Commensurate-incommensurate transitions in rare-gas monolayers adsorbed on graphite and in layered charge-density-wave systems

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Existing theories for commensurate-incommensurate transitions in one-dimensionally-modulated systems show that these transitions are continuous and are associated with domain-wall formation. We consider the effect of domain-wall crossing in two-dimensionally modulated systems with hexagonal symmetry such as rare-gas layers adsorbed on graphite and the layered compound $2H$-$TaSe_2$. We show that if the commensurate-incommensurate transition is continuous, the hexagonal symmetry is broken in the incommensurate phase, while if the transition is first order the hexagonal symmetry can be maintained in the incommensurate phase. The experimental consequences of this prediction are discussed.

I. INTRODUCTION

There exist many physical systems which exhibit phase transitions between commensurate and incommensurate phases. Rare-gas layers adsorbed on graphite form two-dimensional structures which may either be registered or nonregistered with the underlying lattice.[1,2] The charge-density-wave systems tetrathiafulvalenium-tetracyanoquinodimethanide TTF-TCNQ[3] and $2H$-$TaSe_2$ (Ref. 4) exhibit similar transitions in which the ordering quantity is the charge density or a periodic lattice distortion. The rare-gas monolayers and $2H$-$TaSe_2$ are two-dimensionally modulated systems. Other systems, which are modulated in one direction, are liquid crystals which exhibit transitions from cholesteric to nematic phases,[3-6] and XY-like helimagnets[7] which become ferromagnets when subjected to a sufficiently strong magnetic field.

A model for commensurate-incommensurate (C-I) transitions in one-dimensionally modulated systems has been constructed in different contexts by Frank *et al.*,[8] De Gennes,[5] Luban *et al.*,[6] and McMillan.[9] According to these theories the C-I transition is continuous. It has also been found that in the vicinity of the phase transition, the incommensurate phase consists of large areas which are nearly commensurate with the lattice, separated by relatively narrow domain walls or discommensurations, where the phase of the modulated structure changes rapidly. These are in fact the "misfit dislocations" introduced by Venables and Schabes-Retchkiman.[10]

In the present note we consider the C-I transition in two-dimensionally modulated systems. In this case the domain walls may take several orientations, and therefore, one should consider the possibility of wall crossings which does not exist in the one-dimensional (1-D) case. Although the arguments presented here are quite general, we will specifically consider the case where the commensurate phase has a hexagonal symmetry, as found in $2H$-$TaSe_2$,[4] and in rare-gas layers adsorbed on graphite. We find that if the C-I transition is first order the domain-wall structure can be hexagonal, while if the transition is continuous, the domain walls are parallel to one another, thus breaking the hexagonal symmetry. The model used in this paper is similar to the models used by Ying[11] and van der Merwe.[12]

The paper is organized as follows: In Sec. II we introduce the model for domain-wall interaction and discuss its ground-state properties. The effect of finite T is considered in Sec. III. Our results are

summarized and compared with existing experimental data in Sec. IV.

II. DOMAIN-WALL INTERACTIONS

To construct a model for domain-wall interactions we consider the density function $\rho_0(\vec{r})$ of the ordering condensed wave in the commensurate phase. In the rare-gas monolayers case $\rho_0(\vec{r})$ is the mass-density wave of the rare-gas atoms, while for $2H$-$TaSe_2$ $\rho_0(\vec{r})$ is the charge distribution. In both cases $\rho_0(\vec{r})$ has a hexagonal symmetry. We describe the nonregistered or incommensurate phase, by local displacements $\vec{u}(\vec{r})$ of the commensurate structure in the x-y plane. The density function in the incommensurate phase will thus take the form $\rho(\vec{r}) = \rho_0(\vec{r} - \vec{u})$. The energy associated with the local displacement field $\vec{u}(\vec{r})$ is given in a continuum approximation by

$$H = \int H(\vec{u})\, dx\, dy \ , \tag{1}$$

where $H(\vec{u})$ is the energy density. Assuming that one can expand H in power series of u and its spatial derivatives, we find that to second order in u, H takes the form

