Phase-Transition Studies of Germanium to 1.25 Mbar

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New phase transitions in Ge were observed by energy-dispersive x-ray diffraction techniques for pressures up to 125 GPa (1.25 Mbar) as follows: the β -Sn structure to the simple hexagonal (sh) phase at 75 ±3 GPa and to the double hexagonal close-packed structure (dhcp) at 102 ±5 GPa. These are the highest pressures for which a crystalline structure change has been directly observed by x-ray diffraction. Total-energy pseudopotential calculations predict 84 ±10 GPa for the β -Sn to sh phase transition and 105 ±2 GPa for sh to hcp (not dhcp) transition. The role of 3*d* core electrons in increasing the transformation pressures in Ge, as compared to Si, is emphasized.

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There is considerable interest in the phase transitions induced by application of high pressures in the covalent group-IV elements, C, Si, and Ge. For the case of carbon only theoretical predictions are available^{1,2}; however, for Si and Ge both experimental and theoretical studies have been done. Various novel crystalline forms of Si and Ge have been observed under a variety of thermodynamic conditions of temperatures and pressures.³ The interest in the highpressure phase transitions in those elements was further stimulated by the existence of a simple (or primitive) hexagonal phase (sh) in Si observed at a pressure above 13 GPa.^{4,5} This was the first observation of a monatomic system in the sh phase, although the sh phase is known to occur in some binary systems.^{6,7} For pressures up to 50 GPa,^{4,5} Si was found to have a structural transition sequence: cubic diamond to tetragonal to sh to an intermediate structure⁴ and finally to hexagonal close packed (hcp) above 40 GPa. Ge studied in the same pressure range showed only one transition from the cubic diamond structure to the β -Sn structure around 11 GPa.⁴ Pseudopotential calculations were applied to study the sh phase transition in Si^{8,9} and it was shown that the transition is driven by a soft phonon mode. Superconductivity in the sh phase of Si was predicted and experimentally verified and the critical temperature of sh Si is among the highest of the nontransition elements.¹⁰

In this Letter, we report *ab initio* pseudopotential calculations on Ge made by two of us (Chang and Cohen⁸) which suggest the possibility that Ge will transform into the sh and hcp structures at pressures in the megabar range and report experimental measurements made simultaneously and independently by the other authors.

The Ge samples were studied in a diamond-anvil cell by energy-dispersive x-ray-diffraction techniques using the Cornell high-energy synchrotron source. The experimental technique is described in detail elsewhere.^{11,12} Two separate high-pressure experiments were made on Ge samples. A Ge powder of 99.999% purity was ground into fine powder and placed in the $50-\mu m$ hole of the spring-steel gasket. Diamonds of $300-\mu m$ flat area were used and pressure was measured by the ruby fluorescence technique¹³ to 90 GPa. In another ultrahigh-pressure experiment, a Ge-20wt.% Pt mixture was placed in the $25-\mu m$ hole of the spring-steel gasket and pressure was measured from the Pt marker via the isothermal equation of state of Jamieson, Fritz, and Manghnani¹⁴ and the gasket material via the isothermal equation of state of ϵ iron of Brown and McQueen.¹⁵ Diamonds with $300-\mu m$ tips with 5° bevel and flats of 100 μ m were used in the latter experiment. X-ray diffraction measurements were made to pressures of 1.25 Mbar and were terminated only because the scheduled time at the synchrotron ended.

