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Step-density-wave phase of crystalline interfaces

Eugene B. Kolomeisky
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853-2501

Joseph P. Straley
Department of Physics and Astronomy, University of Kentucky, Lexington, Kentucky 40506-0055

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The combined effect of striction and crystallinity can produce a state for vicinal crystalline interfaces, which we call the step-density-wave (StDW) phase due to its resemblance to the charge-density-wave phase of one-dimensional conductors. This phase arises due to a spontaneous periodic distortion of the surface commensurate with the steps, which creates a potential that localizes them. In many cases of interest the energy gain of step localization is greater than the energy cost of the elastic distortion, thus favoring the StDW phase. There is true long-range translational order of the step positions relative to the surface distortion, which makes the StDW phase similar to traditional smooth interfaces. The surface distortion and associated step waves are not fixed rigidly in space, however, but only relative to each other. Therefore, in the absence of pinning by impurities, the combined system of steps with associated surface elastic distortion can move freely in response to an external force (for example, under crystal growth conditions) so that in this respect it resembles a rough interface. In this paper we demonstrate the existence of the StDW phase and study the phase transitions between the rough phase of wandering steps and the StDW phase. [S0163-1829(96)07231-1]

I. INTRODUCTION

This paper will study the phase diagram for a vicinal surface: a crystal interface having wide terraces of a low Miller index face separated by elementary steps. These steps induce an elastic deformation in the bulk of the crystal, and this in turn produces a long-range interaction between the steps.[1] Since the steps are actually a structure of the crystal, their shape and location are discrete on the scale of the lattice, so that in order to regard them as interacting objects of linear topology we will have to introduce a periodic potential at the atomic scale. We will show that a combination of the effects of deformability and crystallinity can lead to a new thermodynamic state of the crystal surface, in addition to the well-understood rough and smooth phases.[2]

Our insight into the behavior of this system was based on an analogy between the steps and the world lines of a one-dimensional electronic liquid placed in a periodic ion lattice. This system has the following properties: when the lattice is undeformable, the quantum system is either a metal or Mott insulator; the insulating phase occurs when the filling factor is rational and quantum fluctuations are sufficiently weak. When the ion lattice is deformable the electron-ion interaction induces an effective electron-electron interaction, and there is another mechanism, first noticed by Peierls,[3] to make an insulator out of the one-dimensional quantum system that does not depend on having a rational filling factor: the lattice distorts spontaneously so that it is modulated at the Fermi wave vector, creating a commensurate potential for the electrons.

In our analogy, the quantum fluctuations of the electrons are equated to the thermal fluctuations of the steps, the metal is equivalent to the rough phase of the wandering steps, and the Mott insulator becomes the flat phase in which the steps are locked in by in-plane periodicity. The deformation-induced effective electron-electron interaction is analogous to the elasticity-mediated interstep interaction found in continuum elasticity theory.[1] We will extend our analogy to show that a vicinal interface of wandering steps can exhibit a Peierls-like state, driven by a spontaneous surface deformation commensurate with the average interstep spacing, which we call the *step-density-wave* (StDW) phase.

In Sec. II we derive a long-wavelength Hamiltonian describing a vicinal interface on a deformable crystal. In Sec. III we demonstrate how this Hamiltonian describes the continuum limit. In Sec. IV we show how a surface elastic deformation can lower the system free energy: first we analyze a low-temperature limit using elementary arguments, and clarify the nature of the distorted state. Then the case of finite temperatures is studied using a renormalization-group approach, leading to a phase diagram and a discussion of the nature of the possible phase transitions. Section V presents some speculations on possible experimental relevance of our findings.

II. LONG-WAVELENGTH HAMILTONIAN

A vicinal surface will have a set of on average parallel and uniformly spaced steps of linear density n. We will choose a coordinate system such that the average slope is along x (the steps are parallel to y), and the outward normal is the z direction. We will describe the conformation of the mth step (regarded as a continuous linear object) located near $x=m/n$ by its displacement $v(x,y)$ in the x direction. The atoms in the crystal are displaced from the lattice sites (of lattice spacing ρ^{-1}) by a displacement field $\mathbf{u}(x,y,z)$. The interacting steps are described by a Hamiltonian of the form

$$H_{\rm steps}=\frac{1}{2}\int dx\ dy[K_1(\partial v/\partial x)^2+K_2(\partial v/\partial y)^2]$$
$$+\int dy\sum_{j,m}V[m/n+v(m/n,y)$$
$$-j/\rho-u_x(j/\rho,y,z=0)],\tag{1}$$

where $V(x)$ is a function that represents the effects of atomicity: it attempts to align the mth step with the jth atomic row on the surface. The gradient part of (1) describes a translationally invariant anisotropic interface with positive stiffness coefficients K_1 and K_2. The Hamiltonian (1) is valid on scales that exceed the mean interstep distance n^{-1} provided that step wandering is small ($|\partial v/\partial x|,|\partial v/\partial y|\ll 1$) and that the temperature T is below the roughening phase transition temperature of the terrace. This Hamiltonian can be put into continuum form by representing the sums using the Poisson sum rule,[4] which replaces $m/n\to x$, $j/\rho\to x'$, while keeping track of the higher Fourier components of the sum. Assuming the integral $V=\int_{-\infty}^{\infty}V(x)dx$ is finite allows us to approximate $V(x)=V\delta(x)$, thus giving in the long-wavelength limit

$$H_{\rm steps}=\frac{1}{2}\int dx\ dy[K_1(\partial v/\partial x)^2+K_2(\partial v/\partial y)^2]$$
$$+\rho nV\sum_{p,q}\int dx\ dy[1-(\partial v/\partial x)][1-(\partial u_x/\partial x)]\exp 2\pi i[(nq-\rho p)x-nqv+\rho pu_x].\tag{2}$$

