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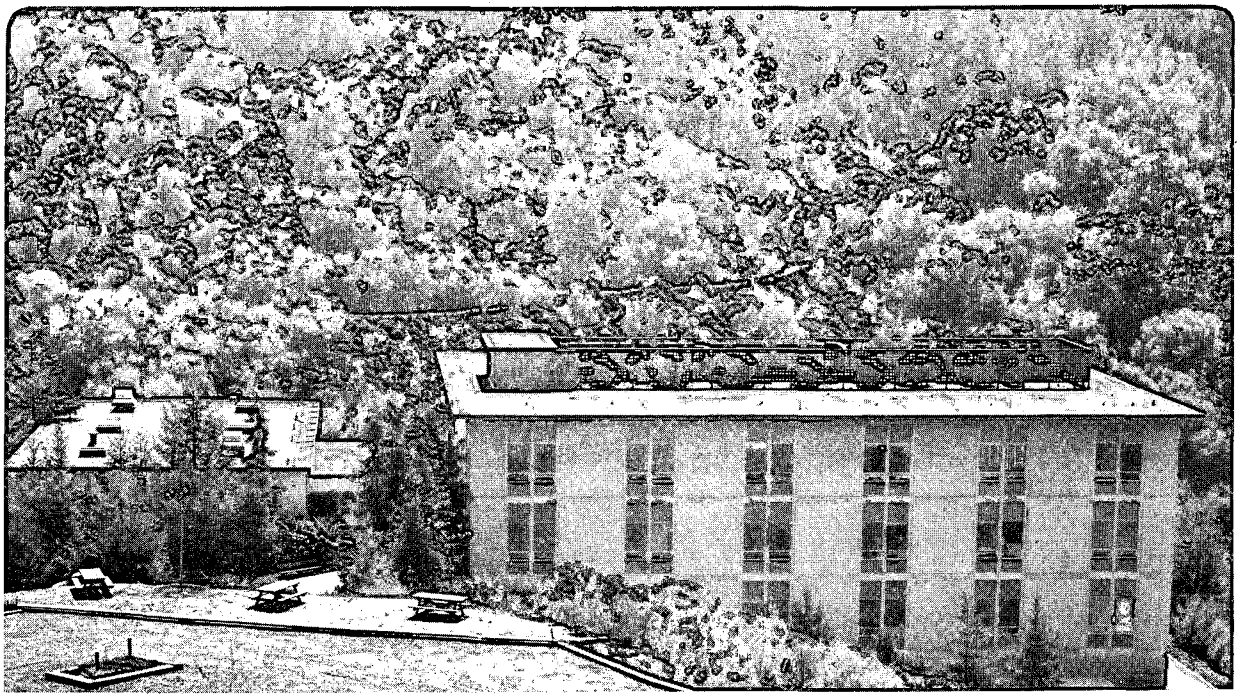

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PHENOMENOLOGICAL GINZBURG-LANDAU THEORY OF CHARGE-DENSITY-WAVE SPECTRA*

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Abstract

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.

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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 non-linear fashion the conductivity of the solid [3,7]. This interesting non-linear conduction process has been the subject of very extensive investigations, both theoretical [1,2,10–16] and experimental [9,7,17].

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 non-equilibrium state. Concurrently, the structure of the equilibrium state is drastically modified by the presence of the pinning impurities and exhibits very complex properties.

It is the purpose of this contribution to formulate a phenomenological model which describes these static phenomena. 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 [18,19]. It applies to one-dimensional CDWs. 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).

In section II, a reasonable 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 discussion of the behavior of the order parameter and the CDW wavelength. The response of the chain to impurities, both in the normal state and in the condensed phase is discussed in section IV. Finally section V contains the conclusions.

II. THE MODEL

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

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

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 can be written as

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

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

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

where

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

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

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

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

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

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

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

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

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

Finally, the impurity contribution to the free energy is

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

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 m^{th} 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 [20].

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 non-zero value. There is a finite range of wavenumbers in the interval between q_- and q_+,

$$q_\pm = Q_0(\sqrt{1+\mid\beta\mid} \pm \sqrt{\mid\beta\mid}) \quad ,$$

where f_q is negative. For any q in this range n_q may have a finite amplitude. Moreover, one cannot say that n_q vanishes whenever f_q is positive since the fourth-order term couples different wavenumbers.

The first step to solve the problem is to look for the periodic solutions by applying periodic boundary conditions. In this case, for a given length a, the condition $n(x+a) = n(x)$ is assumed. The solution for $n(x)$ is then found by minimizing the free energy. In a second step, the free-energy density per unit length, F/L, is minimized with respect to a. If the infinite system has a periodic solution with a wavelength λ, then the solution in the case of periodic boundary conditions has a wavelength a/ν (ν an integer) very close to the value of λ. On the other hand, if there is an aperiodic solution for the infinite system, then one can expect to see a long-wavelength solution for large values of a. It has been found that there is indeed a periodic solution with wavelength close to $2\pi/Q_0$, and there is no indication of the existence of aperiodic solutions.

Therefore the free energy (1)-(6), for negative B and no impurities, yields a CDW with a well-defined periodicity, i.e., a fundamental wavenumber 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 wavenumber Q and its odd-order harmonics are non-zero; all other n_q, even those in the interval $q_- < q < q_+$ vanish, since non-vanishing n_q's other than those mentioned above have the effect of increasing F_4 more than they cause F_2 to decrease.

The (odd) harmonic content can be easily analyzed in two limits. Near the transition temperature, for B negative and small,

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

and

$$| n_{(2m+1)Q} | / | n_Q | \quad \propto \quad | \beta |^m \quad , \qquad \text{for} \quad m \geq 1 \quad . \tag{9}$$

On the other hand, for a well established CDW, i.e., for B negative and large, the term in (5) proportional to A can be neglected [21], and

$$F \approx \int \left(\frac{1}{2} B n(x)^2 + \frac{1}{4} C n(x)^4 \right) dx \quad . \tag{10}$$

Therefore, in this limit $n(x)$ takes two values $\pm\sqrt{|B|/C}$, and the CDW looks like a square wave. Non-zero components of n_q are given as

$$n_{(2m+1)Q} = \frac{2\sqrt{|B|/C}}{(2m+1)\pi}(-1)^m e^{i(2m+1)\phi} \tag{11}$$

for non-negative integer values of m and for arbitrary values of the phase ϕ. The "rounding-off" of the square wave takes place over an interval $\Delta x \approx 2\pi/(Q_0\sqrt{8|\beta|})$.