Figure 1 shows patterns of Ge at a pressure of 72 GPa in the β -Sn phase recorded with a 10- μ m pinhole and at 90 GPa in the sh phase recorded with a 20- μ m pinhole. All the ten diffraction peaks at 72 GPa can be indexed on the basis of the tetragonal cell of the β -Sn type. At a pressure of 77.7 GPa, Ge shows almost complete transformation into the simple-hexagonal phase. This transformation between two metallic phases is either isovoluminal or nearly so (volume change less than 0.5%); thus we do not expect a large hysteresis. On this basis the experimental value of the phase transition pressure is 75 ± 3 GPa. All nine peaks at 90 GPa can be indexed on the basis of a simple-



FIG. 1. The energy-dispersive x-ray-diffraction patterns of Ge (a) at 72 GPa in the β -Sn structure taken with a 10- μ m pinhole and (b) at 90 GPa in the simple-hexagonal phase taken with a 20- μ m pinhole. The weak peaks marked \overline{e} and g are respectively an escape peak and a diffraction peak from gasket material. The diffraction angle $\theta = 9.630^{\circ}$. The pressures were measured by the ruby-fluorescence technique.

hexagonal cell. In Fig. 2, the pressure variation of the axial ratio for various phases of Ge is given. The experimental c/a ratio of Ge in the β -Sn phase is remarkably constant (0.550 \pm 0.008) over the complete pressure range of its stability and shows excellent agreement with theory, as shown by the solid line. In the sh phase, the experimental $c/a = 0.930 \pm 0.007$ which is in reasonable agreement with theoretical value of 0.945.

In the second experiment when the sh phase of Ge was pressurized beyond 1 Mbar a new phase transition was observed at a pressure of 102 ± 5 GPa. This is the first crystalline transformation observed above 1 Mbar in any material by x-ray diffraction. The new phase appears to be similar to the so-called intermediate phase reported⁴ in Si between 34 and 39 GPa; above about 40 GPa Si has the hcp structure. The new phase in germanium can be indexed as a double-hexagonal-close-packed structure (dhcp). All the observed



FIG. 2. Axial ratios for β -Sn (c/a), sh (c/a), and dhcp (c/2a) phases of Ge. The solid circles represent the experiment to 90 GPa. The open circles represent the experiment to 125 GPa. The solid lines represent the theoretical calculations.

diffraction-line positions can be explained by this four-layer sequence of hexagonal-close-packed layers although the relative intensities are modified by the presence of stacking faults.¹⁶ The diffraction pattern of the dhcp structure contains all the peaks of the hcp structure as a subset plus additional peaks. The intensities of these additional peaks are exceptionally sensitive to the presence of stacking faults, decreasing very rapidly with the number of stacking faults¹⁶; these additional peaks go to zero when the hcp structure is formed as has been noted in silicon.⁴ Several of the light-rare-earth elements have the dhcp structure at atmospheric pressure while the rare-earth elements in general have this structure at high pressure.¹⁷

For Ge at 125 GPa (1.25 Mbar) the lattice parameters are a = 2.414 Å, c = 8.114 Å, and c/2a = 1.681. This ratio as a function of pressure is shown in Fig. 2. We note that for Si the extra peaks for the intermediate phase denoted by arrows in Fig. 1(d) of Ref. 4 at 39 GPa are located exactly at the expected positions of (101) and (103) peaks of the four-layer structure (all the other peaks fit also) for a = 2.458 Å, c = 8.348 Å, and c/2a = 1.698. It appears from these measurements that the eventual transition of Ge into the hexagonal-close-packed layer sequence of ABAB ... may occur at pressures greater than 125 GPa. It would be interesting to extend the high-pressure studies on Ge to pressures of 2 Mbar. It is also likely that the discontinuity reported in the shock Hugonoit for Ge under shock waves above 1 Mbar¹⁸ is due to the phase transition seen in this study. The detailed equation of state of Ge for all the high-pressure phases to 1.25 Mbar will be presented elsewhere.¹⁶

These two transformations in Ge occur at much

TABLE I. Transformation pressures in gigapascals.

	Silicon		Germanium	
	Expt.	Theory	Expt.	Theory
Diamond to β -Sn	12.5ª	9.3 ^d	10.8 ^e	9.5
β -Sn to sh	13-16 ^{b,c}	12 ^d	75	84
sh to dhcp	34 ^b	41 ^d	102	105 ^g
dhcp to hcp	40 ^b	• • •	f	

^aReference 19.

