

HYSTERESIS TEMPERATURE DEPENDENCE DURING PHASE TRANSFORMATIONS UNDER PRESSURE

É. I. Éstrin

I. P. Bardin Central Scientific-Research Institute of Nonferrous Metallurgy, Moscow
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Data obtained during investigations on the T-p diagrams of materials belonging to various classes of solids (metals (Tl, Sr [1]), ionic salts (RbCl, AgNO₃ [1], TlI [2], RbI [3]), semiconducting compounds of types A^{II}B^{VI} (CdS [4]) and A^{III}B^V (InSb [5]), and others) indicate that in all cases there is considerable hysteresis between transformations with the increase and reduction of pressure. The magnitude of the hysteresis increases sharply with a reduction of temperature (Fig. 1).

Since the location of the hysteresis lines (and not the phase equilibrium line) actually determines

both the region for synthesis of the high-pressure modifications and the region of their (metastable) existence at normal pressure (i.e., their capability of preserving a high-pressure phase), it is of interest to study the occurrence of the hysteresis and its temperature dependence.

It may be shown that the sharp increase in the hysteresis with the reduction of temperature, and the particular shape of the lines at the start of direct or reversible transformations, agree with the law of thermally activated processes in general, and those of phase transformations in particular.

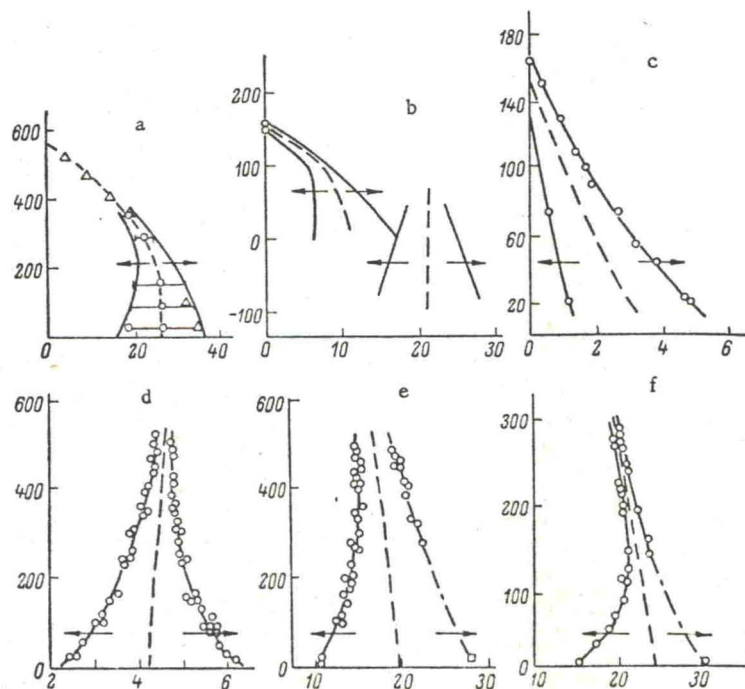


Fig. 1. Hysteresis during phase transformations under pressure: a) Sr [1]; b) AgNO₃ [1]; c) TlI [2]; d) RbI [3]; e) CdS [4]; f) InSb [5]. The abscissa axis is pressure (kbars); the ordinate axis is temperature T (°C).

