Phenomenological Ginzburg-Landau theory of charge-density-wave spectra

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A phenomenological Ginzburg-Landau theory of charge-density waves is presented. It yields, in the absence of pinning impurities, a manifold of stable (equal-energy) states that are independent of the phase of the wave. The pinning of these waves by impurities (both weak and strong pinning) is examined in detail and spectra for various impurity distributions are analyzed in detail. Strong dependence on the wave phase, change in harmonic content, and phase shifts are common features, in addition to the appearance of a continuous background. There is also a plethora of metastable states, many of which have energies close to the ground state. Comparison between the proposed theory and experiment in $NbSe_3$ is satisfactory.

I. INTRODUCTION

Charge-density waves (CDW) are a collective phenomenon observed in low-dimensional solids.[1–9] A strong electron-phonon coupling in those systems, together with particular features of the normal-state Fermi surface, lead to an oscillatory (static) distribution of the electron charge, to which a periodic lattice distortion (PLD) is generally associated. In most cases the CDW and the PLD are incommensurable with the original crystal lattice of the solid. The presence of defects and impurities pins the CDW to the crystal lattice. Under these conditions it cannot contribute to the charge-transport processes, in particular to the electrical conductivity. The presence of a strong enough electric field depins the CDW, makes it "mobile" and, therefore, increases sizably and in a nonlinear fashion the conductivity of the solid.[3,7] This interesting nonlinear conduction process has been the subject of very extensive investigations, both theoretical[1,2,10–20] and experimental.[9,7,21]

In addition to this dynamic effect, the presence of pinning impurities, located at random positions in the lattice, produces a static structural phenomenon (i.e., not a transport phenomenon) which has been also examined in great detail.[9] There are mutually inconsistent conditions—frustration—arising from the different geometrical requirements of the CDW, with its own intrinsic periodicity, and from the location of the pinning impurities throughout the crystal. In its attempt to achieve equilibrium, i.e., a minimum of the free energy, the system encounters a variety of long-lived metastable states, and may be trapped (for long times, even indefinitely) in a nonequilibrium state. Concurrently, the structure of the equilibrium state is drastically modified by the presence of the pinning impurities and exhibits very complex properties.

A vast literature, concerned with theoretical models and calculations for these effects, is in existence. It is thoroughly and clearly summarized in the review article by Grüner,[7] and the collection of articles in the book by Gor'kov and Grüner.[8] They range from classical or semiclassical models to quantum-mechanical formulations, and from analytic solutions of nonlinear equations to numerical simulations. They, however, either lack the inherent simplicity of the variational approach proposed here, or are not susceptible (with a few exceptions[22]) to the quantitative description of the many metastable states introduced by impurity pinning.

It is the purpose of this contribution to formulate a phenomenological model that describes these static phenomena where both the amplitude and the phase modification of the CDW in the presence of impurities are treated in a consistent scheme. In particular it is important to obtain a theory that, in the absence of impurities, yields a CDW state whose energy is phase independent, i.e., a totally mobile (incommensurable) CDW. Pinning impurities would then influence, in varying degrees, the *phase* and the *amplitude* of the CDW, and simultaneously bring to the problem their own geometrical and structural features.

The phenomenological theory proposed here is in the spirit of the Ginzburg-Landau model.[23,24] It applies to one-dimensional CDW's. The natural order parameter for such systems is the *difference* in electronic charge density between the state under study and the normal state, i.e., that state in which the charge distribution is identical in every primitive cell. It is a position-dependent order parameter. Other possible order parameters, such as the local energy band gap and the PLD, are simply proportional to the local electronic charge density. Free-energy contributions of the elastic energy of the PLD and the electron-phonon interactions are assumed to be taken into account in the free-energy expression in an implicit way.

In Sec. II, the free-energy expression for a single chain containing an arbitrary number of impurities is proposed. Section III contains the solution of the model in the absence of impurities and a brief discussion of the behavior of the order parameter, the CDW wavelength, and the

excitation modes. The response of the chain to impurities, both in the normal state and in the condensed phase is discussed in Sec. IV. Finally, Sec. V contains the conclusions.

II. THE MODEL

The free energy is expanded in the customary fashion, up to fourth-order terms

$$F = F_2 + F_4 + F_i \ . \tag{1}$$

Each term contains both short-range and long-range contributions in the single space variable x or, equivalently in the Fourier-transform variable q. The only long-range contribution—small q—is normally caused by the Coulomb interaction.

If $n(x)$ denotes the order parameter—number of electrons per unit length—the most general form of the second-order term with complete translational invariance is

$$F_2 = \frac{1}{2}\int\int f(x-y)n(x)n(y)dxdy \ ,$$

where $f(\eta)$ is an even function of η which may contain δ functions and their derivatives. For the sake of clarity, F_2 will be written in terms of the q variable

$$F_2 = (L/2)\sum_q f_q |\, n_q \,|^2 \ , \tag{2}$$

where

$$f_q = \int f(x)e^{iqx}dx \ ,$$
$$n(x) = \sum_q n_q e^{iqx} \ , \tag{3}$$

and L is the length of the chain. A reasonable choice for f_q is

$$f_q = a_1/q^2 + a_2 q^2 + a_3 \ , \tag{4}$$

where the first is a Coulomb-like term which prevents long-wavelength oscillations, and especially does not permit a charge transfer to the chain from outside ($n_{q=0} = 0$). The second is a derivative-in-x term which prevents very-short-wavelength oscillations. The simplicity of Eq. (2) implies that the transition from the normal to the CDW state occurs when in some region of q space f_q becomes negative. Therefore, it is useful to write f_q in the form