^bReference 4.

^cReference 5.

^dReference 8.

eReference 20.

^fNot observed at pressures as high as 125 GPa.

⁸Present theory predicts a transformation from sh to hcp. The dchp phase is found by present theory to be metastable relative to hcp.

higher pressures than the corresponding transformations in silicon (see Table I). This represents a radical departure from the general observation that an equivalent transition pressure is lower for an element further down a given column of the periodic table. Examples of this general rule include the semiconductor-to-metallic transition in the group IVb elements as follows: diamond (not found even at 275 GPa),¹⁹ Si (12.5 GPa),²⁰ Ge (10.8 GPa),²¹ and Sn (atmospheric pressure); the bcc to fcc transition in the alkali metals,²² K (25 GPa), Rb (7 GPa), Cs (2 GPa); and the semiconductor to metallic transition in the group VIb elements O_2 (not found at 40 GPa),²³ S (50 GPa),²⁴ Se (12 GPa),²⁴ Te (4.5 GPa).²⁴ It is the departure of these two transformations from this general empirical rule which makes the behavior of Ge interesting. We will return to this point in the theoretical section which follows.

Figure 3 shows the calculated crystal energies fitted to the Murnaghan equation of state²⁵ for different phases. Up to 150 GPa, we find that except for the high transition pressures, Ge behaves like Si. The β -Sn, sh, and hcp structures appear as high-pressure phases and the ordering of the structural transitions is the same as that found theoretically in Si.^{8,9} For Ge, the computed structural transition from diamond to β -Sn occurs at 9.5 GPa along the common tangent (dashed line) of the lowest two energy curves. The sh phase in Ge is calculated to be stable at 84 ± 10 GPa and the crystal volume only changes by 0.3% of V_0 , where V_0 is the calculated equilibrium volume in the diamond phase. This is in reasonable agreement with experimental value of 75 ± 3 GPa for the transition pressure and volume change of less than 0.5% at the transition. The large error in theoretical calculated pressure is because the energy curves for the β -Sn phase and sh structures are very close and sharply rising for a wide range of volume. At 105 ± 2 GPa, the



FIG. 3. Crystal energies vs volume. The volumes are normalized by the calculated equilibrium volume of 22.5616 A^3 . Inset: detailed structure of the curve near the transitions. The arrows indicate the transition volumes for the β -Sn to sh and the sh to hcp transitions. From right to left, the arrows are at 0.533, 0.530, 0.506, and 0.493.

sh structure is calculated to transform into the hcp structure with a discontinuous change of volume of 1.3% of V_0 . Experimentally, the sh structure transforms to an intermediate phase at 102 ± 5 GPa which appears to be the dhcp structure. Further theoretical studies are needed to explain the stability of this phase.

The origin of the high transition pressure between metallic phases of Ge appears to be connected with the large 3*d*-core radius for Ge. This core effect influences the energy curves in Fig. 3. The minimum energy volumes for Ge are almost the same for the metallic phases while for Si it decreases when the coordination number increases from β -Sn (coordination =6) to sh (coordination = 8) to hcp (coordination = 12). This difference in behavior is strongly related to the 3dbands in Ge which induce a repulsive motion of the dvalence electrons because of the more repulsive dpseudopotential.²⁶ A constant shift of the sh curve in Si to higher energy which was attempted to explain a possible high transition pressure for Ge⁹ does not represent this core effect. A more appropriate approach is to note that the sh and hcp curves of Ge

resemble that of Si shifted to higher volumes. These shifts result from the *d*-core repulsion and produce a high transition pressure. At the β -Sn to sh transition pressure the *d*-valence-state contribution in Si and in Ge become nearly equal.

It should be pointed out that the compression of Ge to pressures over a megabar results in volumes less than half of the volume at ambient pressure. We note that at these extreme compressions the large 3d cores in Ge might start overlapping and the further theoretical calculations probably have to take into account the core-core overlap effects and probably also the core-polarization effects.²⁷

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