$$H = -A\left[\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y}\right] + B\left[\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y}\right]^2 + C\left[\frac{\partial u_x}{\partial y} - \frac{\partial u_y}{\partial x}\right]^2 + D\left[\left[\frac{\partial u_x}{\partial x} - \frac{\partial u_y}{\partial y}\right]^2 + \left[\frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x}\right]^2\right] + f(\vec{u}) \ , \tag{2}$$

where $f(\vec{u})$ can be any function which has the symmetry of the underlying lattice. The energy expression (2) has the most general form consistent with the hexagonal symmetry. The physical interpretation of the various terms is quite straightforward. The terms A and B represent the energy associated with bulk strain of the adsorbed monolayer, D is the energy associated with shear strain, and C is the energy associated with local rotations. The function $f(\vec{u})$ represents the potential applied by the substrate on the rare-gas monolayer. The lock-in transition takes place as a consequence of the competition between the bulk-strain term A which favors an incommensurate structure and the lock-in potential $f(\vec{u})$. For $|A|$ small compared to $|f|$ the commensurate phase is stable, while for $|A|$ large compared to $|f|$ the incommensurate phase is stable.

We now use the energy Eq. (2) to discuss the C-I transition. Consider first an incommensurate phase with one-dimensional wall structure. Assuming that the domain walls lie in a symmetry direction, we take $u_y = 0$ and allow u_x to depend only on x. The energy Eq. (2) becomes

$$H = -A\frac{\partial u_x}{\partial x} + (B+D)\left[\frac{\partial u_x}{\partial x}\right]^2 + f(u_x, 0) \ . \tag{3}$$

This energy has the same form as the one discussed by McMillan[9] with $f(u_x) = \cos(2\pi u_x)$, and by Luban *et al.*[6] with $f(u_x) = au_x^2$ for $-\frac{1}{2} \leq u_x \leq \frac{1}{2}$, and $f(u_x + 1) = f(u_x)$. For simplicity we adopt the latter form in the present discussion. Minimizing the functional Eq. (1) with H given by Eq. (3) we find in the incommensurate phase, $u_x(x)$ is given by

$$u_x(x) = \tfrac{1}{2}\frac{\sinh(kx)}{\sinh(kl/2)} \quad \text{for } -\tfrac{1}{2}l \leq x \leq \tfrac{1}{2}l \ , \tag{4a}$$

and

$$u_x(x + l) = u_x(x) + 1 \ . \tag{4b}$$

Here $k = [a/(B+D)]^{1/2}$ and l is the distance between adjacent domain walls. In the limit of large l the energy per unit length takes the form

$$E/l = \alpha(1/l) + \beta(1/l)e^{-kl} \ , \tag{5a}$$

where

$$\alpha = \tfrac{1}{2}[a(B+D)]^{1/2} - A \tag{5b}$$

and

$$\beta = [a(B+D)]^{1/2} \ . \tag{5c}$$

In this expression the first term, which is proportional to the domain-wall density, gives the domain-wall energy while the second term represents the interactions between domain walls. Minimizing Eq. (5) with respect to l we find that for $\alpha > 0$, we have $l = \infty$, and the structure is commensurate. For $\alpha < 0$, l becomes finite and the structure is incommensurate with the lattice. Near the transition point l diverges logarithmically

$$l \sim -\log|\alpha| \tag{6}$$

and the transition is continuous. Note that in this case the hexagonal symmetry is broken in the incommensurate phase.

If one wants to consider the possibility of a hexagonal incommensurate phase while keeping the domain-wall picture, one must consider wall crossings. In this case the domain walls form a hexagonal pattern. In the vicinity of the phase transition, where the distance between adjacent parallel walls l, is large, the energy per unit length of the wall and the interac-

tion energy between adjacent parallel walls are not affected by the fact that there exist wall crossings. The energy per unit area associated with wall crossings is proportional to the number of wall crossings per unit areas. We thus take it to be of the form

$$\lambda/l^2 , \tag{7}$$

where λ depends on the parameters A, B, D, and on the specific form of the function $f(\vec{u})$. The energy per unit area, therefore, takes the form

$$E/l^2 = 2\alpha(1/l) + (\beta'/l)e^{-kl} + \lambda/l^2 . \tag{8}$$

The factor 2 in the first term arises from the fact that the total length of the walls per unit area in the hexagonal case is twice as large as in the one-dimensional case. Also note that wall crossings can, in principle, change the coefficient β to β'. However, as we shall see, this does not affect our final result.