The combinations $n[1-(\partial v/\partial x)]$ and $\rho[1-(\partial u_x/\partial x)]$ in (2) describe how the displacements alter density of steps and atoms.

The $p=q=0$ term of the sum (2) contains a term independent of the derivatives $\partial v/\partial x$ and $\partial u_x/\partial x$, as well as terms linear in them. These terms can be dropped: the x derivatives of the fields v and u_x represent the fluctuations in the step and atom density about homogeneity, and so we must impose $\int dx\ dy(\partial v/\partial x)=\int dx\ dy(\partial u_x/\partial x)=0$ if the step and atom density are to be correctly specified by n and ρ, respectively. Then

$$H_{\rm steps}=\frac{1}{2}\int dx\ dy[K_1(\partial v/\partial x)^2+K_2(\partial v/\partial y)^2+2\rho nV(\partial v/\partial x)\partial u_x/\partial x]$$
$$+\rho nV{\sum_{p,q}}'\int dx\ dy\ \exp 2\pi i[(nq-\rho p)x-nqv+\rho pu_x],\tag{3}$$

where the symbol Σ' means that the terms corresponding to $p=q=0$ have been removed from the sum. Finally we have to take into account elastic deformation in the bulk of the crystal induced by the coupling with the step displacement field v. The corresponding energy is given by $H_{\rm bulk}=\int_{z\leqslant 0}dx\ dy\ dz\,\frac{1}{2}\Sigma_{i,k}\sigma_{ik}u_{ik}$, where σ_{ik} and u_{ik} are the components of the stress and strain tensors,[5] respectively, and are related by Hooke's law $\sigma_{ik}=[E/(1+\sigma)][u_{ik}+\sigma/(1-2\sigma)\Sigma_j u_{jj}\delta_{ik}]$ with E and σ being Young's modulus and Poisson's ratio, respectively. Combining $H_{\rm bulk}$ with (3) we get the total Hamiltonian of the system

$$H=\int_{z\leqslant 0}dx\ dy\ dz\ \frac{1}{2}\sum_{i,k}\sigma_{ik}u_{ik}+\frac{1}{2}\int dx\ dy[K_1(\partial v/\partial x)^2+K_2(\partial v/\partial y)^2+2\rho nV(\partial v/\partial x)\partial u_x/\partial x]$$
$$+\rho nV{\sum_{p,q}}'\int dx\ dy\ \exp 2\pi i[(nq-\rho p)x-nqv+\rho pu_x].\tag{4}$$

When the interstep distance n^{-1} is commensurate with the lattice periodicity ρ^{-1} in the x direction (i.e., $nq=\rho p$) and the crystal is undeformable ($u_x=0$), the most relevant terms of the sum in (4) are those with smallest q and p, namely, those reducing to $2\rho nV\int dx\ dy\cos 2\pi nqv$; dropping the rest brings (4) to an anisotropic version of the sine-Gordon problem analyzed by Villain, Grempel, and Lapujoulade[6] in connection with the roughening phase transition of high Miller index crystal faces.

Lyuksyutov[7] considered a Hamiltonian similar to (4) in the context of the closely related problem of solitons of the commensurate phase on an elastic substrate; however, the effects described below were overlooked.

The nonharmonic terms of the Hamiltonian (4) represent the moiré pattern of the step and atom periodicities and can be understood from a phenomenological point of view. A short-ranged interaction between the steps and terrace atoms gives rise to a gradient coupling between v and u_x (regarding two systems as continuous media); the term $2\rho nV(\partial v/\partial x)(\partial u_x/\partial x)$ in (4) is the lowest-order term of this type. Since each subsystem consists of discrete elementary objects (steps and atoms) with some average spacing, each creates an effective periodic potential for the other population, and the effect is described by the sum in (4).

III. CONTINUUM LIMIT

The parameter V entering Eq. (4) can be regarded phenomenologically as the amplitude of the step-atom interaction. However, it is a poorly defined quantity since the steps are not objects that can literally exert or experience a force. The physical meaning of V can be understood by going to the continuum limit.