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

$$Q = Q_0(1 - \tfrac{5}{64}\beta^2) \quad \text{for} \quad |\beta| \ll 1, \tag{12}$$

$$Q \propto \quad |\beta|^{-\frac{1}{4}} \qquad \text{for} \quad |\beta| \gg 1. \tag{13}$$

With the assumption of a temperature-independent parameter Q_0 – as it appears in (5) – the wavenumber Q varies quadratically with $(T_c - T)$ near the transition temperature. This behavior does not conform well with experimental data [22] where it has been found that the variation of Q is linear in $(T_c - T)$.

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 wavevector ($q = 0$) 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 wavevector, a low energy of excitation. The phasons are responsible for the electrical transport properties [7] associated with CDWs. It is of interest to investigate these excitation modes. The way to do that is to follow the prescription set up originally by Landau [23]. It consists of taking the second-order functional derivative of the free energy with respect to the electron density (a generalized inverse susceptibility tensor)

$$\Phi(x;x') = \frac{\delta^2 F}{\delta n(x)\delta n(x')} \quad , \tag{14}$$

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

$$\Phi(x;x') = \ f(x-x') \ + \ 3C \ n(x)^2 \ \delta(x-x') \quad , \tag{15}$$

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

$$\int \Phi(x;x')\psi(x')dx' = \omega\psi(x) \quad . \tag{16}$$

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 [24]

$$\Phi(x \ ; \ x') \ = \ \Phi(x + 2\pi/Q \ ; \ x' + 2\pi/Q) \quad . \tag{17}$$

Bloch's theorem then yields for the eigenfunction

$$\psi_{\alpha k}(x) = e^{ikx} u_{\alpha k}(x) \quad , \tag{18}$$

where α is an index and $u_{\alpha k}(x)$ is a periodic function with period $2\pi/Q$. The quantity k is the wavevector of the excitation. The energy of the excitation is proportional to 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. 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 inversions which result in a spectrum of non-intersecting 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

$$\int \Phi(x;x')\, \delta n(x')\, dx' = -\, V(x) \quad , \tag{19}$$

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 (19) 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

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

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_0 and therefore the wavevector Q_0 "shapes" the charge distribution. In the CDW state, on the other hand, the charge density is crucially affected by the phason modes.

A. Impurities in the normal state

In the normal state, the presence of an impurity causes a screening-charge "pile up" 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

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

where

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

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

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

where ϕ is related to β by

$$\sin^2 \phi \ = \ \beta \quad .$$

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

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

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 peak in the susceptibility $\chi(q)$ in the neighborhood of $q = Q_0$. This behavior is a precursor to the CDW transition [25].

B. Impurities in the CDW phase: Linear-response theory

Because in the natural, pristine state the phase of the CDW is completely undetermined, the "ground state" of the system may be considered to be infinitely degenerate. In order to apply linear-response theory to the CDW phase one needs to determine the phase of the unperturbed charge density $n(x)$ that minimizes the free energy in the presence of infinitesimal (zero-strength) impurities. For real (finite-strength) impurities the charge density becomes

$[n(x) + \delta n(x)]$, where $\delta n(x)$ can be obtained by solving Eq. (19). The phase of the unperturbed charge density $n(x)$ has to be chosen so that the response $\delta n(x)$ is zero for vanishing values of the impurity-potential strength U_0. This can be accomplished by fixing (pinning) the phase so that

$$\int V(x) n(x+b) dx \tag{20}$$

is a minimum as a function of b. Pinning has two implications. First, there is a contribution to free energy that is first-order in $\mid U_0 \mid$, i.e., the phase of the CDW is such that the interaction between the unperturbed charge and the impurity potential, proportional to $\mid U_0 \mid$, is a minimum. Pinning (fixing the CDW phase) is thus the main energy-determining mechanism. Second, and as a consequence, the zero eigenvalue corresponding to the $k = 0$ phason mode drops out from (19) without creating any problems [26]. It is now possible to assume that the function $n(x)$ is redefined so that $\hat{b} = 0$ at the minimum of (20). Such phase-definite charge density is labelled $n_0(x)$.

Even though pinning makes (19) solvable, small eigenvalues of Φ corresponding to the phason modes cause divergences in the Fourier transform of $\delta n(x)$ – denoted by δn_q – at odd multiples of Q (see Fig. 2). The divergent part of δn_q is given by

$$(1/L) \sum_{odd\ l} 2\gamma \frac{l\ Q\ n_{0,lQ}}{q - l\ Q} \quad , \tag{21}$$

where l is the harmonic index, and γ is an l-independent quantity with dimension of length, which is proportional to U_0 and which depends on the temperature and on the impurity distribution. The effect of terms of the form (21) on the total charge density $[n_0(x) + \delta n(x)]$ is to produce a phase shift of the "pinned wave" over an infinite distance (long range). For a few impurities located near the origin, the asymptotic solution for the charge density is

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

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

The phase shift γ is such that positive values indicate displacement of the charge towards the region of the impurities. In general, both positive and negative values are possible for γ. However, for a single impurity, only positive values [27] of γ are observed. It should be noted that γ is a very sensitive function of the temperature; relatively small changes in β produce sizable changes in the phase shift (see Fig. 3), one more indication of the complexity and non-linearity of the phenomena discussed here.

If $\delta n(x)$ is expanded in terms of the eigenfunctions of Φ, one obtains

$$\delta n(x) = (1/L) \sum_k (\gamma'/k) \quad \psi_{0k}(x) \ + \ \ldots \tag{22}$$

where γ' is proportional to γ. Hence, because of the $(1/k)$ factor in (22), phason excitations with small values of wavevector k have divergently large contributions to the response. The divergence of the expansion coefficients in (22) is the result of the absence of a phason gap, $\omega_{0,k=0} = 0$, and an energy of excitation of the phasons – a quantity proportional to $\omega_{0,k}$ – which depends quadratically on the wavevector k. A better calculation, beyond linear response, shows that this kind of divergences is not an artifact of linear-response theory, i.e., the long-range phase shift is a physical (observable) phenomenon.

Terms not included in (21) are well behaved. They change the charge density locally, near the impurity, and their effect dies off quickly, with a finite healing length proportional to $(Q_0 \sqrt{|\ \beta\ |})^{-1}$. When the system is close to the transition temperature, the contribution of amplitudon modes, especially of $\alpha = 1$, increases. This property is in agreement with the observation that in this limit the healing length and the susceptibility diverge [28]. It is because the $\alpha = 1$ excitations, for small k, are in phase with the CDW, while the phason excitations are always out of phase.