The nature of the incommensurate phase and the order of the transition can now be studied by comparing the two energies arising from minimizing the two expressions (5) and (8). For $\lambda < 0$,(i.e., the walls attract each other), the hexagonal incommensurate phase is favored and the transition is first order. The transition occurs at $\alpha = \alpha_c > 0$. For $\lambda > 0$ the transition takes place at $\alpha = 0$ and the *one-dimensional domain-wall* structure is favored. The transition in this case is continuous.

Incommensurate phases with several wall directions have been considered by Ying[11] who neglected interactions between crossing walls and by van der Merwe[12] who considered a model similar to the one presented here. However, apparently he did not reach our conclusions. A model for the C-I transition in $2H$-$TaSe_2$, in which the incommensurate phase is assumed to be hexagonal has recently been studied by Nakanishi and Shiba.[13] They found a first-order transition, consistent with our result for $\lambda < 0$.

In the following we discuss the way the two possible incommensurate phases show up in a scattering experiment. In the commensurate phase one finds three primary diffraction peaks at

$$\vec{q}_1 = (2\pi/3a)(1,0), \quad \vec{q}_2 = (2\pi/3a)[-\tfrac{1}{2}, \tfrac{1}{2}(3)^{1/2}] ,$$

and

$$\vec{q}_3 = (2\pi/3a)[-\tfrac{1}{2}, -\tfrac{1}{2}(3)^{1/2}] .$$

In the hexagonal incommensurate phase these primary peaks shift to $\vec{q}_i' = \vec{q}_i(1+\delta)$, where $\delta \sim 1/l$. Such a diffraction pattern has been observed for $2H$-$TaSe_2$. The fact that the C-I transition is first order in this case, is consistent with our theory. In the one-dimensionally distorted incommensurate phase, however, one finds that the three domains corresponding to the three symmetric diffraction peaks appear at

$$\vec{q}_1' = (2\pi/3a)(1+\delta, 0),$$

$$\vec{q}_2' = (2\pi/3a)[-\tfrac{1}{2} - \tfrac{1}{2}\delta, \tfrac{1}{2}(3)^{1/2}] ,$$

and

$$\vec{q}_3' = (2\pi/3a)[-\tfrac{1}{2} - \tfrac{1}{2}\delta, -\tfrac{1}{2}(3)^{1/2}] .$$

The diffraction pattern of the two other domains is obtained by rotating this structure by $\pm\frac{1}{3}2\pi$. Since all three domains contribute to the diffraction pattern, each peak splits into three peaks in the incommensurate phase. Clearly, in both cases, the domain-wall structure gives rise to secondary diffraction peaks.

III. FINITE-TEMPERATURE CONSIDERATIONS

Whereas the discussion of the ground state (in classical mechanics) can easily be generalized to an arbitrary-space dimensionality d, the effect of finite temperature depends crucially on d. For $d = 1$, there is of course no phase transition; complete registry can never be obtained. For $d \geq 3$, the incommensurate phase can again be described by a succession of rigid walls, provided the temperature is lower than the roughening transition temperature.[14] Therefore, a low but nonvanishing temperature should not modify the conclusions of Sec. II. For higher temperatures, however, the C-I transition is expected to be first order,[15] irrespective of the symmetry of the incommensurate phase.

The case $d = 2$, which corresponds to adsorbed layers, is special because the roughening transition temperature is zero; walls are strongly distorted at any nonvanishing temperature. This is related to the well-known fact that strictly speaking a two-dimensional solid cannot exist at nonvanishing temperature.[16] In the similar case of an XY ferromagnet[17] no long-range order exists at $T \neq 0$. We conclude that the theory given in Sec. II is probably not valid for $d = 2$ except at zero temperature. It would be correct in the case of infinite wall stiffness. However, for practical application to adsorbed layers, the stiffness may well be sufficient at low temperature and the effects of surface defects are probably larger than temperature effects, so that direct comparison of experimental data to predictions of Sec. II is not unreasonable.