Let us assume that the discreteness effects accumulated in the sum in (4) can be neglected; later we will find when this assumption is justified. Then the part of the Hamiltonian (4) dependent only on the elastic degrees of freedom reads as follows:

$$H_{\mathrm{el}}=\int_{z\leqslant 0} dx\ dy\ dz\ \frac{1}{2}\sum_{i,k}\ \sigma_{ik}u_{ik} \\ +\rho nV\int dx\ dy(\partial v/\partial x)(\partial u_x/\partial x). \tag{5}$$

Let us consider the case that the field v depends only on x—this means that the interface consists of straight steps of varying density. Introducing Fourier transforms in x according to the rule $f(x)=\int(dk/2\pi)f(k)\exp ikx$, reduces (5) to

$$H_{\mathrm{el}}/L=\int_{z\leqslant 0} dz\int\ \frac{dk}{2\pi}\frac{1}{2}\sum_{i,k}\ \sigma_{ij}(k,z)u_{ij}(-k,z) \\ +\rho nV\int\ \frac{dk}{2\pi}\,k^2 v(k)u(-k), \tag{6}$$

where L is the system size in the y direction. The coupling between v and u_x in Eqs. (5) and (6) implies that the presence of a vertical profile $\partial v/\partial x$ induces a finite lateral strain $\partial u_x/\partial x$; to eliminate the elastic degrees of freedom from (6), we have to solve a two-dimensional elasticity problem (we ignore for now the y dependence) with the boundary condition $u_x(k,z=0)=u(k)$. The equations of equilibrium in the bulk are[5]

$$\frac{\partial\sigma_{xx}}{\partial x}+\frac{\partial\sigma_{xz}}{\partial z}=0, \tag{7a}$$

$$\frac{\partial\sigma_{zx}}{\partial x}+\frac{\partial\sigma_{zz}}{\partial z}=0. \tag{7b}$$

Two boundary conditions must be given to determine the solution uniquely, one of which is the specified value $u_x(k,z=0)=u(k)$. In his treatment, Lyuksyutov[7] selected as the second boundary condition $\sigma_{xz}(z=0)=0$, which incorrectly asserts the absence of any force parallel to the surface. We will instead use $\sigma_{zz}(z=0)=0$ (no normal force). It can be shown that this is equivalent to choosing $u_z(k,z=0)$ so as to minimize the elastic energy of the bulk.

Under these conditions Eq. (6) simplifies to

$$H_{\mathrm{el}}/L=\frac{E}{4(1-\sigma^2)}\int\ \frac{dk}{2\pi}\,|k|u(k)u(-k) \\ +\rho nV\int\ \frac{dk}{2\pi}\,k^2 v(k)u(-k). \tag{8}$$

The $|k|$ dependence in the first term of (8) implies a long-range interaction via the bulk of the crystal. It can be understood as follows: a surface deformation having a wave number k decays in the bulk over a distance of order $1/|k|$, so that most of the elastic energy is confined in a well-defined layer of this thickness; the total energy per unit area can be estimated by multiplying the elastic energy density (quadratic in k) by the thickness of the layer $1/|k|$ wherein the energy is accumulated.

The significance of having the elastic energy linear in $|k|$ is that thermal fluctuations do not destroy the long-range translational order of the atomic positions along the crystal interface—the surface inherits the long-range order of the three-dimensional crystal.[8] It has an important simplifying consequence for what follows: fluctuations of the field $\mathbf{u}$ can be neglected and their effect is manifested only in the temperature dependence of the elastic constants (assuming that we are far away from the melting point).

The elastic degrees of freedom can now be eliminated from (8): this is equivalent to a minimization over $u(k)$ and subsequent evaluation of (8) at the minimum. This gives us

$$H_{\mathrm{el}}/L=-\frac{1-\sigma^2}{E}\,(\rho nV)^2\int\ \frac{dk}{2\pi}\,|k|^3 v(k)v(-k) \tag{9a}$$

$$=\frac{n^2}{2}\int dx\ dx'\ \frac{\partial v}{\partial x}\,U(x-x')\,\frac{\partial v}{\partial x'} \tag{9b}$$

$$U(x)=\frac{2(1-\sigma^2)}{\pi E}\,\frac{(\rho V)^2}{x^2}\quad \text{as}\ \ x\to\infty. \tag{9c}$$

Equation (9b) describes a nonlocal interaction between the gradients $\partial v/\partial x$ and $\partial v/\partial x'$ at points separated by the distance $|x\text{-}x'|$. Since displacement of the steps along the terrace gives rise to a vertical shift of the interface, there is a local surface slope $nb\ \partial v/\partial x$ (where b is the step height), and then Eq. (9b) can be interpreted as describing an interaction between slopes; in turn, Eq. (9c) has the meaning of an inverse-square interaction between steps mediated by the effects of striction[1,2,9]—the steps of the same sign repel each other while the steps of opposite signs attract, regardless of the sign of the parameter V.