$$f_q = A\left(\frac{q}{Q_0} - \frac{Q_0}{q}\right)^2 + B \ , \tag{5}$$

where $Q_0 = (a_1/a_2)^{1/4}$ is the value of q for which f_q has its minimum. It is assumed that the two constants A and Q_0 are temperature independent, and that B varies linearly in T and changes sign at the transition temperature T_c

$$B = B'\ (T - T_c) \ .$$

The fourth-order term should be positive and short ranged. These conditions are satisfied by the simplest possible form

$$F_4 = (C/4)\int n(x)^4 dx \ . \tag{6}$$

Finally, the impurity contribution to the free energy is

$$F_i = \int V(x)n(x)dx = \sum_m \int U(x - R_m)n(x)dx \ , \tag{7}$$

where $U(x)$ is the potential of a single impurity, $V(x)$ is the sum of all impurity potentials, and R_m denotes the location of the mth impurity.

In the cases considered here all impurities are identical. Their potential is chosen to be a δ function [$U(x) = U_0\ \delta(x)$]. The strength of the potential U_0 and the positions of impurities along the chain R_m are, therefore, the only parameters necessary to describe the effect of impurities.

The free-energy functional F has one natural length scale ($2\pi/Q_0$), the ideal wavelength of the CDW. In addition, F does not contain the lattice constant as a parameter. The model is, therefore, a "continuum" model, and all lattice effects are ignored. This continuum approximation is appropriate for the current problem, but must be reassessed and changed when looking at other effects, such as the incommensurable-commensurable CDW phase transition.[7,25]

There are two independent dimensionless variables in the formulated problem. The first, $\beta = B/4A$, which is linearly proportional to the temperature, is the only parameter needed to describe the condensed phase in the absence of impurities. The other dimensionless variable, which gives the strength of the impurity potential, can be taken to be $u = U_0 Q_0 \sqrt{C/64A^3}$.

III. CDW PHASE WITHOUT IMPURITIES

A. The order parameter

Above the transition point, i.e., when $B > 0$, because all terms in F are non-negative, the order parameter is necessarily zero. When B becomes negative, the system can lower its energy if the order parameter assumes a nonzero value. There is a finite range of wave numbers in the interval between q_- and q_+,

$$q_\pm = Q_0\left(\sqrt{1+|\,\beta\,|} \pm \sqrt{|\,\beta\,|}\right) \ ,$$

where f_q is negative. For any q in this range n_q may have a finite amplitude. The numerically obtained solution of this problem indicates that the minimum-energy solution has a well-defined periodicity, i.e., a fundamental wave number Q—close in value to Q_0—together with its odd harmonics $3Q, 5Q, 7Q, \ldots$. The absence of even harmonics is closely linked with the absence in F, Eq. (1), of a third-order term in $n(x)$. Only one wave number Q

and its odd-order harmonics are nonzero; all other n_q, even when they are in the interval $q_- < q < q_+$ vanish, since nonvanishing n_q other than those mentioned above have the effect of increasing F_4 more than they cause F_2 to decrease.

Near the transition temperature, for B negative and small, the fundamental component of the order parameter is approximately given by

$$| n_Q | \approx \sqrt{| B | /3C} , \tag{8}$$

and the higher harmonics vary as

$$| n_{(2m+1)Q} | / | n_Q | \propto | \beta |^m , \tag{9}$$

for any $m \geq 1$. For a CDW peaked at the origin (i.e., n_Q is a positive real number), the third harmonic n_{3Q} is negative in sign [more generally sign of $n_{(2m+1)Q}$ is $(-1)^m$]. This has the effect of distorting the pure sinusoidal towards a square-wave form. As the temperature is lowered further, the harmonic content increases and the CDW wave form approaches to a true square-wave [i.e., $n_{(2m+1)Q}/n_Q \to (-1)^m/(2m+1)$ in the limit $B \to -\infty$].

It should be noted that, because of the increase of harmonic content with increasing $| B |$, the CDW wave number Q varies with temperature,

$$Q = Q_0(1 - \tfrac{5}{64}\beta^2) \quad \text{for} \quad | \beta | \ll 1, \tag{10}$$

$$Q \propto |\beta|^{-\frac{1}{4}} \quad \text{for} \quad | \beta | \gg 1. \tag{11}$$

With the assumption of a temperature-independent parameter Q_0, as it appears in (5), the wave number Q varies quadratically with $(T_c - T)$ near the transition temperature. This behavior does not conform well with experimental data[26,27] where it has been found that the variation of Q is linear in $(T_c - T)$. This variation has been interpreted as caused by the change of the nesting wave vector $2k_F$. This Fermi-surface change in turn is a result of the thermal change in occupation of the electronic bands, those responsible for the CDW transition.[26] Since the parameter Q_0, the "ideal" wave vector, is related to the nesting wave vector $2k_F$, the linear variation of the CDW wave vector Q can only be described in the current model if Q_0 is assumed to depend linearly on temperature. It should be stressed, however, that the two origins for the variation of Q are unrelated: one is caused by Fermi-surface effects, the second one by the nonlinear CDW effects.