C. Impurities in the CDW phase: Finite-amplitude effects

If there are more than one impurities, and the distances between them is large, the linear approximation – used to reach the conclusions above – breaks down, even for very small values of the impurity potential U_0. Figure 4 displays the calculated asymptotic phase shift for two impurities as a function of the distance between those impurities. For increasing distances magnitude of the phase shift gets larger, indicating that the linear-response approximation is valid for smaller and smaller values of U_0. This can be explained by a simple example. An attractive impurity pins the phase of the CDW so that the maximum of the charge density is at the position of the impurity. For two (attractive) impurities located at a distance that is an integral multiple of the CDW wavelength, the requirements of maximum amplitude at the impurity site can be satisfied for both. If the separation, on the other hand, is not an integral multiple of the wavelength a compromise is necessary. For small values of U_0, little change in the CDW structure takes place, and the impurities cannot be at maxima of the wave. As U_0 increases the structure of the CDW gets disturbed, and the maxima of the waves move towards the impurities: strong pinning takes place (See Figs. 5 and 6). Cross-over behavior between weak and strong pinning regimes is governed by the relative values of two energies: (i) the energy gained by placing the CDW maxima at the positions of the impurities, an energy proportional to $\mid U_0 \mid$ and to the number of impurities; and (ii) the energy increase caused by the wavelength change, which is inversely proportional to the distance between impurities. Therefore, the crossover value of U_0 is inversely proportional to this distance [11]. The unusual behavior of the phase shift shown in Fig. 4 results from this phenomenon.

For a finite density of impurities, the non-linear 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 period 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 cut-off approximation is made whereby the charge-density components in q-space, n_q, are taken to be zero for $| q | > Q_{\max}$ where $Q_{\max}$ is a large wavenumber. 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 non-linear regime. Figures 5 and 6 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 (see Fig. 4): $(R/\lambda) = 1.46$ for Fig. 5, and $(R/\lambda) = 1.54$ for Fig. 6. These two cases are for values of $(R/\lambda) \approx 1.5$, a discontinuous point, so that the phases of $n_0(x)$ differ by exactly π.

In the case of Fig. 5, 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. $\phi = \pi$ at $x = 0$ [see Fig. 5 (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. 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). It corresponds to an energy per unit length $(F/L) = -0.061276\ \ (4A)^2/C$. 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 6 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., $\phi = 0$ at $x = 0$ [see Fig. 6 (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. 6 (b). The results of the finite-amplitude calculation for the minimum-energy state are shown in real space in Fig. 6 (a), and in q-space in Fig. 6 (b). The minimum energy per unit length is now

$(F/L) = -0.062029 \ (4A)^2/C$. 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 states are shown in Fig. 7 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 1. The states are labelled (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 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 wavenumber [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 vanish. 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.

V. DISCUSSION AND CONCLUSION

A Ginzburg-Landau theory of CDWs 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

$$f(x) = -a_1 \mid x \mid /2 - a_2\delta''(x) + a_3\delta(x) + \text{a constant} \quad , \tag{23}$$

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 main properties of the model are:

(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 non-linearity 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 wavevector 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, 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. If there are many impurities, the

long-range phase shifts appear as a change in CDW wavelength.

(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 $(Q_0 \sqrt{|\beta|})^{-1}$.

(9) The model correctly describes the transition between the weak and the strong pinning regimes.

(10) In the strong pinning regime, one observes changes of the wavelength or equivalently changes in the wavevector 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 when one parameter is changed continuously.

(11) In this regime one also observes several metastable states which have their own characteristic wavelength distributions. As a function of the main parameters of the problem, they too show significant variation in ordering, i.e., level crossing which are apparent in Table 1.

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

For real, three-dimensional anisotropic systems interaction between chains is important, an effect ignored here. The CDWs on different chains maintain a constant phase difference between them. If a single impurity is added to one of the chains, the long-range phase shifts on that particular chain tend to alter the phases in the neighboring chains. However, the interchain interactions contribute energies that are proportional to the length of the chains as opposed to the finite energy contributed by the single impurity. Therefore, one can argue that the interchain effect must globally dominate and result in impurity effects that are only local, i.e., short-range changes of charge density and CDW amplitude and wavelength. This argument is clouded by the fact that, as a result of the charge pile-up around the impurity, an effective potential is applied to the neighboring chains through the interchain interactions. Similar phase shifts can be observed on neighboring chains. However, a model which fully includes the interchain interactions is needed to answer this question satisfactorily.

A number of different topics need further investigation, in particular phenomena in the non-linear regime: strong pinning and metastable states. The nature of phase shifts in the case of strong pinning and the stability of metastable states as a function of temperature and impurity potentials are among the interesting and pressing questions that need to be answered. It would be interesting also to develop a time-dependent theory which would explain the complex transport phenomena characteristic of CDW systems.

ACKNOWLEDGMENTS

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[21] Three remarks are in order: (i) The limit of large and negative B is mathematically but not physically meaningful, since the free-energy expansion (1) is only valid for small order parameters, near the transition temperature; (ii) Even though the term proportional to A can be neglected for amplitude considerations, it is that term that determines the value of the CDW wavenumber Q; (iii) It is also the term proportional to A that produces the rounding off of the square CDW, and determines the width of the transition region Δx.

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[24] It should be noted that the actual periodicity of Φ is π/Q, i.e., half the natural wavelength of the CDW system $2\pi/Q$. This extra symmetry arises from the absence of a third-order term in F, which manifests itself as the "electron-hole" symmetry $n(x) \rightarrow -n(x)$. It is nonetheless convenient to plot the excitation modes in the Brillouin zone $-(Q/2) < k \leq (Q/2)$, even though at the zone boundaries the modes are all doubly degenerate (i.e., the bands "stick together").

[25] This precursor behavior in the normal state near the CDW transition is the equivalent to the Kohn anomalies in the normal metallic state, where a singularity in the electric susceptibility caused by the geometry and the topology of the Fermi surface induces observable features in the phonon spectrum.

[26] It should be noted that of all the contribution to the energy arising from the impurity, that corresponding to the $\alpha = 0$, $k = 0$ component is the only one that is first-order in the strength U_0 of the impurity potential. All other components yield second-order terms, proportional to the square of U_0. Moreover, the value of the phase, b, that minimizes (20) guarantees that $V(x)$ is orthogonal to $\psi_{0,k=0}$. Under these circumstances, and only under these circumstances Eq. (19) has a solution: it is determined by all the components of $V(x)$ in the eigenfunctions $\psi_{\alpha k}(x)$ other than $\psi_{0,k=0}$.

