Novel surface state in a class of incommensurate systems

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We study the Landau model of the class of incommensurate systems with a scalar order parameter where the modulated phase is driven by a gradient-squared term with negative coefficient. For example, theoretical studies of cholesteric liquid crystals in a field (electric or magnetic) suggest that such an modulated phase should exist at high chirality. The bulk phase diagram in the presence of a bulk external field which couples linearly to the order parameter exhibits a modulated phase inside a loop in the temperature-field plane, and a homogeneous phase outside. On analyzing the same model for a semi-infinite system, we find a surprising result; the system exhibits surface states in a region where the bulk phase is homogeneous (but close to the modulated region). These states are very different from the well-known surface states induced either by a surface field or by enhanced interactions at the surface, for they exist and are energetically favored even when the sole effect of the surface is to terminate the bulk, as expressed by free boundary conditions taken at the surface. Near the surface, the surface-state order parameter is very different from the bulk value (in fact, it has the opposite sign). When the temperature or the bulk field are varied to move away from the modulated state, we find a surface phase transition at which the surface states become energetically unfavorable, though they continue to exist as metastable states. We then study how a surface field changes the surface phase diagram.

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I. INTRODUCTION

It is well known that a surface field can give rise to wetting phenomena and also that enhanced interactions near a surface can give rise to surface order without bulk order [1]. Nakanishi and Fisher [2] have given a unified picture of wetting and surface ordering at the phenomenological (Landau-theory) level; these effects require that surface terms be added to the bulk free energy. In this article, we report an entirely new surface effect which should occur in a particular class of incommensurate systems. We find that surface states exist and are energetically favored by the mere presence of the surface, without surface terms such as those considered in Ref. [2].

Candidate physical systems for observing these states include highly chiral cholesterics in electric or magnetic field, where a bulk undulating phase was recently predicted to occur [3]. This phase is an undulating structure in which the amount of orientational order varies periodically in conjunction with an oscillation of the direction of the local optic axis. It is expected to occur under appropriate conditions of temperature and a strong aligning electric or magnetic field. As discussed in Sec. III C of Ref. [3], the order parameters for the modulated state are the amplitudes of the harmonics of the modulated density associated with the state, such as the magnetic density in the case of magnetic systems. The free energy that results is identical to that of Landau models in which the coefficient of the gradient-squared elastic terms is negative, necessitating the inclusion of terms quadratic in second derivatives. When the coefficient of the gradient-squared term vanishes, a Lifshitz point occurs in the phase diagram [4]. Therefore other candidates include Lifshitz-point systems such as the magnetic material MnP [5,6], and Langmuir monolayers and diblock copolymers [7] with modulated phases.

Our Landau model gives a bulk temperature-field phase diagram with a closed loop separating the modulated phase (favored inside) from the homogeneous phase. The surprise is that the mere existence of the surface produces a surface state which is energetically favored within a second closed loop well outside the first. Outside the second loop, the surface state exists but it is metastable (the equilibrium solution is simply the homogeneous bulk state). The order parameter in the surface state is not a small perturbation to the bulk order parameter. It differs considerably from the bulk order parameter in a small region close to the surface, decaying to the bulk value away from the surface. The width of this region depends very weakly on the temperature. In particular it does not diverge at any temperature, and thus the state does not wet the surface. In the presence of a surface field (coupling linearly to the order parameter), the surface phase may still occur but the line of surface transitions no longer forms a closed loop. From the above and other evidence, our surface states are very different from the states considered in Refs. [1,2].

This paper is organized as follows. Section II presents the effective Landau-Ginzburg model and then describes analytical and numerical results for the bulk phase diagram. Section III presents analytical and numerical results for the surface states, in the absence of a surface field. Section IV shows how the surface phase diagram is modified by a surface field. Finally Sec. V discusses the results and their possible realization.