B. Excitation modes

The formalism described above yields a CDW with complete phase independence. In other words, the charge-density distribution can be translated uniformly by any length without changing the total free energy of the system. This translation is a zero-energy excitation, the so-called $q = 0$ phason mode. It corresponds to a particular wave vector ($q = 0$) of a continuous branch of excitation modes, the phasons. Although only the $q = 0$ mode has zero excitation energy, the whole branch carries, for any wave vector, a low energy of excitation. The phasons are responsible for the electrical transport properties[7] associated with CDW's. It is of interest to investigate these excitation modes. The way to do that is to follow the prescription set up originally by Landau.[28] It consists of taking the second-order functional derivative of the free energy with respect to the electron density (a generalized inverse susceptibility tensor)

$$\Phi(x;x') = \frac{\delta^2 F}{\delta n(x)\delta n(x')} , \tag{12}$$

which, according to Eqs. (1)–(6), takes the form

$$\Phi(x;x') = f(x-x') + 3C\, n(x)^2\, \delta(x-x') , \tag{13}$$

and then determine its eigenvalues ω and eigenfunctions $\psi(x)$

$$\int \Phi(x;x')\psi(x')dx' = \omega\psi(x) . \tag{14}$$

In these equations $n(x)$ is the CDW that minimizes F, and has a *fixed* (but arbitrary) phase. The quantity Φ, as defined above, is symmetric and periodic[29]

$$\Phi(x;\ x') = \Phi(x + 2\pi/Q; x' + 2\pi/Q) . \tag{15}$$

Bloch's theorem then yields for the eigenfunction

$$\psi_{\alpha k}(x) = e^{ikx} u_{\alpha k}(x) , \tag{16}$$

where α is an index and $u_{\alpha k}(x)$ is a periodic function of x with period $2\pi/Q$. The quantity k is the wave vector of the excitation. The energy of the excitation[28,30] is proportional to the square root of the eigenvalue $\omega_{\alpha k}$. By taking an appropriate linear combination of $\psi_{\alpha k}$ and $\psi_{\alpha,-k}$, real-valued eigenfunctions can be obtained. A typical dispersion relation $\omega_{\alpha k}$ is shown in Fig. 1. The excitations corresponding to the lowest band ($\alpha = 0$) are phasons. For the special case of $k = 0$, $\omega_{0,k=0}$ is zero, and $\psi_{0,k=0}(x)$, which is proportional to $dn(x)/dx$, corresponds to the uniform translation of the CDW. As expected, $\omega_{0,k}$ has, for small values, a quadratic dependence on k. Thus, phason modes are very sensitive to applied external potentials, such as impurities (because of the low excitation energies). At the zone boundaries $k = \pm Q/2$, all bands, including the phasons, are degenerate in pairs, i.e., all bands "stick together." It is, therefore, possible (although not desirable) to describe all modes in a double-zone scheme, in the interval $-Q < k \leq Q$.

In addition to the phason there are infinitely many other modes, each with finite energies throughout the zone. They all involve amplitude modulation and are generically called "amplitudons." The lowest amplitudon mode ($\alpha = 1$, $k = 0$) has an eigenvalue $\omega_{1,k=0}$ which varies linearly with B, i.e., an "excitation gap" which is proportional to $(T_c - T)$ in the vicinity of T_c. Therefore, low-energy amplitudons may play an important role in the response of the CDW system to impurities near the transition temperature. At low enough temperatures (large and negative B) the importance of the amplitudons decreases, their energy increases, and there are level in-

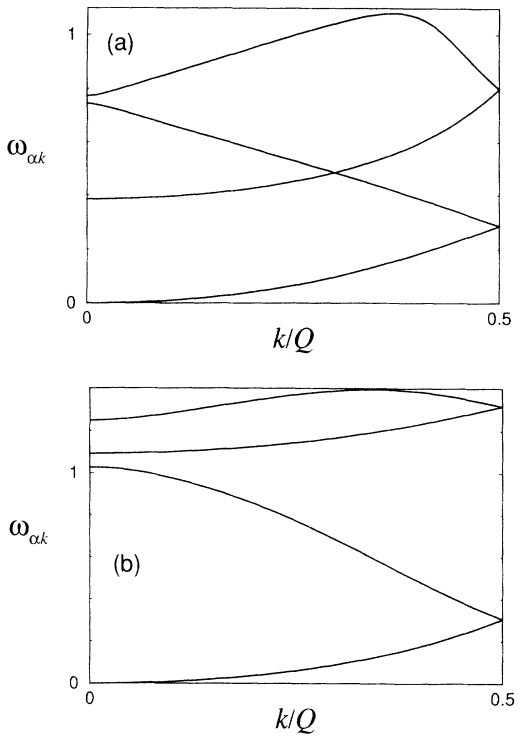

FIG. 1. The dispersion relation (spring constant *versus* wave vector) for the collective excitations: (a) $\beta = -0.2$ and (b) $\beta = -0.6$. Only the lowest four modes are shown in each case.

versions which result in a spectrum of nonintersecting pairs of "stuck-together" bands [see Fig. 1(b)].

