Tetragonal-monoclinic phase transition in two-dimensional crystals

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(Submitted 15 April 1985)
Zh. Eksp. Teor. Fiz. **89**, 1067–1070 (September 1985)

A uniaxial two-dimensional crystal is shown to be thermally unstable at all temperatures at the tetragonal-monoclinic transition point. The form of the phase diagram near the transition is found.

A great many adsorbate-substrate systems are known today in which uniaxial two-dimensional crystals form (see Ref. 1 for more details). The adatoms in these crystals are constrained to move in a single direction (because of the pronounced anisotropy of the potential relief of the substrate, for example). These uniaxial crystals are incommensurate with the substrate for a wide range of covering coefficients θ (defined as the number of adatoms divided by the number of atoms in the top layer of the substrate). A continuous phase transition from tetragonal to monoclinic symmetry is observed in a wide variety of incommensurate crystals as θ changes[2,3]; we will refer to this as the $T-M$ transition below.

A complex superstructure (lattice of solitons or domain walls) is present[4] in incommensurate crystals near the point at which the crystal and substrate are commensurate. As we move away from this point, the potential of the substrate merely modulates the lattice of adatoms slightly. For simplicity we will consider the case when the incommensurate crystal supports a quasiacoustic mode,[4] i.e., the substrate is effectively smooth as far as the crystal is concerned. We thus arrive at a uniaxial two-dimensional crystal model described by a Hamiltonian of the form

$$H=\frac{1}{2}\int dx\,dy\left[\lambda_1\left(\frac{\partial u}{\partial x}\right)^2+\lambda_2\left(\frac{\partial u}{\partial y}\right)^2\right]. \tag{1}$$

Here λ_1 and λ_2 are the elastic moduli and $u\equiv u_x$ is the unique nonzero component of the displacement vector. Figure 1a shows the tetragonal lattice and the direction of the displacement vector. In the monoclinic phase the lattice is inclined at an angle φ; however, there is no change in the distance between the atomic rows (which extend along the x axis), because this distance is determined by the topography of the potential surface of the substrate (cf. Ref. 1). Figure 1b shows a unit cell of the monoclinic phase.

At $T=0$, the free energy density F near the $T-M$ transition point θ_0 can be expanded in powers of the inclination angle φ. If φ changes continuously then F should be given by the Landau expansion

$$F=F_0+\alpha(\theta_0-\theta)\varphi^2+\gamma\varphi^4 \tag{2}$$

for a phase transition of the second kind[5] (for definiteness we will assume that the monoclinic phase forms as θ increases). Then for $\theta<\theta_0$ the average value of φ is zero and the tetragonal phase is present, while for $\theta>\theta_0$ the angle $\varphi_0=(\alpha(\theta-\theta_0)/2\gamma)^{1/2}$ is nonzero and a monoclinic lattice forms. If $\theta<\theta_0$ then $\varphi=\partial u/\partial y$, i.e., $\alpha(\theta_0-\theta)\equiv\lambda_2$. Thus, λ_2 vanishes at the transition point and one must analyze the higher order y-derivatives. The Hamiltonian H and the correlation function

$$G=\langle\exp[i(2\pi/a)(u(x,y)-u(0))]\rangle$$

therefore have the form

$$H=\frac{1}{2}\int dx\,dy\left\{\lambda_1\left(\frac{\partial u}{\partial x}\right)^2+\lambda_3\left(\frac{\partial^2 u}{\partial y^2}\right)^2\right\},$$

$$G\propto\exp\left(-\left(\frac{2\pi}{a}\right)^2 g(x,y)\right), \tag{3}$$

$$g\approx\frac{T}{\lambda_1}\left[\frac{|x|}{4\pi}\frac{\lambda_1^{1/2}}{\lambda_3^{1/2}}\right]^{1/2}\left(y^2\ll\frac{\lambda_3^{1/2}}{\lambda_1^{1/2}}|x|\right),\qquad g\approx\frac{T}{(\lambda_1\lambda_3)^{1/2}}|y|,$$

$$\left(y^2\gg\frac{\lambda_3^{1/2}}{\lambda_1^{1/2}}|x|\right)$$

at the $T-M$ transition point. The exponential decay of G implies that no translational order is present in the system at $\theta=\theta_0$ for any $T>0$. The analysis in Ref. 6 shows that nematic ordering can occur in a system with Hamiltonian (3) for $0<T<T_1$.