II. MODEL AND BULK PHASE DIAGRAM

In this section we introduce the model used in the rest of the article, and we study the bulk phase diagram, especially

the transition line separating the homogeneous and modulated states. The bulk free energy F_b is the spatial integral of the density $\mathcal{F}_b$, which is the following functional of the scalar order parameter $\phi(x)$:

$$\mathcal{F}_b[\phi]=-h\phi+\frac{1}{2}r\phi^2+\frac{1}{4}\phi^4-\frac{1}{2}(\phi')^2+\frac{1}{2}(\phi'')^2, \quad (1)$$

where $\phi'=d\phi/dx$. We have scaled the order parameter, the energy and the unit of length to simplify the coefficients, and so h and r are the rescaled ordering field and temperature variables, respectively. The corresponding Euler-Lagrange equation is

$$\phi''''+\phi''-h+r\phi+\phi^3=0. \quad (2)$$

Nakanishi and Fisher [2] examined a very different model; the gradient-squared term appeared with a positive coefficient, the $(\phi'')^2$ term was omitted, and surface terms were added. Their model, without the surface terms, applies to the usual Ising model with ferromagnetic interactions; it has only the disordered and homogeneous (ferromagnetically ordered) phases, and its bulk (r,h) phase diagram consists of a first-order line at $h=0$ and $r<0$ which terminates at a critical point at $r=0$. The model of Eq. (1), but without the $(\phi')^2$ term, exhibits a Lifshitz point at $h=r=0$ and a first-order line for $r<0$.

Without the bulk field h, the model (1) has a disordered phase at high temperature (T), a second-order transition at $r=1/4$ to a modulated phase, and a strong first-order transition at $r\approx-1.2$ to one of two degenerate homogeneous phases; the modulated phase is almost sinusoidal over its entire range, and its wave number is almost independent of T. In the (r,h) plane, the modulated phase occupies a closed loop [8,5,9]. Outside this loop, the energetically favored phase is the homogeneous phase, with order parameter ϕ_0 found from

$$-h+r\phi_0+\phi_0^3=0; \quad (3)$$

its free-energy density is $\mathcal{F}_0=-h\phi_0+1/2r\phi_0^2+1/4\phi_0^4$.

Figure 1 gives the bulk phase diagram, as found for the most part by numerical solution of the Euler-Lagrange equation (2) with periodic boundary conditions. The homogeneous-modulated transition is second-order near $r=1/4$, but otherwise first order. The second-order segment and the tricritical points at its ends are found analytically in the following.

We consider a spatially modulated order parameter and expand it in harmonics. If q is the wave number of the modulated structure and ϵ is the amplitude of the leading harmonic, then the order parameter takes the form

$$\phi(x)=\phi_0+\epsilon\cos(qx)+\epsilon^2[\phi_2\cos(2qx)+\overline{\phi}_2]+O(\epsilon^3), \quad (4)$$

where ϕ_2 and $\overline{\phi}_2$ are constants to be determined. Inserting this order parameter in the free energy (1) and integrating over a period, one finds the following expansion of the free energy (per unit volume):

$$\langle\mathcal{F}_b\rangle=\mathcal{F}_0+\epsilon^2\mathcal{F}_2+\epsilon^4\mathcal{F}_4+O(\epsilon^6) \quad (5)$$

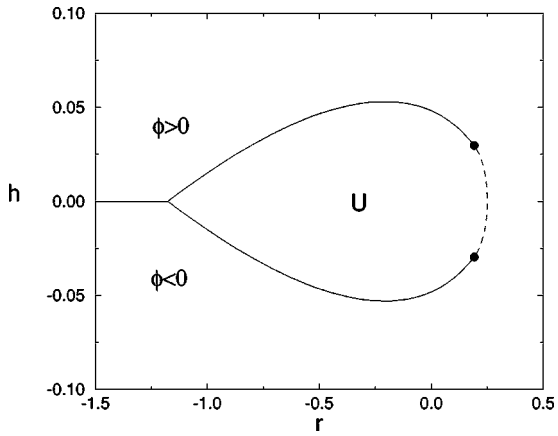

FIG. 1. The (r,h) bulk phase diagram corresponding to model (1). The undulating state (U) is energetically preferred inside the loop, and the homogeneously ordered state outside it. The transition between the states is either first-order (solid line) or second-order (dashed line); two tricitical points (solid circles) separate the two types of transition. The first-order segment was found by numerical solution of the Euler-Lagrange equation, the second-order segment from Eq. (8), and the tricritical points from Eq. (10). At lower temperatures, a first-order transition at $h=0$ separates the two homogeneously ordered states $\phi>0$ and $\phi<0$.

with coefficients

$$\mathcal{F}_2=\frac{1}{4}\left(r+3\phi_0^2-\frac{1}{4}\right), \quad (6)$$

$$\mathcal{F}_4=\frac{1}{4}(r+3\phi_0^2+2)\phi_2^2+\frac{1}{2}(r+3\phi_0^2)\overline{\phi}_2^2+\frac{3}{2}\phi_0\overline{\phi}_2+\frac{3}{4}\phi_0\phi_2+\frac{3}{32}. \quad (7)$$