Previous continuum treatments[1,2] did not determine uniquely the sign of the interstep interaction for oppositely oriented steps: the step was treated as a localized surface force distribution $\mathbf{f}\delta'(x)$ where the vector $\mathbf{f}$ lies in the $x-z$ plane: f_x describes a local stretch of the surface (it is independent of the step sign) while f_z is a local torque that tends to twist the crystal (it changes its sign if the step direction reverses). The standard way to present the interaction of steps 1 and 2 separated by a distance x is to write it as[1,2]

$$U_{12}(x)=\frac{2(1-\sigma^2)}{\pi E}\,\frac{\mathbf{f}_1\cdot\mathbf{f}_2}{x^2}, \tag{9d}$$

where the vectors $\mathbf{f}_1$ and $\mathbf{f}_2$ describe the force distribution associated with the steps 1 and 2. Comparing this with Eq. (9c) we conclude that (i) $f_x=0$, i.e., there is no local stretch associated with the step; (ii) $f_z=\rho|V|$, i.e., we have identified the phenomenological parameter V introduced in Eq. (2). However, it is also true that $f_z=\alpha b$ where α is the surface tension of the terrace;[1,2] then we can write

$$\rho|V|=\alpha b. \tag{10}$$

An important feature of (10) that attests to the coherence of the approach is that there is no dependence on the elastic properties of the bulk, something that should have been expected from the outset. We note that in Eq. (4) the parameter V also controls the strength of the effects of crystallinity, and one should be able to describe the problem of the roughening phase transition of a high Miller index face in the undeformable limit using it. This is indeed the case, as taking the undeformable limit does not affect Eq. (10).

IV. THE EFFECTS OF CRYSTALLINITY

So far we have neglected the effects of crystallinity accumulated in the sum in Eq. (4), and now we determine their importance. In the undeformable limit these effects are unimportant over a wide range of temperatures between the roughening transition temperature of the terrace and the roughening phase transition temperature of the vicinal interface. The latter is very low:[10,2] a single step is a one-dimensional object, and thus has its roughening transition temperature at $T=0$. The nonelastic part of the interstep interaction will make the roughening temperature finite but it will remain low in the dilute limit. We are always assuming that the interstep distance is much larger than the period of the in-plane crystallinity, and therefore from now on we ignore very weak effects of commensurability of interstep spacing n^{-1} and lattice periodicity ρ^{-1} along the terrace.

When the crystal is deformable, a surface elastic deformation can induce its own potential commensurate with the interstep spacing; the effect will be the strongest when the period of this potential is the same as that of the step array. We can determine whether the surface deformation happens by calculating the system free energy and showing that it is decreased.

A. Effective Hamiltonian

The instability is implicit in the $p=q=\pm 1$ terms of the sum in (4). Dropping the rest we rewrite (4) as follows:

$$H=\int_{z\leqslant 0} dx\,dy\,dz\,\frac{1}{2}\sum_{j,k}\sigma_{jk}u_{jk}+\frac{1}{2}\int dx\,dy[K_1(\partial v/\partial x)^2+K_2(\partial v/\partial y)^2+2\rho nV(\partial v/\partial x)\partial u_x/\partial x]$$
$$+2\rho nV\int dx\,dy\,\cos[2\pi(n-\rho)x-nv+\rho u_x]. \tag{11}$$

The oscillatory dependence on x in the last term will integrate to zero if v and u_x are slowly varying. However, when there is a static surface distortion

$$u_x=u_0(x)=d\,\sin 2\pi(n-\rho)x, \tag{12}$$

with some small amplitude d (to be determined), the integrand has a nonoscillatory part that acts like a commensurate potential for the steps, which can be found by expanding in powers of d. There are still oscillatory terms, but these will be dropped.

The cross-gradient term in (11) couples the distortion of the lattice (12) to the step array. This shifts the equilibrium positions of the steps, requiring the introduction of a new step displacement field

$$w=v+\rho nVu_0/K_1, \tag{13}$$

which eliminates the term linear in $\partial v/\partial x$.

The distortion (12) costs elastic energy, which can be evaluated from the first term of Eq. (8). There will also be some change of the elastic energy associated with redistribution of steps (13). Putting all this together and neglecting the fluctuations of the elastic degrees of freedom [see the discussion after Eq. (8)], we reduce Eq. (11) to the form with diagonal harmonic part

$$H=\tfrac{1}{2}\int dx\,dy\Big[K_1(\partial w/\partial x)^2+K_2(\partial w/\partial y)^2-2\pi\rho^2 nVd$$
$$\times(1+n^2V/K_1)\int dx\,dy\,\cos 2\pi nw+\int dx\,dy\,\mathscr{E}_{\text{el}}(d), \tag{14a}$$

where

$$\mathscr{E}_{\text{el}}(d)=\frac{\pi E|n-\rho|}{2(1-\sigma^2)}\left[1-\frac{2\pi(\rho nV)^2|n-\rho|(1-\sigma^2)}{K_1E}\right]d^2. \tag{15a}$$

The expression in the square brackets of (15a) may become negative implying an instability even in the continuum limit.

However, the sign and the value of the correction to unity in (15a) are not reliable, because the wave number of the distortion (12) does not belong to the domain $k<n$, which is the range of validity of the dependent on v part of the Hamiltonian (4). We will assume that the leading-order terms (in a small-V limit) dominate the physical behavior, so that Eqs. (14a) and (15a) can be reduced to

$$H=\tfrac{1}{2}\int dx\,dy\Big[K_1(\partial w/\partial x)^2+K_2(\partial w/\partial y)^2$$
$$-2\pi\rho^2 n|V|d\int dx\,dy\,\cos 2\pi nw+\int dx\,dy\mathscr{E}_{\text{el}}(d), \tag{14b}$$

$$\mathcal{E}_{\mathrm{el}}(d)=\frac{\pi E|n-\rho|}{2(1-\sigma^2)}\,d^2\equiv\tfrac{1}{2}Ad^2, \tag{15b}$$

where A plays a role of generalized elastic constant. In the prefactor of the cosine term in (14b) we have written $|V|$ instead of V because the sign of this term can be reversed by a homogeneous shift of the field w. Thus regardless of the sign of the step-atom interaction V, commensuration of the step array with the surface deformation lowers the system energy; this lowering can compensate for the increase of the elastic energy $\mathcal{E}_{\mathrm{el}}(d)$. The resulting decrease in the energy will now be calculated, regarding d to be a fixed parameter. This gives a free-energy expansion similar to that of the Landau theory for phase transitions,[11] with d being the order parameter. Then we will discuss the conditions under which the free-energy minimum occurs for nonzero d.