IV. DISCUSSION AND CONCLUSIONS

We have analyzed, using a simple phenomenological model, the C-I transition in hexagonal two-

dimensionally modulated systems. We have found that if the C-I transition is continuous, the hexagonal symmetry is broken in the incommensurate phase while if the transition is first order the incommensurate phase can be hexagonal. This result is consistent with the experimentally observed first-order C-I transition in $2H$-$TaSe_2$, which results in a hexagonal incommensurate phase. The situation is not so clear for adsorbed monolayers on graphite: experimentally, the transition seems to be continuous[1,2] and Eq. (6) is satisfied[1,10] with reasonable accuracy. However, this implies an orthorhombic distortion, which has not been experimentally observed so far. It would be of interest to see whether a reinterpretation of existing experiments[1,2] can confirm this orthorhombic distortion.

The arguments presented in this work apply also to the case where the domain walls are rotated away from symmetry directions. This orientational epitaxy has been discussed by Novaco and McTague[18] within the harmonic approximation and by Villain[19] by using a pseudoharmonic theory. Our model neglects interactions with lattice distortion. It has been argued[20] that interaction of walls with shear modes in bulk systems leads to a first-order transition from commensurate to incommensurate structure. This process does not work for adsorbed films.

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[1]M.D. Chinn and S.C. Fain, Jr., Phys. Rev. Lett. 39, 146 (1977); J. Phys. 38, C4-99 (1977).
[2]M. Nielsen, J.P. McTague, and W. Ellenson, J. Phys. 38, C4-10 (1977).
[3]R. Comes, S.M. Shapiro, G. Shirane, A.F. Garito, and A.J. Heeger, Phys. Rev. Lett. 35, 1518 (1975); P. Bak and V.J. Emery, Phys. Rev. Lett. 36, 978 (1976).
[4]D.E. Moncton, J.D. Axe, and F.J. DiSalvo, Phys. Rev. Lett. 34, 734 (1975); Phys. Rev. B 16, 801 (1977); J.A. Wilson, F.J. DiSalvo, and S. Mahajan, Adv. Phys. 24, 117 (1975).
[5]P.G. de Gennes, Solid State Commun. 6, 163 (1968).
[6]M. Luban, D. Mukamel, and S. Shtrikman, Phys. Rev. A 10, 360 (1976).
[7]L.P. Regnault, P. Burlet, and J. Rossat-Mignod, Physica B 86, 660 (1977); L.P. Regnault, Troisieme cycle thesis, (University of Grenoble, 1976) (unpublished).
[8]F.C. Frank and J.H. van der Merwe, Proc. R. Soc. London A 198, 205, 216 (1949) and 200, 125 (1949).
[9]W.L. McMillan, Phys. Rev. B 14, 1496 (1976).
[10]J.A. Venables and P.S. Schabes-Retchkiman, Surf. Sci. 71, 27 (1978); J. Phys. 38, C4-105 (1977).
[11]S.C. Ying, Phys. Rev. B 3, 4160 (1971).
[12]J.H. van der Merwe, J. Appl. Phys. 41, 4725 (1970).
[13]K. Nakanishi and H. Shiba, J. Phys. Soc. Jpn. 44, 1465 (1978).
[14]H.J. Leamy, G.H. Gilmer, and K.A. Jackson, *Surface Physics of Materials,* edited by Blakely (Academic, New York, 1975) Vol. 1, 121.
[15]P. Bak and D. Mukamel, Phys. Rev. B 19, 1604 (1979) (preceding paper).
[16]B. Jancovici, Phys. Rev. Lett. 19, 20 (1967).
[17]F. Wegner, Z. Phys. 206, 465 (1967).
[18]A.D. Novaco and J.P. McTague, Phys. Rev. Lett. 38, 1286 (1977); J. Phys. 38, C4-116 (1977).
[19]J. Villain, Phys. Rev. Lett. 41, 36 (1978).
[20]A.D. Bruce, R.A. Cowley, and A.F. Murray, J. Phys. C 11, 3591 (1978).