The free energy has already been minimized with respect to the wave number q, giving $q=\sqrt{1/2}+O(\epsilon^2)$. The homogeneous phase is unstable to a modulated perturbation when $\mathcal{F}_2<0$. Provided that $\mathcal{F}_4>0$ then, a second-order transition occurs at

$$h=\pm\frac{2}{3\sqrt{3}}\left(\frac{1}{8}+r\right)\sqrt{\frac{1}{4}-r}. \quad (8)$$

When $\mathcal{F}_4$ is negative, the transition to the modulated phase is first order. To find the tricritical points separating the continuous and first-order segments, we minimize $\mathcal{F}_4$ with respect to ϕ_2 and $\overline{\phi}_2$ and then set the result equal to zero. On the line $\mathcal{F}_2=0$, $\mathcal{F}_4$ is minimized by $\phi_2=-2\phi_0/3$ and $\overline{\phi}_2=-6\phi_0$; the minimum value is

$$\mathcal{F}_4=\frac{3}{32}-\frac{19}{4}\phi_0^2, \quad (9)$$

and so the two tricritical points are located at

$$r=29/152, \quad h=\pm\sqrt{6/19^3}. \quad (10)$$

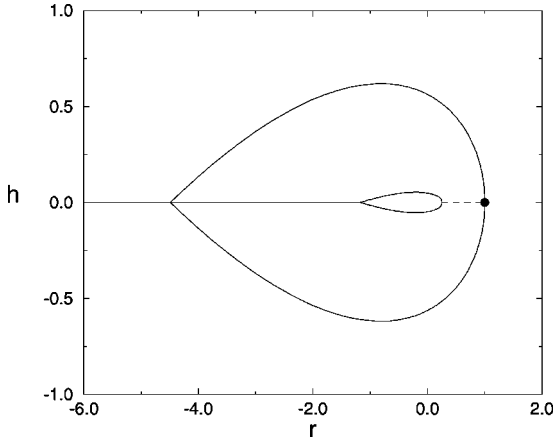

FIG. 2. The (r,h) surface phase diagram for $h_s=0$. The surface states are energetically favorable inside the outer loop (with the qualification noted in the text), and the homogeneous states outside. The transition is first order except at the isolated point $r=1$, $h=0$ (indicated by a dot) where it is continuous. The inner loop is the loop of Fig. 1 (the scale precludes display of details). The leftmost of the three horizontal lines at $h=0$ is the bulk transition between the ordered states $\phi>0$ and $\phi<0$. At the rightmost line (dashed), the surface state changes discontinuously and the bulk state continuously. At the middle line, both surface and bulk states change discontinuously.

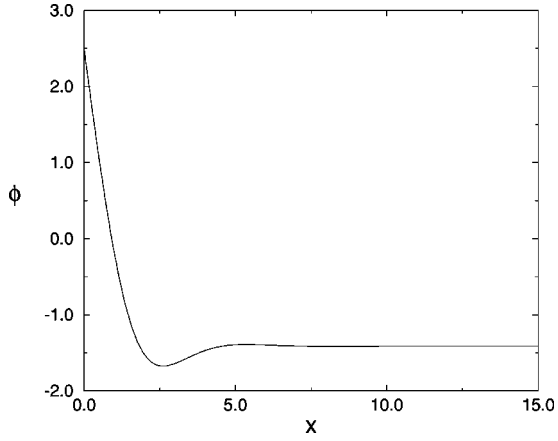

FIG. 3. Order parameter $\phi(x)$ of the surface state for parameters $r=-2$, $h=0^-$, and $h_s=0$. The order parameter is large and positive near the surface; it crosses zero and then decays to the bulk value for large x.

III. SURFACE PHASE DIAGRAM

In this section we consider the surface phase diagram of the model (1) for a semi-infinite system, with no surface field. The presence of the surface generally produces states localized near the surface, and the states are energetically favored in part of the phase diagram. We studied the surface states in the region where the bulk phase is homogeneous, and examined their transitions with varying temperature and the external field. Only a cursory examination was made in the region where the bulk is modulated; in this region, we found many solutions of the Euler-Lagrange equation, so many that a detailed analysis was felt unjustified at this time. That is, surface states and surface phase transitions may exist inside the bulk modulated loop, but have not been studied.