[27] The positive values of the phase shift γ for a single impurity, regardless of whether it attracts or repels charge, can be understood based on the fact that the "phase pinning" of the CDW, given by (20), depends on the sign on the potential. Hence the phase shift depends only on the magnitude but not on the sign of the impurity potential

[28] For a single impurity, a susceptibility can be defined as the charge density at the site of impurity divided by the value of the impurity potential. For many impurities other definitions can be given.

FIGURES

FIG. 1. The dispersion relation for the collective excitations: (a) $\beta = -0.2$; (b) $\beta = -0.6$. Only the lowest four modes are shown in each case.

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 phase shift γ for a single impurity as a function of the temperature parameter β.

FIG. 4. The phase-shift, γ, as a function of R/λ for two impurities, where R is the distance between two impurities and λ is the wavelength of the CDW. The discontinuities at half-integer wavelengths are the result of a phase slip of the unperturbed CDW. Note that when the impurities are separated by an integral number of wavelengths γ does not vanish and it takes the same value.

FIG. 5. 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.

FIG. 6. Charge density for two impurities and conditions identical to those of Fig. 5, but with the impurities located at $\pm 0.77\lambda$. The unperturbed CDW has a phase 0 at the origin.

FIG. 7. Charge density for the lowest three metastable states in the case of Fig. 5. Note that whereas the ground state, Fig. 5, 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 1.

TABLES

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 cut-off at $Q_{\max} = 20Q = 40\ \pi/\lambda$. The energy density of the chain without impurities is $F/L = 0$ in the normal state, and $F/L = -0.043950\ (4A)^2/C$ in the CDW state.

	$R = 1.46\lambda$ 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

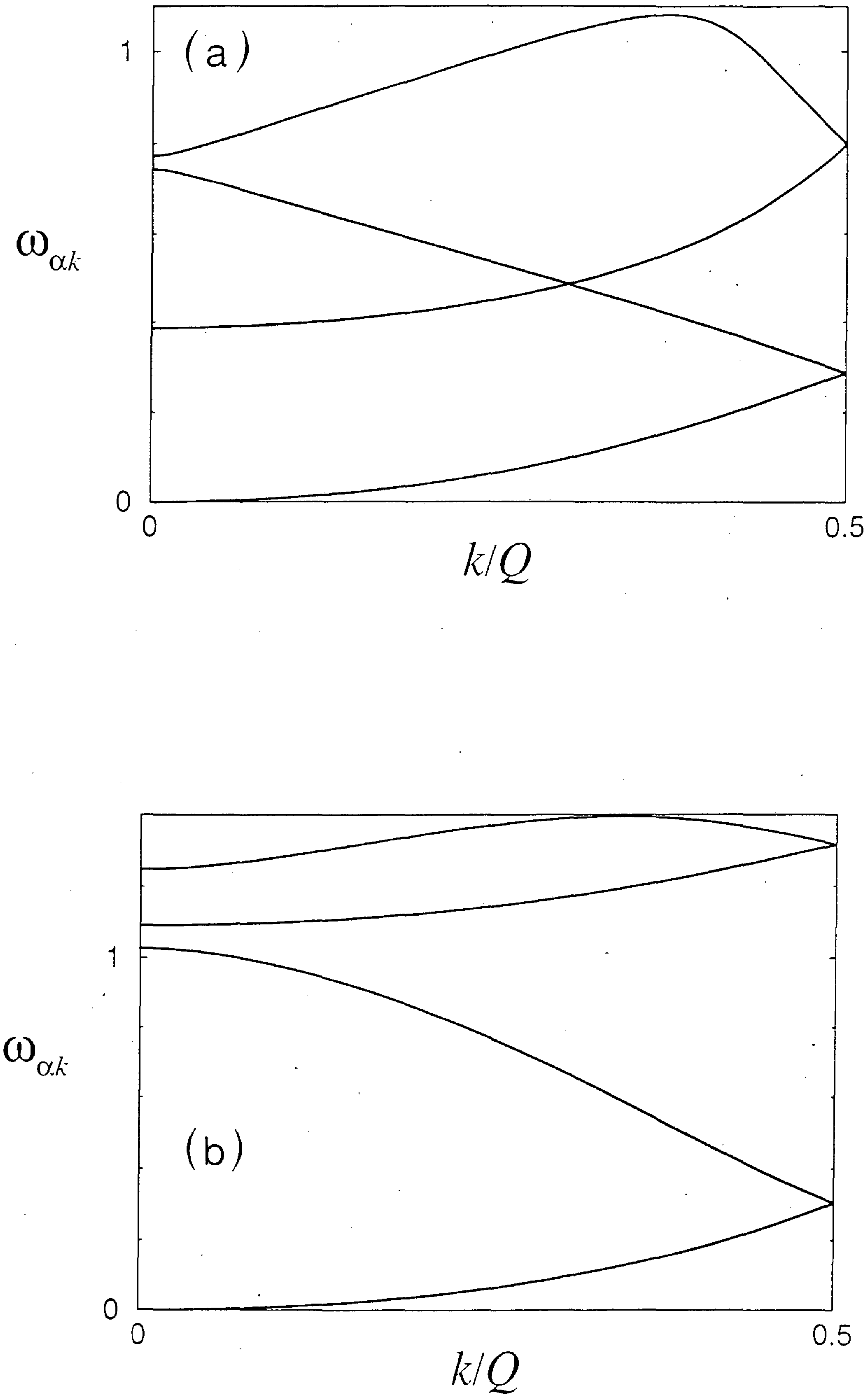
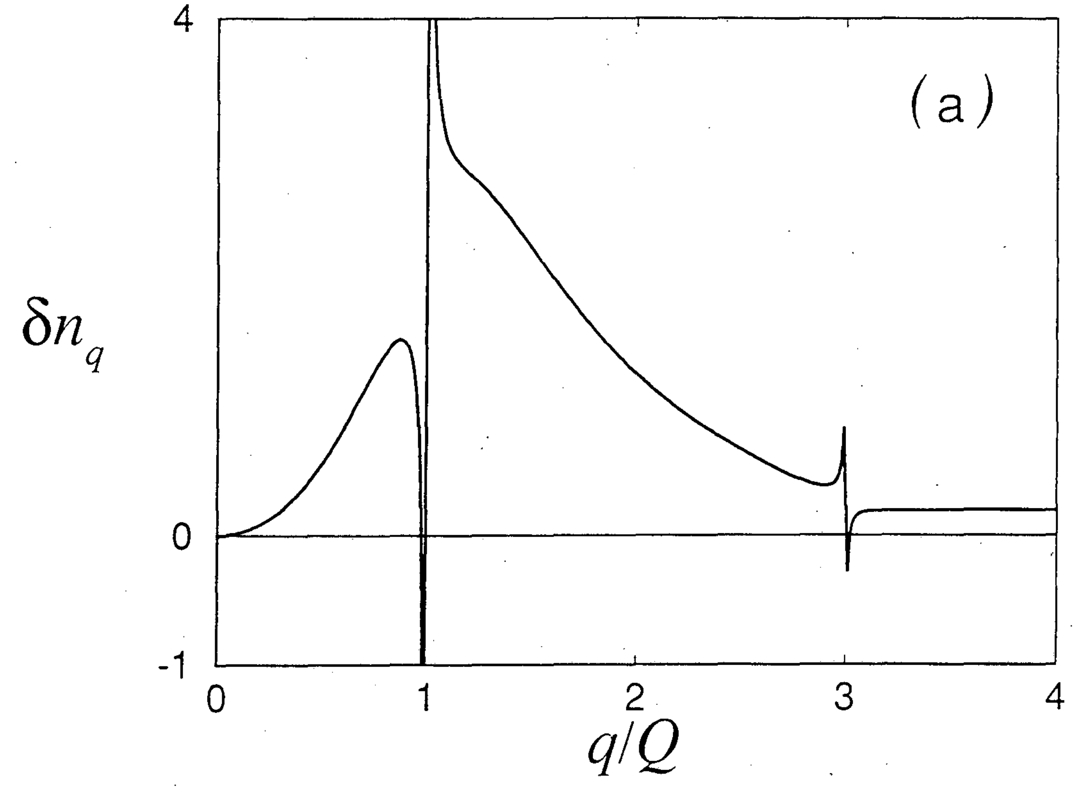