IV. EFFECT OF IMPURITIES

The linear response of the charge density to a given impurity distribution can be found by solving

$$\int \Phi(x;x')\ \delta n(x')\ dx' = -\ V(x)\ , \qquad (17)$$

where $\delta n(x)$ is the difference between the charge density of the system and its constant, unperturbed value. It is evident from the form of (17) that the small eigenvalues of Φ play a crucial role in the behavior of the perturbed charge density. In the *normal state*, since $n(x) = 0$, the inverse susceptibility takes the form

$$\Phi(x;x') = f(x-x')\ ,$$

and the eigenvalues of Φ are simply $\omega_q = f_q$ for each (plane-wave) eigenstate $\psi_q(x)$. The lowest eigenvalue corresponds to $q = Q_0$ and, therefore, the wave vector Q_0 "shapes" the charge distribution. In the CDW state, on the other hand, the charge density is crucially affected by the phason and low-energy amplitudon modes.

(a) Impurities in the normal state. In the normal state, the presence of an impurity causes a screening-charge "pileup" in its environment. There are two regimes where the distribution of the charge behaves differently. If the temperature is high, $\beta \geq 1$, the charge density (in the linear approximation) decays exponentially. For a single impurity at the origin

$$n(x) = \frac{-U_0}{8A\sqrt{\beta(\beta-1)}}\left(\frac{1}{\xi_-}e^{-|x|/\xi_-} - \frac{1}{\xi_+}e^{-|x|/\xi_+}\right)\ ,$$

where

$$1/\xi_\pm = Q_0\left(\sqrt{\beta} \mp \sqrt{\beta-1}\right)\ .$$

In the physically more interesting region close to the transition temperature, $0 < \beta < 1$, Friedel oscillations accompany an exponential decay of charge density

$$n(x) = \frac{-U_0 Q_0}{2A\sin 2\varphi}e^{-Q_0 \sin\varphi|x|}\cos(Q_0\cos\varphi\ |\ x\ |\ +\varphi)\ ,$$

where φ is related to β by

$$\sin^2\varphi\ =\ \beta\ .$$

Therefore, a small impurity causes oscillations whose amplitude and whose healing length

$$\xi\ =\ 1/\left(Q_0\sqrt{\beta}\right)$$

go to infinity as the transition point is approached. These oscillations are induced by the small value of the function f_q at the minimum, i.e., at $q = Q_0$. In other words, near the transition temperature, there is a giant peak in the susceptibility $\chi(q)$ of the coupled electron-phonon system in the neighborhood of $q = Q_0$. This behavior is a precursor to the CDW transition.[31]

(b) Impurities in the CDW phase: linear-response theory. The most important effect of impurities is the pinning of the phase of the CDW to a value determined by the sign of the impurity potential and impurity distribution. This phase is equal to the phase of the CDW for vanishingly small values of the impurity potential. The linear-response theory can then be applied to find the change in charge density δn_q in the presence of impurities. The results for a single impurity at the origin for two different temperatures are shown in Fig. 2. At large distances from the impurity, the CDW displays a phase shift which can be described by

$$n(x) = n_0(x+\gamma),\ x \to +\infty\ ,$$

$$n(x) = n_0(x-\gamma),\ x \to -\infty\ ,$$

where $n_0(x)$ is the zeroth-order pinned solution and γ is the amount of the phase shift in units of distance. The dominant feature in the spectra, which is the divergence of the response at the odd multiples of the fundamental wave vector Q, is the result of this long-range phase shift of the CDW. This behavior is caused by the large contribution of the gapless phason mode to the response.

Apart from this effect, the CDW is also modified locally. For a single impurity the local modulation is in

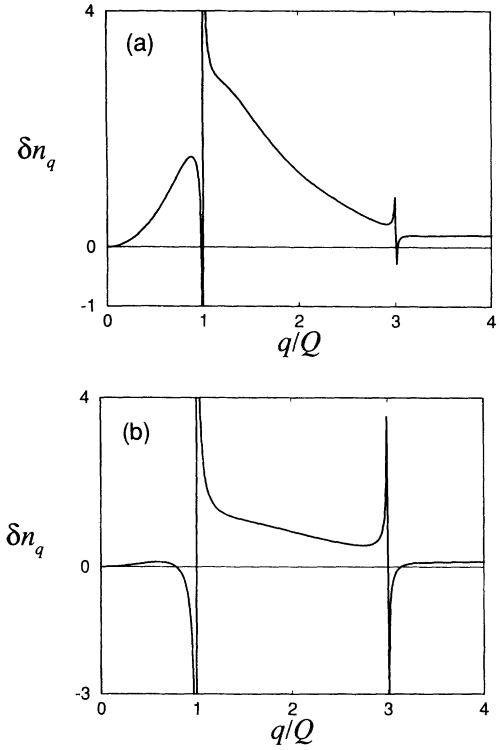

FIG. 2. The linear response of the charge density (arbitrary units) to an attractive impurity at the origin for (a) $\beta = -0.2$ and (b) $\beta = -0.6$. At Q and $3Q$, δn_q diverges to infinity for an infinite chain length, although n_Q and n_{3Q} are still finite. These curves are obtained with the application of periodic boundary conditions to a long chain (with a length of 100 wavelengths) and, therefore, δn_q is finite for all q.