We consider a system occupying the half-space $x\geqslant 0$, and we assume that the order parameter depends only on x. The bulk energy F_b is found by integrating the density of Eq. (1). In this section, we treat the surface very simply, by assuming that it merely terminates the bulk; we thus take free boundary conditions at the surface. In Sec. IV, however, we assume that the surface also applies a local ordering field h_s; then the total energy is F_b+F_s, where

$$F_s=-h_s\phi_s \tag{11}$$

and ϕ_s is the order parameter at $x=0$. The general boundary conditions are then

$$\phi_s'+\phi_s'''-h_s=0,\quad \phi_0''=0. \tag{12}$$

We solved the Euler-Lagrange equation (2) numerically subject to the boundary conditions (12). This equation can have many solutions, depending on the bulk field h and the temperature variable r. Figure 2 gives the surface phase diagram for $h_s=0$, as found from examining these solutions. The surface states are energetically favorable inside the outer loop of the figure (with the qualification noted above), and the homogeneous states outside; the surface states exist (as solutions of the Euler-Lagrange equation) outside this loop but are only metastable there. An interesting feature is that the surface orders at $r=1$ for $h=0$, but the bulk orders only at $r=1/4$. Many more surface states were found at lower temperatures, but they were always metastable.

Figure 3 shows a typical profile of the surface state in the ordered region, for a small and negative bulk field (to break the symmetry) and $h_s=0$. The order parameter decays to the bulk value (which is negative) far from the surface, but it is large and positive near it; the overshooting and the damped oscillations result from a complex decay constant, as shown below. Correspondingly, when the bulk field is positive, the order parameter of the surface state is negative near the wall and then decays to the positive bulk value. Thus at $h=0$ there is a first-order transition at which the surface state changes sign.

To provide an analytical understanding of these numerical results and also those of the next section, we present the following stability analysis of the homogeneous bulk state. The analysis is valid when the deviation of the order parameter from the bulk value is small.

The order parameter is written as $\phi=\phi_0+\psi$, where ϕ_0 is given by Eq. (3) and ψ is the deviation. The free-energy density $\mathcal{F}=\mathcal{F}_b-\mathcal{F}_0$ associated with ψ is

$$\mathcal{F}=\frac{1}{2}(r+3\phi_0^2)\psi^2+\phi_0\psi^3+\frac{1}{4}\psi^4-\frac{1}{2}(\psi')^2+\frac{1}{2}(\psi'')^2. \tag{13}$$

The energy is minimized by an order parameter ψ which satisfies the Euler-Lagrange equation

$$(r+3\phi_0^2)\psi+3\phi_0\psi^2+\psi^3+\psi''+\psi''''=0. \tag{14}$$

To prepare for the next section, we include also the surface free energy (11). The boundary conditions are then

$$\psi'(0)+\psi'''(0)-h_s=0,\quad \psi''(0)=0. \tag{15}$$

For $h_s=0$, the homogeneous bulk state $\psi=0$ is clearly a solution of Eqs. (14) and (15). This solution is stable over some region of the (r,h) plane, but it becomes unstable at the transition to the bulk modulated state.

To study the surface states, we solve Eqs. (14) and (15) perturbatively in ψ. The expansion starts from the solution

$$\psi_1(x)=Ae^{-\alpha x}+A^*e^{-\alpha^* x} \tag{16}$$

of the linearized Eq. (14). The amplitude A and the decay constant α are both complex; the latter (with positive real part) is found from

$$\alpha^2=\frac{1}{2}(-1+i\gamma), \tag{17}$$

where $i=\sqrt{-1}$ and $\gamma=[4(r+3\phi_0^2)-1]^{1/2}$. The condition $\psi_1''(0)=0$ in Eq. (15) gives the amplitude A in terms of $m=\psi(0)$ as

$$A=\frac{m}{2}\left(1-\frac{i}{\gamma}\right). \tag{18}$$

It is convenient to take m as the expansion parameter.