FIGURE 1



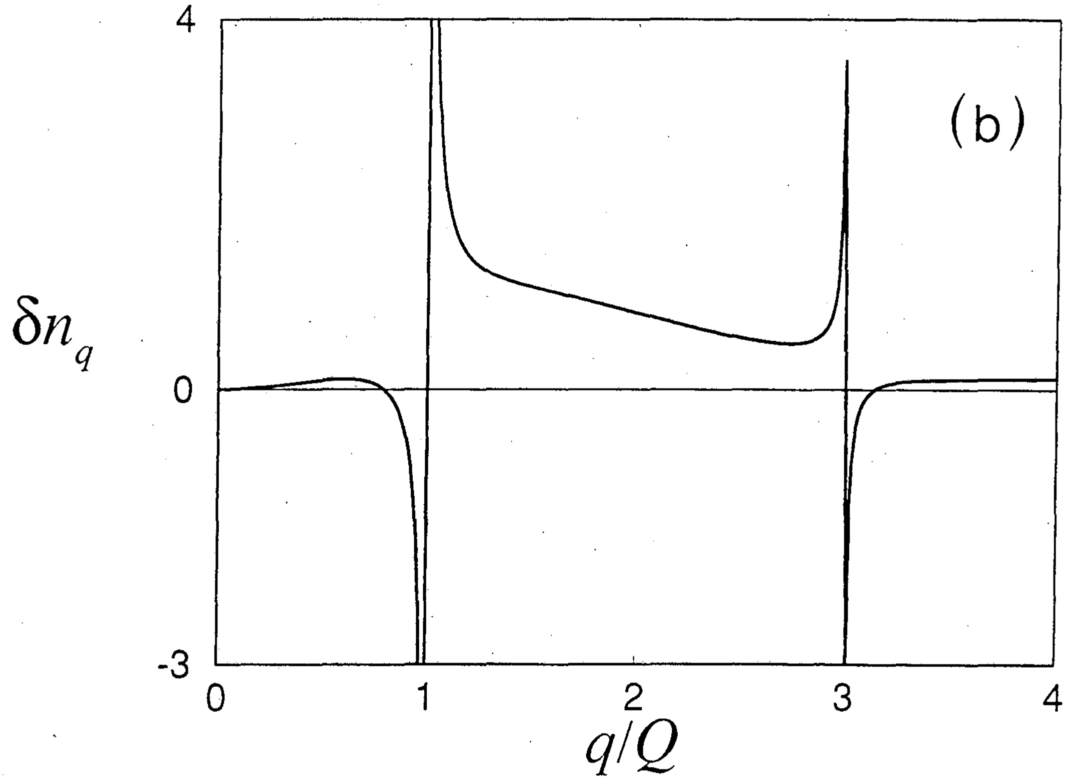


FIGURE 2