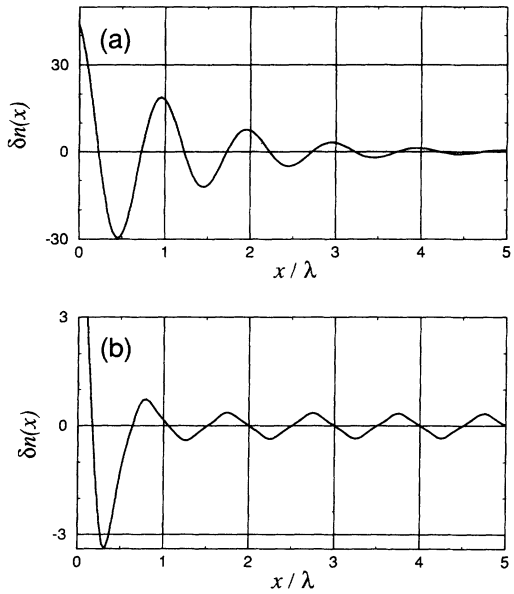

FIG. 3. The linear response of the charge density to a single impurity ($u = -1$) at the origin for (a) $\beta = -0.01$ and for (b) $\beta = -0.2$. In (a) the dominant response is the Friedel oscillations of the electronic charge density in phase with the CDW contributed mostly by the lowest amplitudon modes and with a healing length $\xi \approx 1.13\lambda$. In (b) the healing length is considerably smaller. Friedel oscillations die quickly within a wavelength and the dominant response appears as a long-range phase shift contributed mostly by phasons.

phase with the CDW increasing the local amplitude of the CDW (hence can be termed as Friedel oscillations) and is mostly the response due to the lowest energy amplitudon mode. As explained in the previous section, as the temperature approaches to T_c from below, the "excitation gap" of the lowest amplitudon mode decrease resulting in larger contribution of the in-phase response of the charge density in such a way that the response is divergent at $T = T_c$. Moreover, the healing length of the in-phase response increase in this limit with a temperature dependence $\mid \beta \mid^{-1/2}$. Therefore, the in-phase Friedel oscillation created by a single impurity becomes the dominant response as the transition temperature is approached (the response is divergent as one approaches T_c from below similar to what happens when approaching from above). This qualitative behavior can be seen in Fig. 3. If there are many impurities, then the phase of the CDW at the position of each impurity is the important quantity that determines the response. In such a case "gapless" phason modes significantly contribute to the local response. The overall effect is the change of the CDW wavelength in both neighborhoods of the impurity.

(c) Impurities in the CDW phase: finite-amplitude effects. Linear-response theory is not valid when either the impurity potential is large or the concentration is small.[11] In the present formulation of the problem, one can obtain the charge density by using numerical methods.

For a finite density of impurities, the nonlinear problem has been solved under the assumption of periodic boundary conditions (i.e., the impurity distribution and the charge density are assumed to have a fixed, predetermined period). The artificial period of the distribution, $a = M\lambda$, is chosen as an integral multiple M of the CDW wavelength λ at the given temperature. The impurity concentration c is defined as the number $c = (N/M)$, corresponding to N impurities per length a. For sufficiently large a and for constant N/M the solution should depict the features of the infinite system, where the impurities are distributed randomly.

To obtain the solutions a cutoff approximation is made whereby the charge-density components in q space, n_q, are taken to be zero for $\mid q \mid > Q_{\max}$, where $Q_{\max}$ is a large wave number. The solutions are then obtained by minimization of the free energy, Eq. (1) with respect to n_q, following standard numerical procedures.

A change in the CDW wavelength, and the presence of several metastable states are found to be the characteristic features in the nonlinear regime. Figures 4 and 5 show the charge density for the minimum-energy state for two distributions in an $N = 2$, $M = 10$ case, i.e., two identical impurities ($u = -0.1$), in a period $a = 10\ \lambda$ at a temperature given by $\beta = -0.5$. The distances between the impurities in the two cases were chosen close to a discontinuity of the CDW phase at $R = 3\lambda/2$. For

infinitesimally small and negative impurity potentials the phase of the CDW, φ, measured at the midpoint of the two impurities, is equal to 0 when the impurity separation is slightly larger than $3\lambda/2$, (i.e., at the midpoint the charge density is a maximum). If the separation is slightly smaller than $3\lambda/2$ the phase is $\varphi = \pi$ (i.e., the charge density is a minimum at the midpoint). The charge density in real space and in momentum space for $(R/\lambda) = 1.46$ is shown in Fig. 4, and for $(R/\lambda) = 1.54$ is shown in Fig. 5.

In the case of Fig. 4, where the shortest distance between the impurities is $R = 1.46\lambda$, the unperturbed distribution $n_0(x)$ that minimizes the free energy exhibits a minimum at the midpoint, i.e., $\varphi = \pi$ at $x = 0$ [see Fig. 4(a), upper panel]. Its Fourier spectrum contains a negative component at $q = Q$, and a positive one at $q = 3Q$, as shown by the open circles in Fig. 4(b). The results of the finite-amplitude calculation for the minimum-energy state are shown in real space in Fig. 4(a), and in q space in Fig. 4(b). It corresponds to an energy per unit