B. The case of zero temperature

The easiest case to analyze is that of zero temperature when there are no fluctuations. Putting $w=0$ in (14b) and taking into account (15b) we find the system energy per unit area as a function of the distortion amplitude d:

$$\mathcal{E}(d)=\tfrac{1}{2}Ad^2-2\pi\rho^2 n|V|d. \tag{16}$$

This expression has a minimum at

$$d_{\mathrm{eq}}=2\pi\rho^2 n|V|/A \tag{17}$$

and the value of the energy at the minimum is

$$\mathcal{E}(d_{\mathrm{eq}})=-2(\pi\rho^2 n|V|)^2/A. \tag{18}$$

We conclude that in the deformable case ($A\neq\infty$) the effects of crystallinity induce an instability (12) at zero temperature, for an arbitrarily small magnitude of the interaction V.

C. The nature of distorted state

The energy gain of commensuration in (16) is linear in d, implying a nonzero generalized force acting on the undistorted lattice, which can only be balanced by the elastic restoring force at finite d. Therefore we can safely conclude that the distorted state is stable at least at sufficiently low temperatures (explicit criteria will be derived below).

In the undeformable limit ($u_x=0$) and with no commensuration between the interstep spacing n^{-1} and the lattice periodicity along the terrace ρ^{-1}, the Hamiltonian (4) is symmetric with respect to an infinitesimal shift of the field v. If n and ρ are commensurate, then necessarily this symmetry is broken at zero temperature, and we are inside the flat phase. However, this effect of commensurability becomes irrelevant above the corresponding roughening transition temperature, which is very low. Therefore for an incommensurate ratio n/ρ at any temperature or for a commensurate ratio above the roughening transition temperature of the vicinal interface, the system is translationally invariant—physically this means that the step array can be displaced along the terrace without any energy cost. Moreover, at finite temperature, the step array can be considered as a two-dimensional classical crystal of lines with only algebraic correlations present,[12] and the steps would wander freely.

For a deformable crystal at sufficiently low temperature the surface distortion (12) arises spontaneously due to the strongly relevant cosine term in (14b). Translational symmetry in w will be broken, true long-range order of step positions sets on, and step wandering will be strongly suppressed on length scales exceeding the correlation lengths ξ_x and ξ_y, which can be estimated (at zero temperature) by expanding the cosine function to second order in w, and using the expression (17) for d_{eq}:

$$\xi_x n\cong(K_1/\rho^2 n|V|d_{\mathrm{eq}})^{1/2}\cong(K_1A)^{1/2}/\rho^2 n|V|, \tag{19a}$$

$$\xi_y n\cong(K_2/\rho^2 n|V|d_{\mathrm{eq}})^{1/2}\cong(K_2A)^{1/2}/\rho^2 n|V|. \tag{19b}$$

This would suggest that the distorted state is not qualitatively different from the ordinary flat phase.[2]

However, another important feature of the traditional flat phase is its response to a weak external force:[2] at $T=0$ there is no response at all, while at finite temperature the interface advances exponentially slowly via a two-dimensional nucleation mechanism. This is not the case for our distorted phase. The breaking of translational symmetry means that the step array cannot move relative to the commensurate potential created by the surface distortion, but these are not rigidly fixed in space and can move together, for example, under conditions of crystal growth.

Indeed a translation of the lattice distortion would correspond to having in (12) an extra phase φ: $u_x=d\sin 2\pi[(n-\rho)x+\varphi]$. Then all the transformations following Eq. (12) can be repeated with the result that the field w in the argument of the cosine in Eqs. (14) would be replaced by $w+(\varphi/n)$. Thus we can shift the position of the minima of the distortion-induced potential freely with no cost in energy, allowing the step array itself to move. Thus without impurities (both on the surface and in the bulk), the vicinal interface in the distorted state can grow continuously, as can the rough vicinal interface in the undeformable limit.[2] The difference is that the surface wave (12) moves when the train of steps does (but with a different velocity, because this is the moiré pattern of steps and atoms; the long-wavelength part of the induced potential does move with the steps). This is rather similar to the physical picture of electronic transport via charge-density-wave motion in quasi-one-dimensional materials.[13]

