

# Conditions for a phase transition in solids under nonhydrostatic compression

V. V. Avilov

*L. D. Landau Institute of Theoretical Physics, Academy of Sciences of the USSR*

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The effect of shear stresses on the thermodynamic conditions for the appearance of nuclei accompanying a first-order phase transition in a solid is examined. It is shown that external shear stresses decrease the phase transition pressure compared to purely hydrostatic compression.

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On the basis of simple thermodynamic considerations, we examine the effect of shear stresses on first-order phase transitions in solids. Although there is a large amount of experimental data on this problem,<sup>1</sup> a theoretical explanation of the observed regularities has not been given. In the approximation of a spherical nucleus in an elastic isotropic medium, we obtain a relation between the hysteresis parameters with a phase transition and the elastic moduli of both phases. The phase transitions accompanying the action of external shear stresses, observed in many experiments,<sup>2</sup> are examined theoretically. For the example of the phase transition in hydrogen, we examine the construction of phase diagrams in the pressure-shear plane. We propose a new mechanism for plasticity, related to a phase transition in the presence of shear, when the nucleus of the new phase is unstable relative to the reverse phase transition.

Let us assume that the substance can exist in two phases. We denote by  $f_i$  and  $v_i$  the free energy and volume (per atom) of both phases,  $K_i$  the modulus of volume compression, and  $\sigma_i$  the Poisson coefficient ( $i = 1, 2$ ). We shall examine the conditions for a phase transition in the presence of hydrostatic uniform compression of phase 1 by pressure  $p$ . Let the nucleus consist of  $n$  atoms, occupying at  $p = 0$  a sphere with radius  $R$ . In order to calculate the pressure  $p'$  inside the nucleus, we shall use the solution of the problem of deformation of a medium with a spherical cavity.<sup>3</sup> The displacement of the medium at the boundary of the nucleus is

$$\Delta R = -\frac{pR}{3K_1} + \frac{(p' - p)(1 + \sigma_1)R}{6K_1(1 - 2\sigma_1)}. \quad (1)$$

On the other hand, the volume of the nucleus is determined by the equation of state of the new phase  $4\pi(R + \Delta R)^3/3 = nv_2(p')$ . Using the equations of the theory of elasticity and assuming that the relative jump in the phase volumes is small, we obtain

$$p' = p + \frac{\Delta v(p)}{v_1(p)} K', \quad \Delta v(p) = v_2(p) - v_1(p), \quad (2)$$

where

$$K' = \left[ \frac{3}{4G_1} + \frac{1}{K_2} \right]^{-1}, \quad G_1 = \frac{3(1 - 2\sigma_1)}{2(1 + \sigma_1)} K_1. \quad (3)$$

We can see that with the transition into the phase with higher density the pressure within the nucleus is less than  $p$ .

To describe the phase transition, we shall use the local chemical potential  $\mu_i = f_i + p'v_i$ , where the free energy  $f_i$  includes the energy of shear deformations, introduced by Gibbs (see Ref. 4). The nucleus will grow if at its boundary the quantity

$$\Delta \mu = \mu_2 - \mu_1 \tag{4}$$

is negative. Shear stresses occur in phase 1, and the nucleus is compressed hydrostatically. Using the equations from the theory of elasticity<sup>3</sup> for the magnitudes of the shear stresses and for  $f_i$ , we obtain

$$\Delta \mu = \Delta \mu_h + \delta \mu,$$

where

$$\Delta \mu_h = \mu_2(p) - \mu_1(p), \quad \delta \mu = \frac{K'}{2\nu_1(p)} [\Delta v(p)]^2. \tag{5}$$

The quantity  $\Delta \mu_h$  is calculated in the absence of shear stresses. We can see that  $\delta \mu$  is positive and, therefore,  $\Delta \mu$  vanishes at higher pressures than  $\Delta \mu_h$ . If we are examining the reverse transition from phase 2 into phase 1, then the shift in the chemical potential is determined by Eqs. (3) and (5), if the indices 1 and 2 are interchanged. Shear stresses now appear in phase 2, so that  $\Delta \mu = \Delta \mu_h - \delta \mu$ .

Figure 1 shows the transition of hydrogen from the molecular phase to the metallic phase and it also shows the reverse transition. The equation of state for the molecular phase is taken from the experiment of Ref. 5, for the metallic phase the calculation of Ref. 6 is used, and we assume that  $\sigma = 0.35$  both for the molecular phase<sup>7</sup> and for the metallic phase. We can see in this figure the hysteresis region characteristic of the first-order phase transitions.