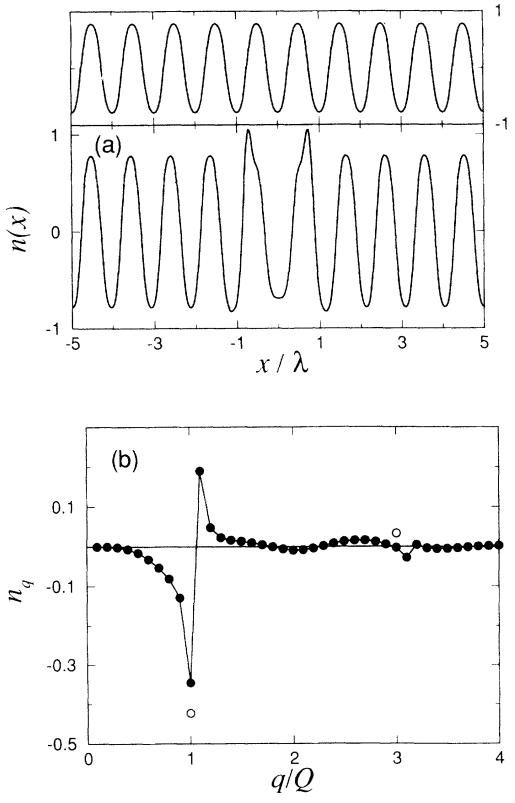

FIG. 4. Charge density (a) in x space and (b) in q space for two impurities located at $\pm 0.73\lambda$. The unperturbed CDW (the minimum energy state for vanishing impurity potential) is shown in the upper panel in (a) and by open circles in (b). The solid line in (b) is a guide to the eye. Since $n(x)$ is an even function of x, n_q is a real quantity. Periodic boundary conditions with period $a = 10\lambda$ are used. The potential of the impurities is $u = -0.1$ and the temperature of the system $\beta = -0.5$. The unperturbed CDW has phase π at the origin. The shift of the CDW wave vector can be clearly seen for the third harmonic.

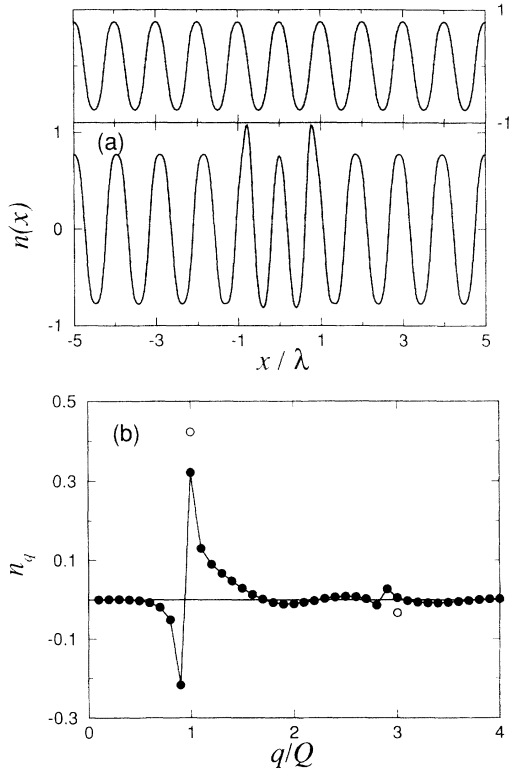

FIG. 5. Charge density for two impurities and conditions identical to those of Fig. 4, but with the impurities located at $\pm 0.77\lambda$. The unperturbed CDW has a phase 0 at the origin.

length $(F/L) = -0.061\,276(4A)^2/C$. It can be seen that, in addition to a continuous background in q space that develops because of the impurities, there is change in the shape of the singularities at $q = Q$ and $q = 3Q$, as well as a shift of these features towards higher values of q.

Figure 5 shows the case where the shortest distance between the impurities has been increased to $R = 1.54\lambda$, i.e., slightly larger than $(3\lambda/2)$. Here the unperturbed distribution $n_0(x)$ that minimizes the free energy has a maximum at the midpoint, i.e., $\varphi = 0$ at $x = 0$ [see Fig. 5 (a), upper panel], and its Fourier spectrum includes a positive component at $q = Q$ and a negative one at $q = 3Q$ as shown by the open circles in Fig. 5(b). The results of the finite-amplitude calculation for the minimum-energy state are shown in real space in Fig. 5(a), and in q space in Fig. 5(b). The minimum energy per unit length is now $(F/L) = -0.062\,029(4A)^2/C$. There is also a continuous background but the shifts of the $q = Q$ and $q = 3Q$ singularities are towards lower values of q.

An important feature of these calculations is, in all cases, the existence of many low-energy metastable states. Three of the lowest-energy metastable states are shown in Fig. 6 for the case of impurity separation $R = 1.46\lambda$. The energies of all of the metastable states determined numerically for both impurity separations are listed in Table I. The states are labeled (μ, ν) according to the number of cycles (number of minima) observed between the two maxima at the impurities in the longer interval (μ) and in the shorter one (ν). This classification

TABLE I. Energies of stable and metastable states for $N = 2$ impurities, of strength $u = -0.1$, and for an imposed periodicity $a = M\ \lambda$ of $M = 10$ wavelengths. The temperature is $\beta = -0.5$. Two impurity separations R are chosen. The free energy per unit length F/L is given in units of $(4A)^2/C$. Reciprocal space was cutoff at $Q_{max} = 20Q = 40\ \pi/\lambda$. The energy density of the chain without impurities is $F/L = 0$ in the normal state, and $F/L = -0.043\,950(4A)^2/C$ in the CDW state. It should be noted the energies are slowly convergent functions of the cutoff Q_{max} and the energies listed here will change slightly when a larger value of the cutoff is used. However, the energy differences between states are insensitive to the cutoff, and hence the ordering of the states does not change when larger values of Q_{max} are used.

