Strictive superstructures in two-dimensional phase transitions

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It is shown that a strictive correlation between the order parameter and the lattice deformation leads to the appearance of superstructures in a broad class of second-order phase transitions on crystal surfaces in two-dimensional systems.

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Two-dimensional phase transitions can occur only in different monomolecular layers that are adsorbed on crystal surfaces. As we show below, a unique capillary-strictive correlation between the order parameter and the lattice deformation in a crystal occurs under these conditions in many cases (for example, in ferroelectric transitions, at the surface gas-liquid critical points, in phase transitions due to variation of the equilibrium shape of crystals). It is known[1,2] that striction can greatly change the transition in ordinary, three-dimensional systems. Instead of a uniform phase, a phase with a space-modulated order parameter should develop at the transition point in our case. If the strictive correlation is weak, than the modulation period will be macroscopically large.

Suppose that η is the order parameter corresponding to the phase transition on a plane crystal surface $z = 0$ in a two-dimensional system. In the absence of strictive effects the free surface energy α near the transition point has the usual form

$$\alpha = \alpha_0 + \frac{1}{2} \sum_{\mathbf{k}} (at + gk^2) \left| \eta(\mathbf{k}) \right|^2, \qquad (1)$$

where $\mathbf{k}$ is a two-dimensional wave vector, $\eta(\mathbf{k})$ are space harmonics of the Fourier order parameter, a and g are positive constants, and $t = T - T_c$. We dropped the fourth-order terms in Eq. (1) because thay are not important for our purpose.

The lattice deformation, which is described by the strain tensor u_{ik}, is accompanied by a variation of the surface energy $\delta\alpha$. The relation between $\delta\alpha$ and u_{ik} is linear for a small deformation: $\delta\alpha = \alpha_{ik} u_{ik}$. The values of α_{ik} have an arbitrary nature (see Ref. 3) typical of surface values. This arbitrariness can be eliminated by introducing the condition $\alpha_{ii} = 0$, which is equivalent, as can easily be seen, to the usual condition for the absence of surface particles. The total free strain energy is

$$F_d = \int d^3x \frac{1}{2} \sigma_{ik} u_{ik} + \int d^2x \, \alpha_{ik} u_{ik},$$

where σ_{ik} is the volume stress tensor; the first integral is taken over the volume of the crystal and the second integral over the surface $z = 0$. The equilibrium condition in the volume $\partial\sigma_{ik}/\partial x_k = 0$ makes it possible to convert the volume integral to a surface integral

$$F_d = \int d^2x \left(\frac{1}{2} \sigma_{iz} u_i + \alpha_{\mu i} \frac{\partial u_i}{\partial x_\mu} + \alpha_{iz} \frac{\partial u_i}{\partial z} \right), \tag{2}$$

where $\mu = 1.2$.

Suppose that the symmetry of the crystal face $z = 0$ is such that it allows linear relations of the type

$$\alpha_{ik} = \gamma_{ik} \eta, \tag{3}$$

where γ_{ik} are constants such that $\gamma_{ii} = 0$. Thus, we obtain the following expression from Eq. (2) for the contribution $\alpha_d = F_d/S$ (S is the surface area) of the lattice deformation to the surface energy

$$\alpha_d = \sum_{\mathbf{k}} \left\{ ik_\mu \gamma_{\mu i} \eta^*(\mathbf{k}) u_i(\mathbf{k}) + \gamma_{iz} \eta^*(\mathbf{k}) \frac{\partial u_i}{\partial z}(\mathbf{k}) + \frac{1}{2} \sigma_{iz}(\mathbf{k}) u^*_i(\mathbf{k}) \right\}. \tag{4}$$

The derivatives $\partial u_i/\partial z$ for $z = 0$ can, in principle, be expressed in terms of u_i for $z = 0$ by solving the volume equilibrium equations. As a result,

$$\frac{\partial u_i}{\partial z}(\mathbf{k}) = G_{ik}(\mathbf{k}) u_k(\mathbf{k}), \tag{5}$$

where the components of G_{ik} tensor are first-order, homogeneous functions of the wave-vector components. For an elastically isotropic crystal,

$$G_{\mu\nu} = \frac{1}{k} \left(k^2 \delta_{\mu\nu} - \frac{k_\mu k_\nu}{3 - 4\sigma} \right), \quad G_{zz} = \frac{2(1 - 2\sigma)}{3 - 4\sigma} k,$$

$$G_{\mu z} = G_{z\mu} = -\frac{ik_\mu}{3 - 4\sigma},$$

where E and σ are Young's modulus and Poisson coefficient, respectively.

We emphasize that when only the conditions (5) are valid, i.e., when the volume-

equilibrium conditions are satisfied, is the surface energy a definite function of only the u_{ik} tensor. Otherwise, the part of the crystal adjacent to the surface, and hence the surface itself, are not in equilibrium.

Minimizing the surface energy (4) with respect to $u_i(\mathbf{k})$ for the specified $\eta(\mathbf{k})$, we obtain the expression

$$a_d = -\sum_{\mathbf{k}} f(\mathbf{k})\, k\, |\eta(\mathbf{k})|^2, \tag{6}$$

where $f(\mathbf{k})$ is a positive, homogeneous, zeroth-order function of the wave-vector components. In the isotropic case we have

$$f(\mathbf{k}) = \frac{1+\sigma}{Ek^2}\left\{\frac{(1-2\sigma)^2}{(3-4\sigma)(1-\sigma)}k^2\gamma_{\mu\mu}^2 + \frac{32\sigma^2-52\sigma+21}{(3-4\sigma)^2}(\gamma_{z\mu}k_\mu)^2\right.$$

$$+\left[\left(\delta_{\mu\nu}-\frac{k_\mu k_\nu}{k^2}\right)\gamma_{\nu\lambda}k_\lambda\right]^2 + (1-\sigma)\left[\frac{1}{k}\gamma_{\mu\nu}k_\mu k_\nu - \frac{\sigma}{1-\sigma}k\gamma_{\mu\mu}\right]^2$$

$$\left.+\left[\left(\delta_{\mu\nu}-\frac{k_\mu k_\nu}{k^2}\right)\gamma_{z\nu}\right]^2 k^2\right\}.$$

The expressions (1) and (6) determine the total free energy that describes the phase transition under consideration. We can see that, because of strictive effects, the transition occurs at a higher temperature than T_c to a state characterized by a finite wave vector $k_0 \sim f/g \sim \gamma^2/Eg$. If, as often occurs, the crystal is weakly strained ($E \gg \gamma^2/ga$, where a is the interatomic spacing), then the strictive energy will be small and the period $1/k_0$ of the superstructure will be large as compared with the interatomic spacing.

In conclusion, we emphasize that our findings do not pertain to the transitions from paramagnetic states to magnetically ordered states, since η in this case changes its sign due to time inversion and all γ_{ik} are equal to zero.

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