Let us consider some possible melting mechanisms near the $T-M$ transition. If $\theta<\theta_0$, the Hamiltonian describing the system is given by (1) with $\lambda_2\to 0$ as $\theta\to\theta_0$. The Hamiltonian (1) is isomorphic to the Hamiltonian in the XY model, in which case dislocations (vortices in the XY model) are responsible for the phase transition.[7] In the low-temperature phase the dislocations are bound together in pairs, while in the high-temperature phase depairing occurs and breaks up the order. The transition temperature is given by the expression[7]

$$T_2=(a^2/8\pi)(\lambda_1\lambda_2)^{1/2}, \tag{4}$$

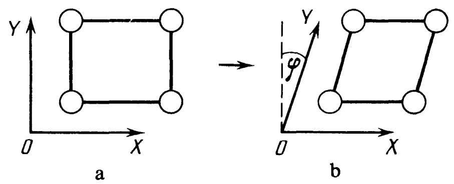

FIG. 1. Unit cells for the tetragonal (a) and monoclinic phases (b).

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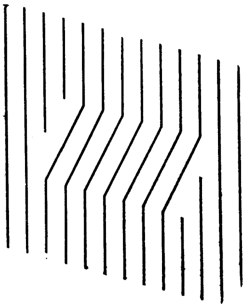

FIG. 2. An antiphase domain (the lines show the atomic rows).

$$T_2 \propto \Delta^{1/2}, \quad \Delta = |\theta - \theta_0|. \tag{5}$$

In addition to dislocations, domain-wall excitations may occur between domains φ_0 of opposite signs in the monoclinic phase (see Fig. 2), and this provides another possible melting mechanism. There are two types of domain walls, which lie along the X and Y axes, respectively. Walls along the X axis resemble magnetic domain walls in uniaxial crystals,[8] and their energy per lattice period along the X axis is given by

$$J_1 = (2a/3\gamma)(\lambda_3 \alpha^3 \Delta^3)^{1/2} \propto \Delta^{3/2}. \tag{6}$$

Walls along the Y axis are similar to small-angle grain boundaries, which are known to consist[9] of a series of dislocations spaced a distance $l = a/2\varphi_0$ apart. The wall energy is the sum of the energy of the dislocation in a region of radius l plus the energy of the core. The first contribution is of order

$$(\lambda_1\lambda_2)^{1/2} a^2 \ln (l/b) \propto \Delta^{1/2} \ln (1/\Delta).$$

The second contribution does not vanish as $\Delta \to 0$ because the dislocation has a finite energy $E \sim (\lambda_1 \lambda_3)^{1/3} a^2/b$ at $\Delta = 0$ (Ref. 6). The asymptotic expression for the wall energy J_2 per lattice period is therefore

$$J_2 \sim Eb/l \propto \Delta^{1/2}. \tag{7}$$

We next estimate the transition temperature for melting due to formation of antiphase domains. If we neglect excitations of the dislocation-pair type, the melting of the monoclinic phase into a liquid will be isomorphic to the anisotropic Ising model with exchange constants J_1 and J_2. The expression for the transition temperature T_3 is[10]

$$\operatorname{sh} \frac{J_1}{2T_3} \operatorname{sh} \frac{J_2}{2T_3} = 1; \tag{8}$$

for $\Delta \to 0$

$$T_3 \sim \frac{J_2}{\ln (J_2/J_1)} \propto \frac{\Delta^{1/2}}{\ln (1/\Delta)}.$$

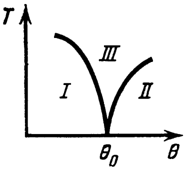

FIG. 3. Phase diagram; θ_0 is the point at which the transition occurs from the tetragonal (I) to the monoclinic (II) phases; region III corresponds to an anisotropic liquid.

The melting temperature T_2 for the dislocation mechanism [cf. (5)] is $\propto \Delta^{1/2}$, i.e., in principle we have $T_2 > T_3$ as $\Delta \to 0$, and the melting of the monoclinic phase near the $T - M$ transition should be isomorphic to the Ising model. Of course, because of the slow divergence of the logarithm $\ln(1/\Delta)$, it is quite possible that $T_2 < T_3$. However, in either case a square-root cusp dependence of the melting temperature on Δ should be observed experimentally. Figure 3 shows a typical phase diagram (the possible nematic phase at $\theta = \theta_0$ is not indicated). We note in closing that an unordered phase was in fact observed between the tetragonal and monoclinic phases in the above experiments.[2,3]

I am deeply grateful to V. L. Pokrovskiĭ for a discussion and valuable comments, and also to V. K. Medvedev and A. G. Fedorus for explaining the experimental situation.

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Translated by A. Mason