	$R = 1.46\lambda$ and $R = 8.54\lambda$		$R = 1.54\lambda$ and $R = 8.46\lambda$
State	F/L $[(4A)^2/C]$	State	F/L $[(4A)^2/C]$
(9,1)	-0.061276	(8,2)	-0.062029
(9,2)	-0.061239	(9,2)	-0.061767
(8,2)	-0.061189	(9,1)	-0.060267
(8,1)	-0.060565	(8,1)	-0.059866
(10,1)	-0.058281	(10,2)	-0.058212
(10,2)	-0.057923	(7,2)	-0.057640
(7,2)	-0.056426	(10,1)	-0.057027
(7,1)	-0.054622	(7,1)	-0.054260
(11,1)	-0.052932	(11,2)	-0.052572
(11,2)	-0.052438	(11,1)	-0.051517
(6,2)	-0.045738	(6,2)	-0.047333
(6,1)	-0.042413	(6,1)	-0.042310

scheme is very informative since it provides a graphical description of how the CDW gets either compressed or expanded. In the situation chosen here there are approximately 8.5 cycles in the large interval and 1.5 cycles in the smaller one.

All metastable states display shifts in the singularity of charge density in q space, similar to those described for the ground states.

It is apparent that a small change in the distribution of impurities can cause drastic changes in the spectrum of the system. Singularities in q space may shift to higher or to lower values of the wave number[9] and energy level inversions may occur, as occurs for the ground states of two cases investigated here. A similarly rich structure is seen when the impurity potential changes strength: inversions of states take place, and some metastable states may change stability. For example, for the $N = 2$, $M = 10$, $R = 1.46\lambda$ case, the (9,1) state, is the lowest-energy state for small values of u, but it is replaced by the (9,2) state at larger values of u.

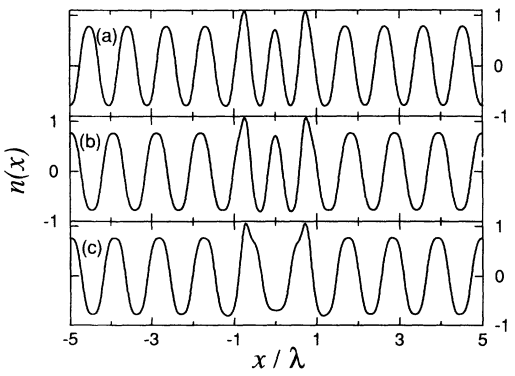

FIG. 6. Charge density for the lowest three metastable states in the case of Fig. 4. Note that whereas the ground state, Fig. 4, has a (9,1) structure, the metastable states are (a) (9,2), (b) (8,2), and (c) (8,1). The energies of these states are given in Table I.

V. DISCUSSION AND CONCLUSION

A Ginzburg-Landau theory of CDW's on a single chain has been proposed, developed, and its consequences explored. The model yields reasonable results, in agreement with observation in real systems such as monoclinic $NbSe_3$.

This agreement is in spite of the fact that the Coulomb-like term of the function $f(x)$, as defined by Eqs. (3)–(5), has an unphysical property. The inverse Fourier transform of Eq. (4) diverges, yielding

$$f(x) = -a_1 \mid x \mid /2 - a_2\delta''(x) + a_3\delta(x) + \text{ a constant }, \tag{18}$$

which grows without bound as $\mid x \mid$ increases. However, since the average value of $n(x)$ vanishes, and in all cases considered here the Fourier transform of $n(x)$ does not contain large terms for small q, this deficiency in $f(x)$ does not create any problems. Any other model that uses a different f_q would display behavior similar to the one found here, provided that f_q goes to infinity for very small and very large values of q, and that it has two local

minima at Q_0 and $-Q_0$.

The function f_q is of central importance in this theory. Through Eq. (2) it determines the energy required to create not only an electronic charge-density distribution, but also the elastic energy of the lattice distortion and the electron-phonon interaction energy. It, therefore, determines the linear response of the coupled electron-phonon system to externally applied static fields in the normal state. For this reason it can be related to the microscopic properties of the electron gas. The short-range (small q) and the long-range (large q) behavior of f_q is consistent with such calculations (which determines a_1 and a_2). However, for intermediate values of q close to the minimum, f_q is quite sensitive to the normal-state Fermi surface and to the temperature. The minimum of f_q is at $Q_0 = 2\,k_F$ and the curvature of f_q at this point is strongly temperature dependent in such a way that a cusp exists at $T = 0$ (and, therefore, these properties are not determined solely by constants a_1 and a_2). For finite temperatures however, f_q is analytic and the form in Eq. (5) is appropriate around the transition temperature when the variation of the curvature with respect to temperature is insignificant.

