

It may be seen from the table that at pressures above 25,000 kg/cm<sup>2</sup>, the discrepancies in the data get as high as 30%. On this basis, Kennedy and La Mori made the assumption that the values for the transition pressures in barium, found by Bridgman from the jump in electrical resistance at 80,000 kg/cm<sup>2</sup>, and in bismuth, found by Bandy at 125,000 kg/cm<sup>2</sup>, are too high by ~30%.

An additional comparison of the results of studies on a number of substances made on Kennedy and La Mori's equipment with similar work done on the same substances under purely hydrostatic pressure shows the following. The transition point in thallium found by Kennedy and La Mori to be 37,414 kg/cm<sup>2</sup> lies near the T1III-T1II transition branch of the p, T diagram for Tl found for pure hydrostatic pressure [9], i.e., along a line corresponding with "superheating" (transition from the more dense to the less dense modification).

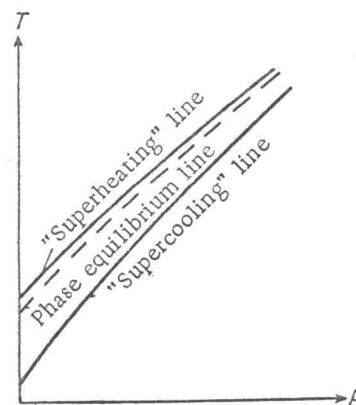
The limit of coexistence between the high and low pressure phases InSbI-InSbII, found using equipment similar to that described by Kennedy and La Mori [10], coincides almost exactly with the "hot" boundary of the InSbI-InSbII transition on the p, T diagram of InSb taken for purely hydrostatic pressures [11], with, as in the case of thallium, the InSb I-InSb II transition occurring with considerable hysteresis under hydrostatic pressure.

Thus, a comparison of these data with the values for the transformation hysteresis observed by Kennedy and La Mori (see table) shows that in addition to the large discrepancies mentioned above in the values of the transition pressures, especially for thallium and cesium, there is also a large discrepancy in the values for the hysteresis of the transitions studied.†

Having hysteresis in these transformations is, generally speaking, not very surprising, since hysteresis is the usual phenomenon in phase transitions of the first kind such as these transformations are. The hysteresis may be accounted for by the fact that it is usually rather difficult to satisfy the conditions for establishing true equilibrium in the system. If however it is in some way possible to make the system approach the equilibrium state, it is obvious that there will be less hysteresis. Theoretical considerations and the experimental facts also show that the hysteresis in a transformation as a rule increases as the temperature of the transformation is reduced, and that the hysteresis may be reduced to where it disappears completely by increasing the temperature of the transformation [9, 12]. A large effect is exerted on the pressure and temperature of the transformation, as well as on the hysteresis associated with it, if there are impurities in the substance undergoing the phase transformation.

The experimentally determined values of the transition pressure given in the table are the mean of the transition pressures when raising and lowering the pressure in the experiment. It may be shown that these values are not the equilibrium parameters of the transition, i.e., they do not define the pressure at which the thermodynamic

potentials of the two phases are equal. The probability of a transition between two phases will be greater, the greater the energy of the atoms and the lower the activation energy of the transition. At low temperatures (small  $kT$ ) the activation energy is considerably greater than the energy of the atoms, and hence the transition probability is relatively small, i.e., the transition accompanies superheating and supercooling (for practically realizable rates of change in the temperature and pressure of the system). However, true equilibrium is not reached exactly at the temperature found by averaging the transition temperatures found in heating and cooling. The transition probability increases as the temperature is raised, while it drops as the temperature is lowered. Thus, the superheating is, as a rule, small in comparison with the supercooling. We have a similar picture in isothermal phase transformations, i.e., where the transition is brought about by raising and lowering the pressure. In this case, the transition probability and the associated transition rate decrease as the pressure is increased, and, conversely, increase as the pressure is dropped. In this sense, increasing the pressure is equivalent to lowering the temperature. Accordingly, it may be concluded a priori that the mean values of the transition temperature and pressure from the "direct" and "reverse" processes (raising and lowering the temperature or pressure in the isobaric or isothermal process respectively) are not the equilibrium phase transformation parameters, when appreciable hysteresis is present. Obviously, the true equilibrium curve in the p, T plane must pass closer to the superheating line and not through the averaged points between the superheating and the supercooling lines. This is made clear by the figure, where a possible position of the equilibrium line between the two phases is shown dotted.



In [2, 10], the measurements were made under quasi-hydrostatic conditions, where the conditions of the experiment, the lack of packing rings, and the rotation of the piston leave reason to suppose that displacement forces were acting [14].

† For bismuth under hydrostatic conditions, a hysteresis of 1000 kg/cm<sup>2</sup> was found for the Bi I-Bi II transition, and 900 kg/cm<sup>2</sup> for Bi II-Bi III [13].