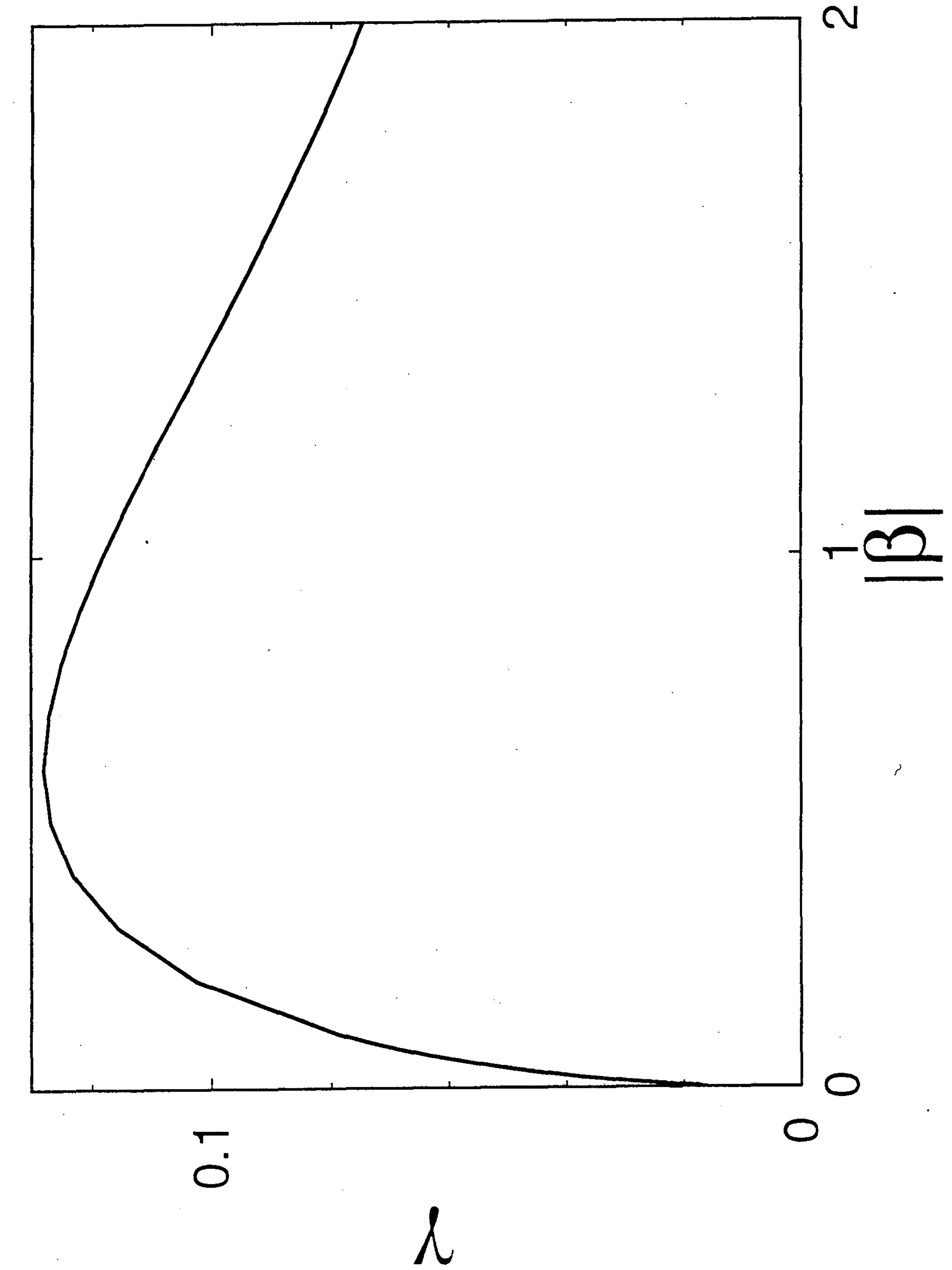


FIGURE 3

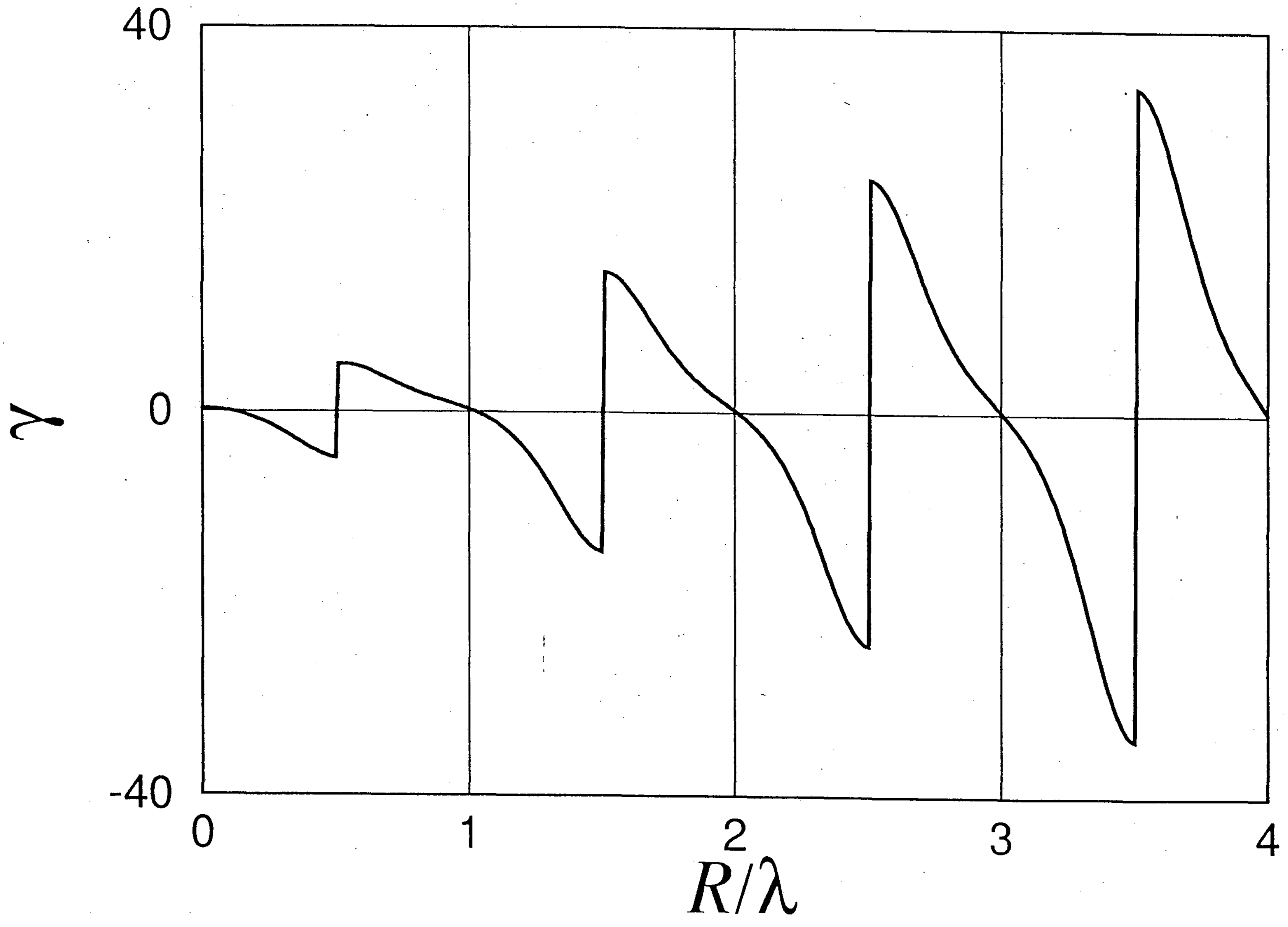


FIGURE 4