D. Finite temperatures

To study the case of finite temperature we introduce the space and field variables

$$x=x_1,\quad y=x_2(K_2/K_1)^{1/2},\quad nw=W, \tag{20}$$

which bring the field-dependent part of the Hamiltonian (14b) into the standard sine-Gordon form

$$H/T=\frac{1}{2}\frac{\pi}{g}\int d^2x(\nabla W)^2-\delta n^2\int d^2x\,\cos 2\pi W, \tag{21}$$

where we have introduced the dimensionless parameters

$$g=\frac{\pi T n^2}{(K_1K_2)^{1/2}}, \tag{22}$$

$$\delta = \frac{2\pi\rho^2 |V| d}{Tn} (K_2/K_1)^{1/2}. \tag{23}$$

The parameter g (22) is the ratio of the temperature to a characteristic energy of the step array. However, g is also the exponent that describes the algebraic decay of density correlations in the two-dimensional crystal of steps.[6]

In certain cases g (22) can be calculated explicitly. The form of the Hamiltonian (1) implies that the elastic constant K_1 can be expressed in terms of the macroscopic compressibility of the step array

$$K_1 = n^2 d^2 F/dn^2, \tag{24}$$

where $F(n)$ is the free energy of the step crystal, while the constant K_2 is the bending rigidity and can be expressed in terms of the stiffness coefficient γ of individual step

$$K_2 = \gamma n. \tag{25}$$

When the underlying interstep interactions decay faster than $1/x^2$, the free energy $F(n)$ has the small-n expansion[2]

$$F(n) = \alpha + \beta n + \pi^2 T^2 n^3 / 6\gamma + \cdots , \tag{26}$$

where β is the step free energy. Equations (22), (24), (25), and (26) lead to the *universal* result $g=1$ first derived by Schulz[14] in the context of the commensurate-incommensurate transition in two dimensions. The universal value $g=1$ can be approached in the vicinal limit $n \to 0$ from both above and below depending on underlying interactions.

If direct interstep interactions contain an inverse-square tail, then for several special values of the amplitude of the inverse-square interaction the exponent g has been calculated by Sutherland[15] who found for a marginal attractive case that $g=2$. For even stronger values of inverse-square attraction the collection of steps is totally unstable against a collapse that allows us to argue that the domain $g>2$ is unphysical. Therefore for what follows only the range $0 \leqslant g \leqslant 2$ will be considered.

The parameter δ (23) is the dimensionless strength of the commensurate potential induced by the distortion (12); it is conveniently regarded as a measure of distortion (12) as it is linear both in d and $|V|$.

The evolution of the parameters of the Hamiltonian under a renormalization-group transformation is given by the Kosterlitz equations[16]

$$\frac{d\delta}{\delta} = (2-g) \frac{da}{a}, \tag{27a}$$

$$dg = -g^3 \delta^2 \frac{da}{a}, \tag{27b}$$

$$d\mathcal{F} = -\frac{T^2 n^2}{K_2} \delta^2 \frac{da}{a^3}, \tag{27c}$$

where the last equation describes the contribution to the free energy $\mathcal{F}$ of the short-wavelength degrees of freedom that have been integrated out. Nonuniversal numerical factors of order unity dependent on the cutoff procedure have been dropped from (27b) and (27c). Here a is the current length scale and Eqs. (27) are valid as long as $\delta(a) \ll 1$. The macroscopic behavior of the system is determined by the solution of Eqs. (27) in the limit $a \to \infty$ where the "initial" scale a_0 is set by the interstep distance n^{-1} and the initial value for $\delta(a_0 = n^{-1})$ is given by the parameter δ (23).

As we have already noted, the physically interesting values of g belong to the range $0 \leqslant g \leqslant 2$, and according to (27a) the induced potential $\delta(a)$ is *relevant* whenever the parameter g is less than 2. Then translational symmetry is broken, and the thermal fluctuations will be suppressed on scales exceeding the correlation length ξ, which we will take to be the scale a at which $\delta(a)=1$. For scales less than ξ, $\delta(a) \ll 1$ and (for $g<2$) we can ignore the renormalization of g described by Eq. (27b). Then the solution to (27a) has the form

$$\delta(a) = \delta(na)^{2-g}, \tag{28}$$

where we used the initial condition $\delta(a_0 = n^{-1}) = \delta$. This determines the correlation length ξ via the definition $\delta(a=\xi) = 1$:

$$\xi n \cong \delta^{-1/(2-g)} = \left[\frac{2\pi\rho^2 |V| d}{Tn} (K_2/K_1)^{1/2} \right]^{-1/(2-g)}. \tag{29}$$

This can be compared with Eq. (19a) by putting $g=0$ in the exponent of (29), leading to the same dependence on $\rho^2 |V| d$. The extra factor $(K_2/K_1)^{1/2}$ in (29) is unimportant—it is due to the change of variable (20), $y = x_2 (K_2/K_1)^{1/2}$; but there is a remaining difference in the prefactors of (29) and (19a). This is not too surprising, because the case $T=0$ is outside the range of the perturbative renormalization group $\delta \ll 1$, and merely means that as the temperature goes down, the dependence (29) (in terms of the original variables x and y) will cross over to (19a). We have no theory for the crossover; however, the important point is that the exponent of the dependence (29) is reproduced exactly for $0 \leqslant g < 2$ already in the limit $\delta \ll 1$. The exponent of (29) diverges approaching $g=2$ implying an essential singularity; this can be studied taking into account the renormalization of g (27b).