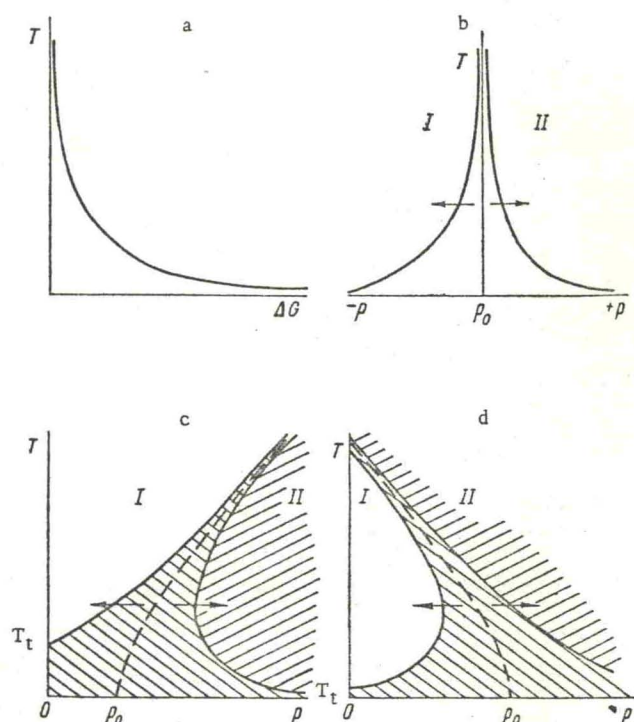


Fig. 2. Diagram illustrating the nature of the hysteresis during phase transformations under pressure, with its temperature dependence. a) Temperature dependence of the thermodynamic stimulus (ΔG) necessary to achieve a specific rate for a thermally activated process; b) the same as (a), but for the case of a phase transformation under the pressure: $\Delta G = (p - p_0)\Delta V$; c, d) T-p diagrams of materials with $dT/dp > 0$, and $dT/dp < 0$, respectively. The regions for synthesis and metastable existence of the high-pressure phase are cross-hatched. The abscissa represents pressure (kbars) and the ordinate temperature, T ($^{\circ}\text{C}$).

The rate of a thermally activated process is a monotonically increasing function of the thermodynamic stimulus ΔG , and the temperature T . The process is experimentally determinable when its rate attains some final (measurable) value. At high temperatures, this experimentally determinable process rate is achieved with a small thermodynamic stimulus. On reduction of temperature, the mobility declines, and the same process rate is achieved at still a larger stimulus. At the limit ($T \rightarrow 0$), the thermodynamic stimulus necessary to produce a specific process rate is infinitely great, and the process does not occur at all.

Thus, the thermodynamic stimulus necessary to attain a specific rate for a thermally activated process has two asymptotic limits: $\Delta G \rightarrow 0$ at $T \rightarrow \infty$, and $\Delta G \rightarrow \infty$ at $T \rightarrow 0$ (Fig. 2a). A dependence analogous to Fig. 2a should be observed for all thermally activated processes. The thermodynamic stimulus is produced by a change of ex-

ternal parameters - magnetic or electric field, mechanical stresses, etc. For the case of phase transformations under pressure, the role of the thermodynamic stimulus is reflected by the value $(p - p_0)\Delta V$, where p_0 is the equilibrium pressure of the phase, and ΔV is the change in volume during the transformation. According to the above, the hysteresis $(p - p_0)$ during phase transformations under pressure should satisfy the conditions: $(p - p_0) \rightarrow 0$ at $T \rightarrow \infty$ and $(p - p_0) \rightarrow \infty$ at $T \rightarrow 0$, i.e., it should have the appearance shown in Fig. 2a, or for actual cases of $dT/dp > 0$ and $dT/dp < 0$, the appearance shown in Fig. 2c and 2d, which are actually observed (cf. Figs. 1 and 2a, 2d).

A transformation on increase of pressure can in principle be realized at any desired low temperature,¹ since the increase in stimulus in this case is not limited by anything (except the technical capabilities of producing still higher pressures). For transformations during reduction of pressure, a natural limit to the increase of stimulus develops on attainment of $p = 0$. In this connection, a transformation during reduction of pressure occurs only at temperatures above the point of intersection of the line for start of the $\text{II} \rightarrow \text{I}$ transformation with the temperature axis (points T_t on Fig. 2c, 2d). At lower temperatures, the high-pressure phase becomes metastable.

Analogous laws may also exist in absence of pressure for the case of diffusionless (metastable) transformations in solid solutions. In such a case, the thermodynamic stimulus equals the difference between the thermodynamic potentials of the two phases of the same composition.

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¹In considering the effect of pressure on mobility it may turn out that on increase of pressure the lower temperature limit for the transformation is not 0°K , but some higher temperature.