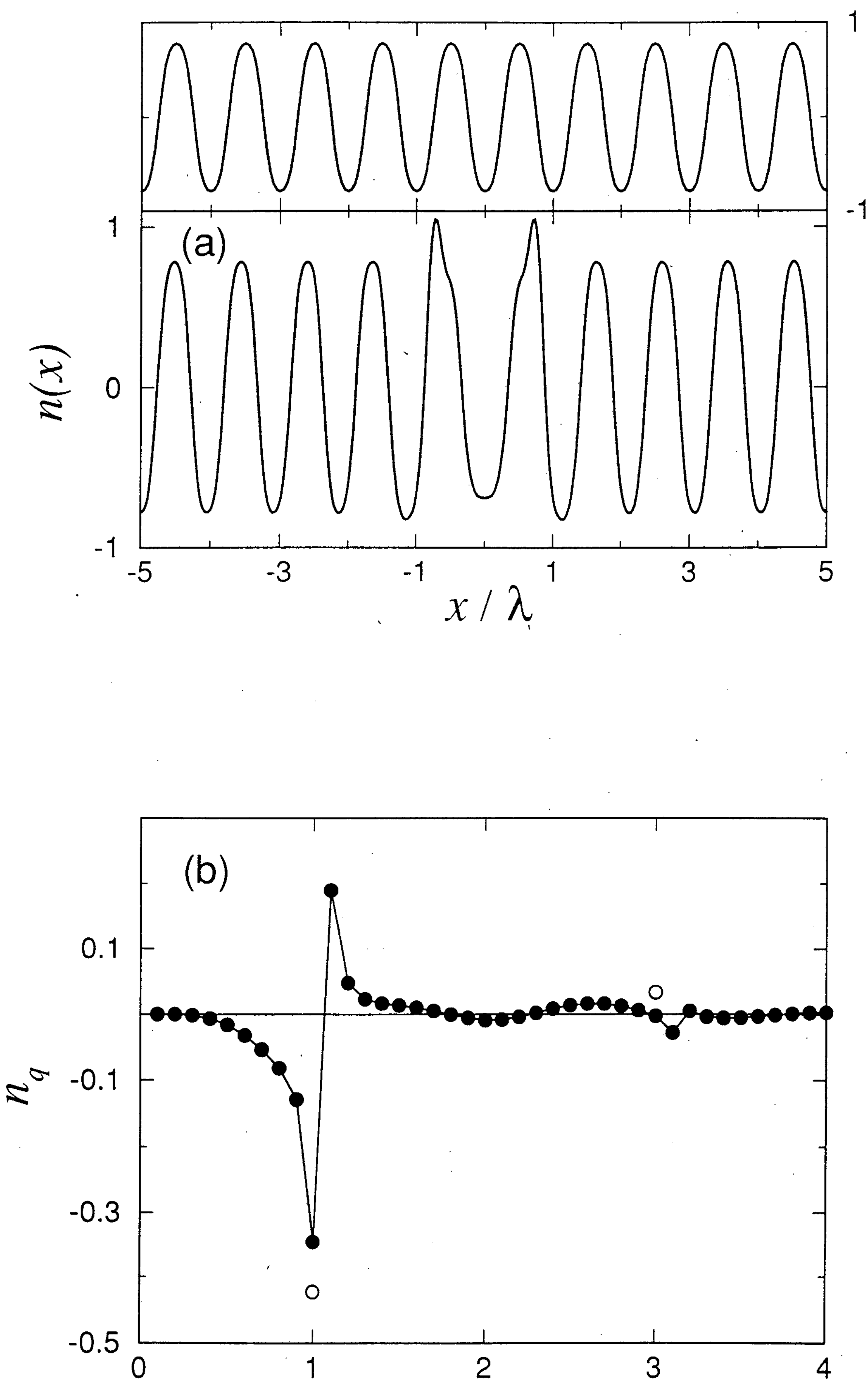
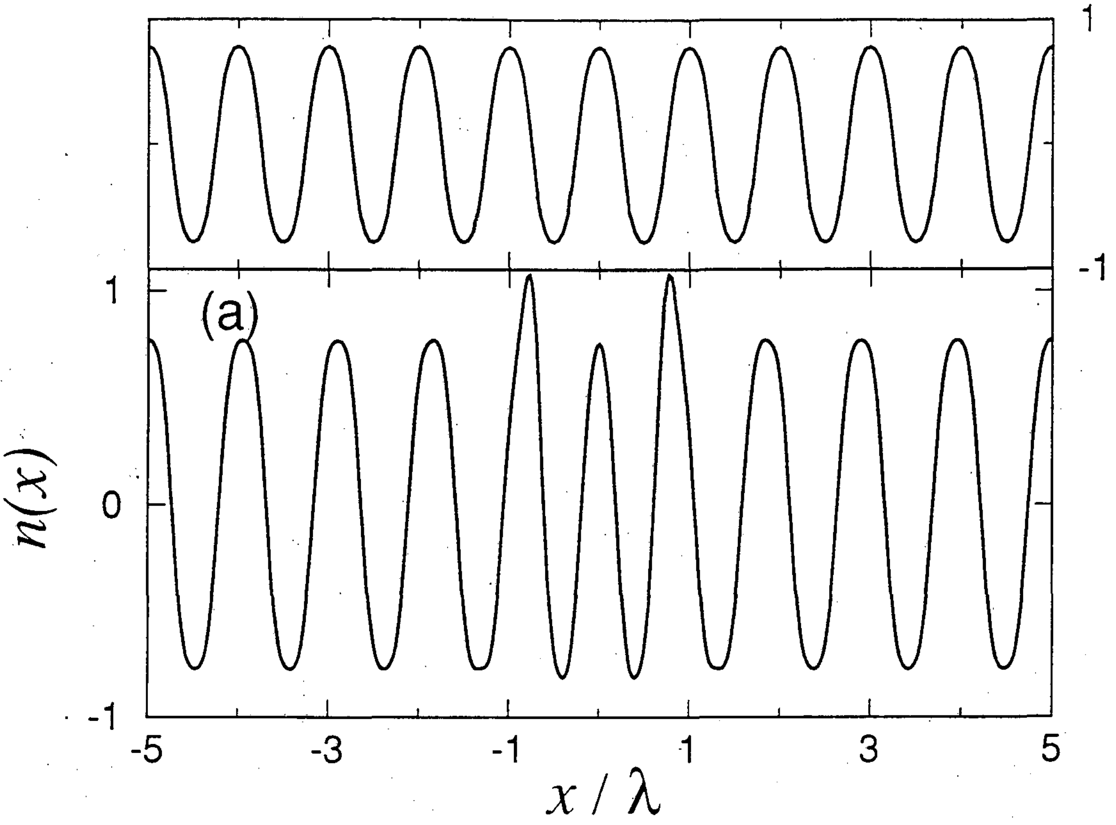