To find the free-energy gain of commensuration of the step array and surface distortion (12) we integrate Eq. (27c) with $\delta(a) = \delta(na)^{2-g}$ (28) from $a_0 = n^{-1}$ to $\xi = n^{-1} \delta^{-1/(2-g)}$ (29). Omitting an overall undetermined factor of order unity, we find for the free energy change

$$\mathcal{F}_{\text{com}} = -\frac{T^2 n^4}{K_2} \frac{1}{2(1-g)} [\delta^{2/(2-g)} \cdot \delta^2]. \tag{30a}$$

The case of $g=1$ is obviously marginal; the limit at $g=1$ is

$$\mathcal{F}_{\text{com}} = \frac{T^2 n^4}{K_2} \delta^2 \ln \delta. \tag{30b}$$

Equation (30a) can be compared with the second term of the zero-temperature result (16): putting $g=0$ in the exponent of (30a), and remembering that δ (23) is linear in $|V|d$, we see that (30a) and (16) agree that there is a term in the free energy that is linear in $|V|d$.

The functional form (30) suggests that it would be more convenient to regard δ (23) (instead of d) as an order parameter.

E. Marginal case $g=1$

For the marginal $g=1$ case we combine (30b) with (15b) and express d in terms of δ (23). As a result the Landau expansion in terms of the order parameter δ will have the form

$$\mathcal{F}(\delta)=\frac{T^2n^4}{K_2}\left(\frac{\delta^2}{\lambda^2}+\delta^2\ln\,\delta\right), \tag{31a}$$

$$\lambda^2=\frac{(1-\sigma^2)\rho^2(\rho nV)^2}{E|n-\rho|K_1}. \tag{31b}$$

Here the parameter λ (which we assume is very small, $\lambda\ll 1$) represents the dimensionless strength of the effects of striction, and we dropped all the numerical constants of order unity.

Looking at (31a) we see that the effects of commensurability (the $\delta^2\ln\delta$ term) lower the free energy more than the elastic energy (proportional to δ^2) raises it. Equation (31a) is minimized for

$$\delta_{\mathrm{eq}}=\exp\left(-\frac{1}{\lambda^2}-\frac{1}{2}\right)\cong\exp(-1/\lambda^2)\quad\text{as}\quad\lambda\rightarrow 0. \tag{32}$$

Substituting this into (31a) and (29) (evaluated at $g=1$), we find

$$\mathcal{F}(\delta_{\mathrm{eq}})\cong-\frac{T^2n^4}{K_2}\exp(-2/\lambda^2), \tag{33}$$

$$\xi(\delta_{\mathrm{eq}})n\cong\exp(1/\lambda^2). \tag{34}$$

We conclude that the usual rough phase of steps is unstable against a spontaneous transition into the StDW phase for an arbitrarily small striction coupling λ. The essential singularities in (32)–(34) are indicative of the marginal case. In-view of the zero-temperature results of Sec. IV B we can expect that for $g\leqslant 1$, an arbitrarily small striction coupling turns the ordinary rough phase of the steps immediately into the StDW phase. We note that Eqs. (31)–(34) have direct analogs in the context of the classical treatment of the Peierls effect for free fermions.[17]

F. The case of $g\neq 1$

For $g\neq 1$ we will have instead of (31a)

$$\mathcal{F}(\delta)=\frac{T^2n^4}{K_2}\left[\frac{\delta^2}{\lambda^2}-\frac{1}{2(1-g)}\left(\delta^{2/(2-g)}-\delta^2\right)\right]. \tag{35}$$

Minimizing with respect to δ we find for the equilibrium order parameter

$$\delta_{\mathrm{eq}}=\left[\left(\frac{(1-g)}{\lambda^2}+1\right)(2-g)\right]^{-(2-g)/2(1-g)}. \tag{36}$$

For $g=1$ this reduces to Eq. (32); for $g<1$ and $\lambda\rightarrow 0$ it simplifies to

$$\delta_{\mathrm{eq}}\cong\lambda^{(2-g)/(1-g)}. \tag{37}$$

Substituting this in (35) and (29), we find

$$\mathcal{F}(\delta_{\mathrm{eq}})\cong-\frac{T^2n^4}{K_2}\lambda^{2/(1-g)}, \tag{38}$$

$$\xi(\delta_{\mathrm{eq}})n\cong\lambda^{-1/(1-g)}. \tag{39}$$

We see that extrapolated to the case $g=0$, both (38) and (39) predict the same dependence on V and the elastic constants of the crystal as do the zero-temperature results (18) and (21).

For $g>1$ Eq. (36) predicts a finite δ_{eq} only for

$$\lambda^2>\lambda_c^2=g-1, \tag{40}$$

while for $\lambda^2\leqslant\lambda_c^2$, the free energy (35) is minimized by $\delta_{\mathrm{eq}}=0$. We conclude that for $g>1$ and sufficiently weak striction coupling $\lambda^2<\lambda_c^2$, the ordinary rough phase of steps is stable with respect to the distortion (12). When the striction coupling exceeds a critical value (40), a phase transition into the StDW phase takes place with exponents that can be read from Eq. (36). The critical value (40) is small for g close to unity, which is within the range of the small-λ theory we have presented. A better theory is necessary to find critical λ_c away from $g=1$; however, we claim that all the exponents we found so far are exact.