Let us assume now that the system contains not only an external hydrostatic compression  $\sigma_{ij} = -p\delta_{ij}$ , but also shear stresses, given by the parameter  $s$ , so that the

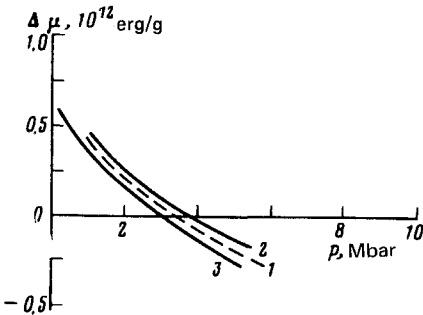


FIG. 1. Difference of chemical potentials of metallic and molecular hydrogen as a function of pressure under hydrostatic uniform compression: 1)  $\Delta \mu_h$ ; 2) and 3)  $\Delta \mu$  with the transition out of phase 1 into phase 2 and the reverse, respectively.

components of the shear tensor  $\sigma_{xx}^s = \sigma_{yy}^s = s$ ,  $\sigma_{zz}^s = -2s$ , while all the remaining components  $\sigma_{ij}^s = 0$ . Because of the spherical symmetry of the nucleus, the change in the free energy of the entire system contains contributions that are linear only with respect to the trace of the external stress tensor and, therefore, only contributions to the free energy can be quadratic with respect to  $s$  and there are no cross terms proportional to the products  $ps$  and  $p's$ . In the case of a phase transition, removal of shear stresses is thermodynamically favorable, so that we assume, as before that the nucleus is hydrostatically compressed by a pressure  $p'$ . The change in the chemical potential of phase 1, due to external sheere stresses, after averaging over the surface of the nucleus does not depend on  $p$  and  $p'$ . We obtain its value from the solution of the problem of the deformation of the medium with a spherical cavity in the presence of purely shear stresses at infinity.<sup>3</sup> The final result is

$$\Delta\mu = \Delta\mu_h + \delta\mu - 15 \frac{s^2 v_1(p) (1 - \sigma_1^2)}{K_1(7 - 5 \sigma_1) (1 - 2 \sigma_1)} \quad (6)$$

We see that the correction to the chemical potential due to external shear stresses is always negative and, therefore, the pressure of the transition  $p$  to the new phase decreases. Figure 2 shows the phase diagram of hydrogen in the  $ps$  plane at zero temperature. Curve 1 corresponds to vanishing of the total  $\Delta\mu$ .

For the new phase to be stable it is necessary that the pressure inside the nucleus  $p'$  fall into the hysteresis region in Fig. 1, i.e.,  $\Delta\mu(p') < 0$  with the reverse phase transition. The dashed line in Fig. 2 shows the boundary of stability of the nucleus  $p = 3.5$  Mbar. At lower pressures, the nucleus of the metallic phase is unstable relative to the appearance of nuclei of the molecular phase within it. Since external shear stresses are eliminated, as a result of the phase transition, this situation corresponds to the appearance of a new mechanism of plastic deformations. Figure 2 also shows the trajectory of the system under single sided compression; a similar situation is realized in diamond anvil setups. As the pressure is increased, the shear stresses increase proportionally to  $p$  (segment  $OA$ ). At  $p = 1.8$  Mbar, plastic deformations of the specimen, due to virtual

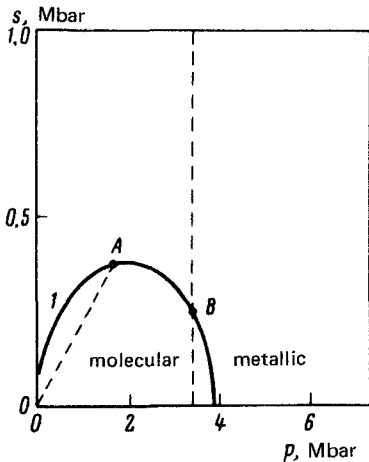


FIG. 2. Phase diagram of hydrogen in the  $p$ - $s$  plane.

phase transition, i.e., the transition to the unstable phase, should appear and later the dependence  $s(p)$  can be interpreted as the dependence of the yield stress on  $p$  (section  $AB$ ). The boundary of stability of the nucleus of the metallic phase is reached at  $p = 3.5$  Mbar (point  $B$ ). Under purely hydrostatic compression, the transition pressure is approximately 3.8 Mbar.

The approximation of a spherical nucleus, examined above, is valid at the early stages of growth of the nucleus, when the surface energy of the interface separating the phases ( $\propto R^2$ ) is not small compared to  $n\Delta\mu \propto R^3$ . As  $R$  is increased, deviation of the nucleus from a spherical shape becomes an advantage; the gain in free energy  $\propto R^4$  is not examined here. The surface energy likewise determines the kinetics of the phase transition. It determines, in each specific case, the probabilities of two competing processes of removing shear stresses: appearance of nuclei and plastic deformations without a phase change.

Aside from decreasing the phase-transition pressures,<sup>1,2</sup> the application of shear stresses in the experiment will permit obtaining new phases, which cannot be obtained with purely hydrostatic compression (see, for example, Ref. 8).

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