One important property of the form of f_q in Eq. (4) is that the wave vector of the CDW can change slightly without costing too much energy. Examples of this kind of changes of Q were given in the previous section which are forced on the CDW by the presence of impurities. It is seen that this change in Q not only depends on the configuration of the impurity distribution but also on the (metastable) state. Since the CDW wave vector is related to the Fermi wave vector by $Q = 2k_F$, these changes are interpreted as changes in the Fermi surface. This picture conforms well with a recent experiment[9] on $NbSe_3$, where it has been observed that details of the Fermi surface are strongly dependent on the impurity pinning and the metastable state in which the system has settled. A similar phenomenon is present[32–34] in the normal state of $NbSe_3$ where, depending on the type and concentration of the impurities, the lattice distortions adopt a changing periodicity. The current theory has been applied[35] to this phenomenon with satisfactory results.

The long-range Coulomb interaction between the electrons ensures that the effects of impurities are completely *screened* at long distances. The characteristic length scale for the decay of the charge disturbance is ξ, the healing length, which diverges to infinity as the transition temperature is approached from both sides. This conclusion remains true for any impurity potential $U(x)$ that either decays faster than $f(x)$ or is proportional to $f(x)$ for large values of $|\,x\,|$, whatever the form of $f(x)$. Consequently it can be argued that the model is particularly well suited for CDW systems that have metallic character, such as $NbSe_3$, because of the screening effects.

In the presence of a single impurity, the charge-density response displays oscillations in both the normal and CDW phases with a wave vector close to Q_0. In the CDW phase the wave vector of these oscillations is identical with the CDW wave vector Q. Since Q_0 is related to the nesting vector of the Fermi surface $2k_F$, it can be claimed that these are Friedel oscillations. However, one distinct nature of these oscillations is that they decay exponentially (except at T_c), unlike the Friedel oscillations in real materials which decay with a power law.[36] The Friedel oscillations are caused by the singular behavior of the wave-vector-dependent susceptibility at $2k_F$. However, in the current model the wave-vector dependent susceptibility is $[\,-1/f(q)\,]$ and it is a smooth, nonsingular function for all finite q. To be able to describe long-range Friedel oscillations one has to include the singularities in the model f_q from the beginning. On the other hand, true singularities in the susceptibility exist only at $T = 0$. For a finite temperature it can be claimed that the current approach should work well, and that the Friedel oscillations have a finite range.

The main properties of the model described here are the following.

(1) The harmonic content of the charge density is found to increase with decreasing temperature. This property follows naturally from the increase of the magnitude of n_Q and the nonlinearity of the equations. The increased harmonic content makes the CDW look like a square wave, a consequence of the special form chosen for F_4.

(2) Increasing harmonic contribution with decreasing temperature implies that the CDW wave vector Q decreases as the temperature is lowered, which follows from the fact that higher harmonics contribute larger energies because of the q^2 term in Eq. (5).

(3) The model exhibits "electron-hole" symmetry, invariance under the sign change of the charge density $[n(x) \rightarrow -n(x)]$, i.e., a dependence of the free energy only on even powers of $n(x)$.

(4) Because of the "electron-hole" symmetry there are no even harmonics in the spectrum n_q.

(5) Also because of the "electron-hole" symmetry all collective excitations are degenerate at the boundaries of the Brillouin zone.

(6) Impurities produce a variety of effects in the CDW phase, the most important one being the fixing of the otherwise undetermined phase (pinning).

(7) A second important effect of the impurities consists of long-range phase shifts of the CDW, shifts that essentially extend to infinite distances. This effect appears as a divergence in the spectrum of n_q at the odd multiples of the fundamental wave vector Q. The phase shifts and the divergences result from the large contribution of low-energy phason modes.

(8) A third effect is a local disturbance of the charge density in the neighborhood of the pinning impurities, an effect that heals over short distances—a healing length proportional to $\left(Q_0\sqrt{|\,\beta\,|}\right)^{-1}$.

(9) In the strong pinning regime, one observes changes of the wavelength or equivalently changes in the wave vector of the singularity in the q space. These changes in magnitude and shape of the charge-density spectra have a strong dependence on the impurity positions and also on the strength of the impurity potential; it is possible to observe discontinuous transitions between states when one parameter is changed continuously.

(10) In this regime one also observes several metastable

states which have their own characteristic period distributions. As a function of the main parameters of the problem, they too show significant variation in ordering, i.e., level crossings which are apparent in Table I.

(11) Metastable states exist for all temperatures in the CDW state. Numerical results indicate that when the temperature is close to the transition point their stability and abundance is observed to decrease. (i.e., for lower temperatures one is more likely to encounter metastable states.)

(12) The existence of very many metastable configurations makes observation of the true minimum free-energy state difficult, and achieving equilibrium in reasonable times, a doubtful proposition.

For real, three-dimensional anisotropic systems interaction between chains is important, an effect ignored here. The effect of interchain interactions on the metastable states is an interesting subject that needs further investigation. The current theory should be expanded to be able to answer all questions associated with three dimensionality in a satisfactory way. It would be interesting also to develop a time-dependent Ginzburg-Landau theory which would explain quantitatively the complex transport phenomena characteristic of CDW systems.

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[30] The eigenvalues of Eq. (14) yield the "spring constants" of the (bosonic) normal modes, and are, therefore, proportional to the square of the energy quantum. In particular the phason modes have a linear energy dispersion (energy proportional to the wave vector), and the amplitudon gap is proportional to the square root of $(T_c - T)$.
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