For g approaching 2 we would have to take into account the renormalization of g described by Eq. (27b) to find a meaningful limit of Eq. (35). However, there are factors that come into play at smaller g that make this unnecessary. The nontrivial power $[2/(2-g)]$ in the expansion (35) increases with g and is greater than 2 for $g>1$. The first term of (35) (quadratic in δ) comes from the harmonic approximation, but a cubic anharmonicity term proportional to δ^3 certainly cannot be neglected for $2/(2-g)\cong 3$. The presence of a cubic anharmonicity term in the free-energy expansion implies that the character of the phase transition between the rough phase of steps and the StDW phase will change from second order [as described by (36)] to first order at g around 4/3. The exact conditions depend on the relative strength of the anharmonicity term; usually the effects of anharmonicity are numerically weak so that in any case we expect only a weak first-order transition.

Figure 1 shows a schematic phase diagram of the system in terms of the exponent g (22) versus the dimensionless striction coupling λ^2 (31b). The solid curve is the second-order line, while the broken line suggests the locus of the first-order phase transitions between the rough phase of steps (shaded area) and StDW phase.

We can now conclude that the continuum treatment of Sec. III was valid only inside the rough phase.

V. CONCLUSIONS

We have demonstrated that the combined effect of striction and crystallinity can lead to the existence of a thermodynamic phase of vicinal interfaces, the step-density-wave phase, analogous to the Peierls phase of one-dimensional quantum systems, over a wide range of parameters.

The underlying Hamiltonian (4) with some undetermined phenomenological parameters is valid beyond the vicinal approximation, and the exponent g (22) is also a well-defined quantity, so that we believe that the Peierls mechanism of distortion can be operative for most crystalline unidirectional

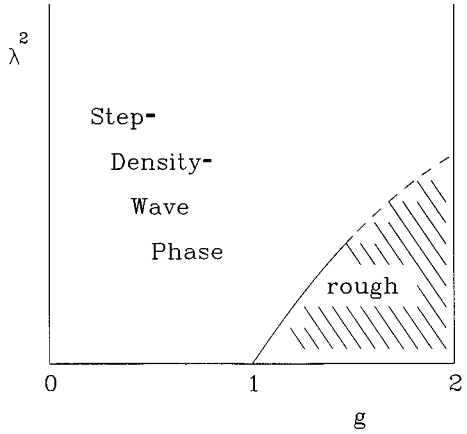

FIG. 1. Schematic phase diagram of the system in terms of the correlation exponent g (22) vs the dimensionless strength of the striction coupling λ^2 (31b). The shaded area corresponds to the ordinary rough phase of steps. The rest is the step-density-wave phase. The solid part of the phase transition line corresponds to the second-order phase transition, and the broken line is a weak first-order transition.

orientations. In the case we have considered, steps running in the y direction, the geometry implied a unidirectional distortion (12). However, a more complicated bidirectional distortion seems possible for more general underlying geometries. The only case for which the Peierls mechanism of surface distortion may not be operative is that of the lowest Miller index interfaces.

Our findings may have relevance to experimentally observed equilibrium crystal shapes. A free-energy expansion of the form (26) for the step array in the vicinal limit implies[2] that the macroscopic shape of the curved interface near a flat edge has the form

$$y=\text{const}\times(x-x_c)^{3/2}, \tag{41}$$

where x_c is the edge position. Experimental observation of this dependence is still a subject of controversy: in some cases, such as equilibrium gold crystals, the intersection of the facets with the curved areas occurs in the form of sharp edges.[18] Recent precise measurements of the equilibrium crystal shape of hcp ^{4}He crystals[19] report on the observation of a vicinal interface state below a critical step density that does not support the prediction (41) either.

The cubic term of the free energy expansion (26) comes from the entropic repulsion of wandering steps. In the StDW phase step wandering is suppressed and the term cubic in step density n may or may not be present. Naively we expect that in this case the leading contribution to the free energy that is nonlinear in n would be the total energy gain due to surface distortion. For example, we found that this contribution is quadratic in n [see Eq. (18)] for low temperatures, thus implying that

$$F(n)=\alpha+\beta n-\text{const}\times n^2. \tag{42}$$

Sàenz and Garcia[20] postulated an expansion of this form to describe the appearance of sharp edges in the equilibrium shape of small gold crystals in the vicinity of (111) facets. We note that in the StDW phase the negative n^2 term cannot be interpreted as an effective $1/x$ attractive interaction between steps, as it originates from collective effects (there is no $1/x$ attraction just between two well-separated steps). Moreover, the presence of such interactions has (almost) been ruled out theoretically[21] even though it describes the experimental data[20] well.

We will not claim that the StDW phase can explain these experimental discrepancies, since we constructed the expansion (42) by hand. However, it is clear that the StDW phase has peculiar properties and needs to be further studied. There is extensive literature on the transitions involving changes in morphology of vicinal interfaces,[22] and maybe this is the domain where the StDW phase has a chance to be observed.

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