

Possible structures and phase transitions on the surface of crystals

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It is shown that two-dimensional first-order phase transitions cannot occur because of strictional effects at the surface of crystals. Restrictions are obtained on the symmetry of equilibrium structures at the surface. The possibility, in principle, of the existence of diverse parquet structures is pointed out.

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We assume that two different phases exist on the surface of a crystal. These can be both the natural surface structures as well as structures of adsorbed atoms. If the phases are in thermodynamic equilibrium, then the surface energies of the crystal in both states are identical for a given face. Since these phases are different, the components of the surface-tension tensor need not be identical.

The surface-tension tensor $\beta_{\mu\nu}(\mu, \nu = 1, 2)$ defines¹ the linear dependence of the surface energy of the crystal on the components of the strain tensor $u_{ik}(i, k = 1, 2, 3)$

$$\int \beta_{\mu\nu} u_{\mu\nu} d^2 x ; \mu, \nu = 1, 2. \quad (1)$$

The total deformation energy with allowance for the volume is

$$\frac{1}{2} \int \sigma_{ik} u_{ik} d^3 x + \int \beta_{\mu\nu} u_{\mu\nu} d^2 x, \quad (2)$$

where σ_{ik} is the stress tensor. If $\beta_{\mu\nu}$ is a function of the coordinates on the plane surface, then we can obtain the boundary condition by varying Eq. (2) with respect to the displacement vector

$$\sigma_{nn} = 0, \quad \sigma_{\mu n} = \frac{\partial \beta_{\mu\nu}}{\partial x_\nu}. \quad (3)$$

We shall restrict our discussion to the isotropic case, where $\beta_{\mu\nu} = \beta \delta_{\mu\nu}$. We assume that $\beta = \beta_1$ in the first phase and $\beta = \beta_2$ in the second; therefore, the condition (3) can be represented in the form

$$\sigma_{nn} = 0, \quad \sigma_{xx} = 0, \quad \sigma_{xn} = (\beta_1 - \beta_2) \delta(x); \quad (4)$$

x, y is the Cartesian coordinate system in the surface plane, with the x axis directed normal to the boundary between the surface phases.

The solution of the equations of elasticity theory with the boundary conditions (4) leads to the following result for the energy (2) per unit length of the demarcation line in some macroscopic region of radius R around this line

$$- \frac{(\beta_1 - \beta_2)^2 (1 - \sigma^2)}{\pi E} \ln \frac{R}{a} . \quad (5)$$

Here E is Young's modulus, σ is the Poisson coefficient, and a is a quantity of the order of the atomic distance. The logarithmic divergence of the energy is attributable to the fact that the strain tensor decreases as R^{-1} . The fact that the energy is negative is obvious even without calculations, since the deformation is energetically favorable in this situation, and the energy (2) is zero in the absence of a strain.

Thus, the formation of boundaries between the phases results in a large energy reduction. Both phases, consequently, tend to mix, i.e., they cannot exist as separate phases. An obvious corollary of this is the impossibility of the occurrence of two-dimensional, first-order phase transitions on the surface of crystals.

We call the primary symmetry of the surface structure a symmetry that is caused by the volume elements of the symmetry. It is clear that the actual symmetry of the surface can either be identical to the primary symmetry or it can be lower. In view of the considered striction instability, complete identity of the components of the surface-tension tensor is necessary in the co-existing phases. For example, assume that the point group of the primary symmetry is C_4 ; then the point group of the actual symmetry can only be C_4 . Let us assume the actual symmetry is C_2 . The surface-tension tensor on such a face has two independent components in the principal axes. The other possible equivalent state differs from the first state by a rotation by C_4 . The components of the surface-tension tensor change from point to point and, therefore, they can experience sudden changes along an arbitrary boundary between the phases. Consequently, the actual point group must coincide with the primary one. The situation is the same in the C_1 , C_3 , and C_{1V} groups. The symmetry at such faces can be lower than the primary symmetry because of an increase in translations. A reduced actual symmetry is possible in the rest of the primary groups: $C_2 - C_2$, C_1 ; $C_{2V} - C_{2V}$, C_{1V} , since the $\beta_{\mu\nu}$ tensor is unchanged after a rotation C_2 , $C_{3V} - C_{3V}$, C_3 ; $C_{4V} - C_{4V}$, C_4 ; $C_6 - C_6$, C_3 ; $C_{6V} - C_{6V}$, C_6 , C_{3V} , C_3 , since the surface-tension tensor in these cases reduces to $\beta\delta_{\mu\nu}$.

It is clear that the obtained restrictions exist at any two-dimensional defects in a crystal-bicrystalline boundaries or packing defects.

We note that the slight logarithmic divergence of the energy (5) can result in the following interesting situation. We add to the deformation energy (5) the energy ϵ of a unit length of the boundary. The sum of the energies can be written in the form (5) with the renormalized quantity $a \rightarrow a^*$. If ϵ is appreciably larger than the multiplier in front of the logarithm in Eq. (5), then $a^* \gg a$. Thus the subdivision of the structure ceases at a size of the order of a^* . A regular, parquet-type, periodic structure must be formed under thermodynamic equilibrium conditions. Each "tile" of this parquet is a phase whose symmetry is forbidden above for a phase of unlimited dimensions. All "tiles" of different orientations are contained in each unit cell of the parquet, so that the parquet, as a whole, has one of the allowed symmetries for a given face.

To avoid a misunderstanding, we must stress that if $a^* \gg a$, then a first-order phase transition (it is easy to prove that this also applies to the one-dimensional

case²) can be observed in two-dimensional systems with dimensions smaller than a^* .

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2. L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Nauka, Moscow, 1976, Part 1, § 163.

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