FIGURE 5



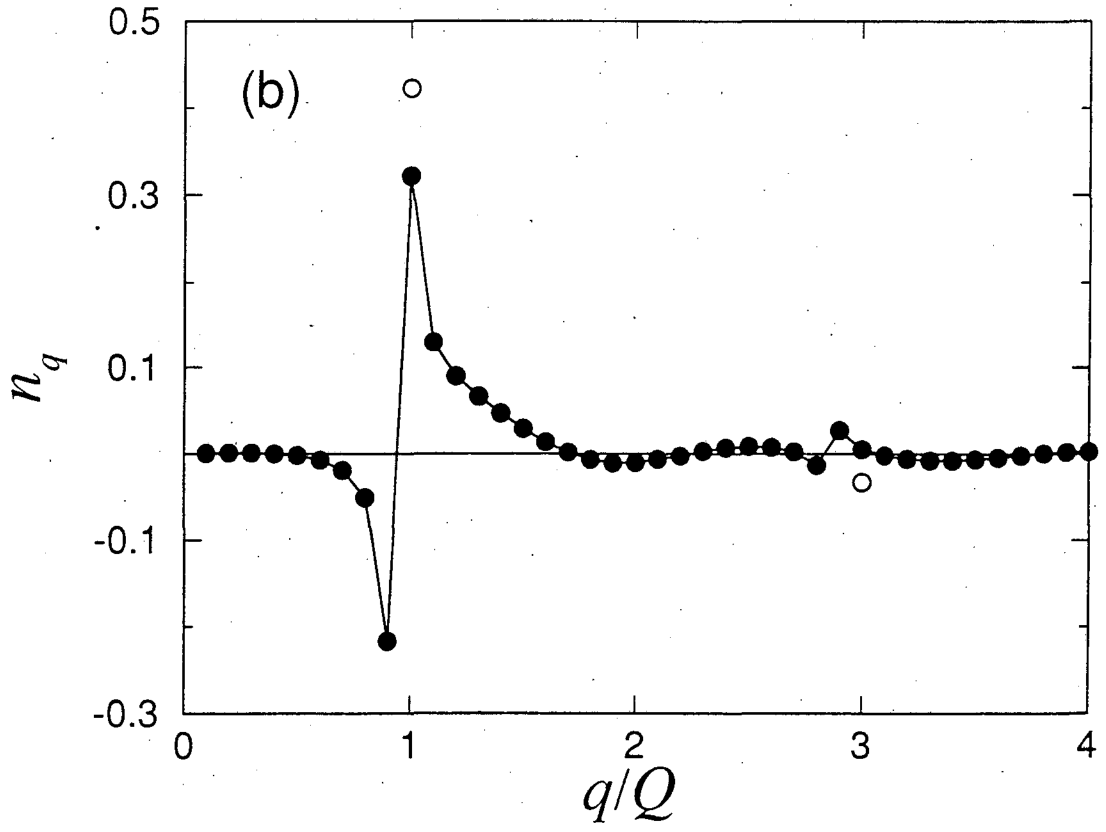


FIGURE 6

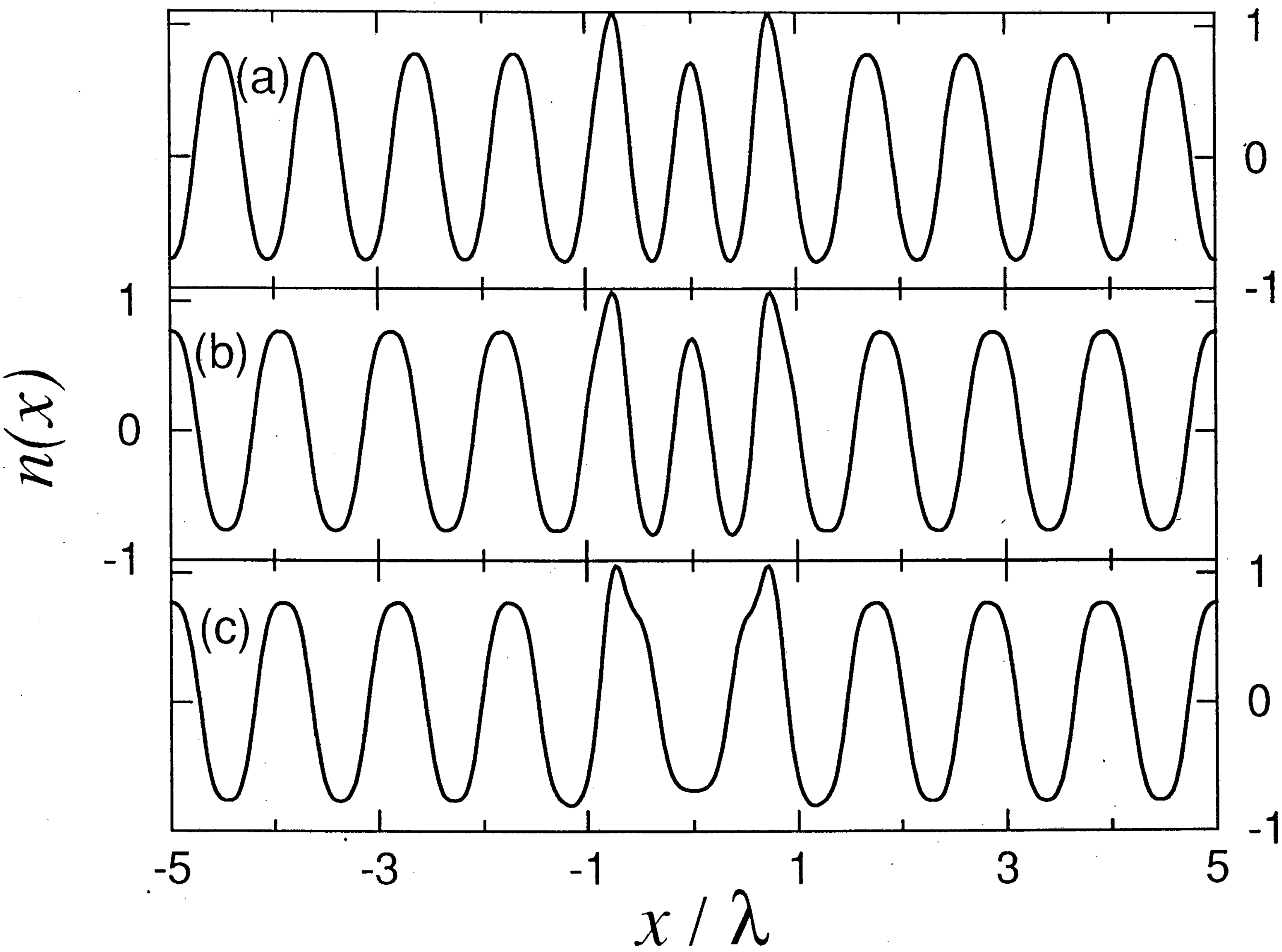


FIGURE 7

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