The solution (16) gives the free energy to order m^2. In order to obtain the free energy to the required order (m^4), one must find the higher-order contributions to ψ. Let $\psi=\psi_1+\psi_2$, where ψ_2 is the nonlinear part of ψ. Inserting this form in Eq. (14), using Eq. (16) and keeping terms to m^3, one finds

$$\psi_2(x)=B_1e^{-2\alpha x}+\frac{1}{2}B_2e^{-(\alpha+\alpha^*)x}+C_1e^{-3\alpha x}$$
$$+C_2e^{-(2\alpha+\alpha^*)x}+De^{-\alpha x}+\text{c.c.} \tag{19}$$

with $\psi_2(0)=\psi_2''(0)=0$ and coefficients

$$B_1=-(3+5\sqrt{3}i)\phi_0m^2/126,$$

$$B_2=-2\phi_0m^2/3,$$

$$C_1=-(27+11\sqrt{3}i)m^3/13104,$$

$$C_2=(3+2\sqrt{3}i)m^3/84,$$

$$D=\left(\frac{5}{14}-\frac{19}{126}\sqrt{3}i\right)\phi_0m^2-\left(\frac{7}{208}+\frac{47}{4368}\sqrt{3}i\right)m^3.$$

On using the result $\psi=\psi_1+\psi_2$ in the free energy (13) and integrating over x, one finds that the free energy of the surface state (per unit area) is given by

$$F=-h_sm+a_2m^2+\frac{2}{9}\phi_0m^3+\frac{3}{56}m^4+\mathcal{O}(m^5), \tag{20}$$

where

$$a_2=-(r+3\phi_0^2)\frac{i}{2\gamma}\frac{\alpha^3-\alpha^{*3}}{\alpha\alpha^*}. \tag{21}$$

The amplitude of the surface structure is determined by minimizing the free energy with respect to m for given surface field h_s. This amounts to satisfying the first condition in Eq. (15). We now use the free energy (20) to discuss the surface phase diagram in the region where m is small.

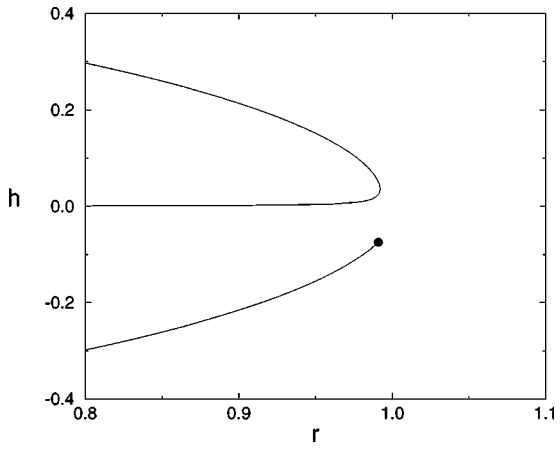

FIG. 4. The high-temperature part of the (r,h) surface phase diagram for $h_s=10^{-4}$. Both transition lines are first order. The lower line ends at a second-order point marked by the solid circle (see text).

Consider first the case $h_s=0$. For zero bulk field h, $\phi_0=0$ and there is no surface state when $a_2>0$ (that is, $\psi=0$). Setting $a_2=0$, one finds a continuous transition at $r=1$ from the disordered bulk state $m=0$ to a surface state with $m\neq0$; this is the second-order point at the right of Fig. 2. For field $h\neq0$, the bulk order parameter ϕ_0 is also nonzero and the free-energy expansion (20) has a cubic term, m^3; this term gives a first-order transition to the surface state, again as found numerically. Near the point $(r=1, h=0)$, m is small and the transition line can be found approximately from the free-energy expansion (20). Away from this point, however, the full free energy must be minimized numerically; Fig. 2 gives the resulting (r,h) surface phase diagram for $h_s=0$.

IV. EFFECT OF A SURFACE FIELD

We consider now the surface phase diagram for nonzero surface field h_s. Positive h_s, for example, tends to increase the order parameters of all states in the region near the surface. The new feature is that the Euler-Lagrange equation must now be solved numerically for what were homogeneous bulk states at $h_s=0$; for lack of a better term, we refer to these surface-field-modified bulk states simply as bulk states. These are the prewetting states considered by Nakanishi and Fisher [2] and others. Figures 4 and 5 give parts of typical phase diagrams for $h_s>0$, as found by numerical solution of Eq. (2). subject to the boundary conditions (12).

