' - U(a,\phi) = 0 \ , \qquad \text{(A1)}$$

$$\phi' - V(a,\phi) = 0 \ , \qquad \text{(A2)}$$

(ii) the free-energy difference vanishes, (iii) the free-energy difference can be written in a form such that the integrand vanishes for all x, and (iv) in the latter form, the integrand is a function times the left-hand side of one of Eqs. (A1) and (A2).

At the triple point, the free-energy expression Eqs. (3.2) and (3.13), the differential Eqs. (3.16) and (3.17) and the first integral Eq. (3.18) reduce to

$$F - F_c = NF_0 \int_{-X}^{X} [\tfrac{1}{2}(a')^2 + \tfrac{1}{2}a^2(\phi'-1)^2 - a^3\cos 3\phi + \tfrac{1}{2}a^4]\, dx \ , \qquad \text{(A3)}$$

$$-a'' + a(\phi'-1)^2 - 3a^2\cos 3\phi + 2a^3 = 0 \ , \qquad \text{(A4)}$$

$$-a^2\phi'' - 2aa'(\phi'-1) + 3a^3\sin 3\phi = 0 \ , \qquad \text{(A5)}$$

$$-\tfrac{1}{2}(a')^2 - \tfrac{1}{2}a^2(\phi')^2 + \tfrac{1}{2}a^2 - a^3\cos 3\phi + \tfrac{1}{2}a^4 = \mathcal{G} \ . \qquad \text{(A6)}$$

To eliminate the quadratic terms in the derivatives from Eq. (A3), we write

$$(a')^2 = \omega(a')^2 - (1-\omega)aa'' + (1-\omega)(aa')' \ , \qquad \text{(A7)}$$

where ω is to be determined. In the first term in Eq. (A7) we use Eq. (A6) and in the second we use Eq. (A4); the third term integrates to zero by virtue of the boundary condition $a'(\pm X) = 0$. We thus obtain

$$F - F_c = NF_0 \int_{-X}^{X} [-\omega a^2(\phi'-1) - \tfrac{1}{2}(5\omega-1)a^3\cos 3\phi + \tfrac{1}{2}(3\omega-1)a^4 - \omega\mathcal{G}]\, dx \ . \qquad \text{(A8)}$$

As a trial expression for ϕ', we therefore take

$$\phi' = 1 - \tfrac{1}{2}(5-\omega^{-1})a\cos 3\phi + \tfrac{1}{2}(3-\omega^{-1})a^2 - \mathcal{G}/a^2 \ . \qquad \text{(A9)}$$

To determine a trial expression for a', we can substitute Eq. (A9) into the first integral [Eq. (A6)]; another method is to substitute Eq. (A9) into Eq. (A5). So that the two expressions have the same form, it is necessary to choose $\omega = \frac{1}{3}$ and to assume that $\mathcal{G} = 0$. We are thus led to the trial expressions given by Eqs. (5.1) and (5.2).

Substitution of Eqs. (5.1) and (5.2) into Eqs. (A4) and (A5) verifies that they are first integrals. Moreover, the conditions

$$a'(0) = a'(X) = a'(-X) = 0$$

are, because of the structure of Eq. (5.1), consequences of the conditions

$$\phi(-X) = 0, \quad \phi(0) = \tfrac{1}{3}\pi, \quad \phi(X) = \tfrac{2}{3}\pi \ ;$$

hence Eqs. (5.1) and (5.2) have the full generality of Eqs. (A4) and (A5).

In conclusion, we point out that the constant $\mathcal{G}$ in the first integral [Eq. (A6)] is zero, as can be verified by substitution. Hence the free energies of the incommensurate and commensurate states are equal at the triple point, whatever the value of $2X$, the distance between discommensurations.

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