lization for non-crystalline material can be a very sluggish process, as evidenced by the behavior of the high-density starting material, Ge IV was inconsistent in its appearance in this work. The proposed Ge III–IV boundary [8] was based on a large number of experiments and the present experiments on non-crystalline material can hardly confirm or disprove the previously proposed boundary. However, the very appearance of Ge III and Ge IV in the present work supports their presence, if not their precise placement, in the phase diagram. The stability field of Ge IV requires further study, especially its relationship with that of Ge II; an earlier proposal [8] placed Ge II metastable to Ge IV over a wide pressure range. Clearly in situ X-ray diffraction measurements after significantly long times at high pressure and low to high temperatures would be of value, but kinetic barriers at low temperatures could well resist the dictates of thermodynamics.

The results obtained for the high-density (6.0 ± 0.3 g/cm^3) non-crystalline Ge seem to be a direct consequence of the high starting density. Table 2 shows the densities of all possible high-pressure phases, and it is evident that the density of the starting material is higher than or equal to that of Ge III or Ge IV, within the experimental errors involved in the determination of the density of the non-crystalline Ge.

From the present results it appears that the following processes variously affect the behavior of non-crystalline Ge: mechanical grinding involving friction between particles and causing within particles fractures and shears that are coarse or sparse on an atomic scale; internal compaction under high pressures creating fractures and shears that are very extensive on an atomic scale. Mechanical grinding apparently releases sufficient strain energy to initiate partial crystallization of Ge I from the high-density, non-crystalline Ge. The low-density, non-crystalline Ge probably has less strain energy related to it, and hence when it is ground no crystallization occurs. However, upon compression, continuous microscopic strains occur on an atomic scale within the low-density non-crystalline Ge, resulting in an increase in its density [6], and the $P\,\mathrm{d}V$ energy related to this over ≈ 100 kbar would be ≈ 4.8 kcal/mol. This energy is apparently sufficient to overcome the activation energy related to the formation of Ge III or the new metallic non-crystalline form [2,3]. For the high-

Table 2
Densities of high-pressure phases of crystalline Ge and non-crystalline Ge.

Phase	Density (g/cm^3)	Remarks
Ge I	5.325	–
Ge II	7.51	from in situ crystallographic data [12]
Ge III	5.89	from crystallographic data on quenched phase
Ge IV	5.846	from crystallographic data on quenched phase
low-density non-crystalline Ge	4.8 ± 0.3	from weight geometry measurements
average density non-crystalline Ge	5.3 ± 0.3	from weight geometry measurements
high-density non-crystalline Ge	6.0 ± 0.3	from weight geometry measurements