



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 ( $\Delta G$ ) 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  $\Delta G$ , 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  $\Delta V$  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,<sup>1</sup> 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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<sup>1</sup>In 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  $0^{\circ}\text{K}$ , but some higher temperature.