Figure 4 shows the high-temperature part of the phase diagram for $h_s=10^{-4}$. The surface field breaks the transitions of Fig. 2 into two first-order lines at which the surface state changes discontinuously. In the region bounded by the upper line and the left vertical (where the bulk field h is positive), the order parameter of the surface state is negative at the boundary $x=0$ $(\phi_s<0)$. The lower line ends at a second-order point. Below this point there is a first-order transition between the paramagnetic state and the surface state with $\phi_s>0$, while above it the two states are indistinguishable. The free-energy expansion (20) can be used to

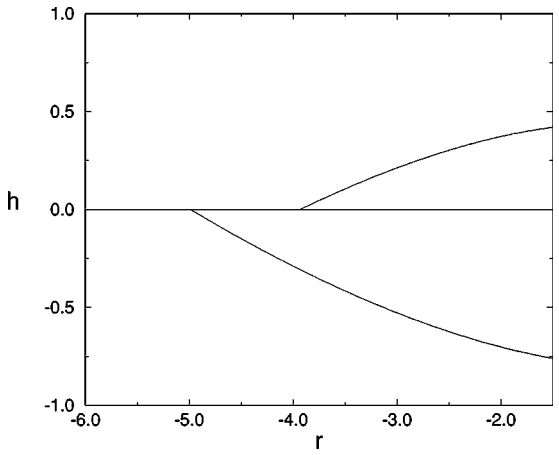

FIG. 5. The low-temperature part of the (r,h) surface phase diagram for $h_s=10^{-1}$. All transitions are first order. The surface field enhances the stability of the lower surface state, for which $\phi(0)>0$ and $\phi(\infty)<0$, and decreases the stability of the other. The leftmost segment of the horizontal line at $h=0$ represents the transition between the two bulk states; these states are not homogeneous in the presence of the surface field. The other segments describe bulk-driven instabilities of the surface states; for example, the lower surface state cannot exist for $h>0$.

find this point to leading order in h_s; the result is

$$a_2=\frac{3}{2}\left(\frac{3}{14}\right)^{1/3}h_s^{2/3},$$

$$\phi_0=-\frac{9}{2}\left(\frac{3}{14}\right)^{2/3}h_s^{1/3}, \tag{22}$$

in good agreement with the numerical results.

Figure 5 shows the low-temperature part of the phase diagram for $h_s=10^{-1}$. Paradoxically, a positive surface field cooperates, rather than competes, with a negative bulk field to enhance the stability of the lower surface state (and it competes with a positive bulk field for the other). These effects occur because the order parameter of the surface state changes sign (as seen in Fig. 3).

V. DISCUSSION

We have developed and analyzed a model to describe the effect of a substrate (or a free surface) on a material which has a bulk phase transition between homogeneous and modulated states. Modulated states tend to form because the free energy of the model contains a term, quadratic in first derivatives of the order parameter, which has a negative coefficient. We treated the surface first as simply terminating the bulk, and then in addition as supplying a surface field coupling linearly to the order parameter.

The important new result of our analysis is the quite unexpected existence of solutions localized at the surface, solutions which exist even if the surface field is zero. These solutions are energetically favored for temperature and field values that are outside but not too far from the closed loop within which the modulated bulk state is stable. When the surface field differs from zero, the loop breaks apart (as shown in Fig. 4 and 5).

We now turn our attention to the applicability of our results to cholesteric liquid crystals in a field [3]. It is obviously desirable to estimate the conditions of chirality, temperature, field, and surface interactions for which the surface states should be observable. To do this, we should examine the relationship between the variables of the theory and the experimental variables, by comparing the expressions for $\mathcal{F}_2$ and $\mathcal{F}_4$ in Sec. II of this paper with the analogous expressions in Sec. III C of Ref. [3]. It is reasonable, however, and far simpler, to expect the loop regions to scale by the same factors; this should be true independent of the strength of surface interactions. From Figs. 1 and 2, the outer (surface-state) loop extends over the range $-4.5\lesssim r<1$ while the inner loop extends over $-1.2\lesssim r<1/4$, about a factor of 4. Accordingly, we estimate the surface-state region to be four times the size of the undulating-state region in temperature. From Ref. [3], the undulating state should occur for intrinsic pitches in the range of 1260–630 nm, at electric fields of the order of a few hundreds of kV/cm, or magnetic fields of roughly 40 T; the temperature width was estimated to be a few tenths of a degree. These conditions are very difficult to achieve and account for the fact that the undulating state has not yet been observed, although some groups plan to attempt the experiments. The surface-state region is expected to be one degree wide. Techniques sensitive to birefringence near the surface, such as Brewster-angle ellipsometry [10,11], may be able to detect the surface states.

The surface states should appear in incommensurate systems where the modulated phase is driven by a negative gradient-squared term. Conditions may be favorable in magnetic Lifshitz-point materials like MnP, or in Langmuir monolayers or diblock copolymers. Other systems in which a modulated phase is driven by a negative gradient-squared term are sodium nitrite and thiourea [12]; related systems are quartz and berlinite, but for these the modulated phase is two dimensional.

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