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Germanium at high pressures

Carmen S. Menoni, Jing Zhu Hu, and Ian L. Spain
Department of Physics, Colorado State University, Fort Collins, Colorado 80523
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X-ray diffraction experiments have been carried out on germanium in a diamond anvil cell to 26 GPa. The pressure at the transition to the metallic phase (II) has been studied in different pressurizing media, giving 10.6±0.05 GPa in a quasihydrostatic medium (4:1 methanol:ethanol mixture), 9.8±0.1 GPa in NaCl, and 8.1±0.3 GPA when the sample was compressed directly between the anvils. The compression curve for phase II has been fitted to a modified Murnaghan equation. Upon release of pressure the transformation from phase II to III (tetragonal) was found at 7.6±0.05 GPa. It was found that the details of the transition depended on the stress condition and rate of decompression.

I. INTRODUCTION

High-pressure phase transitions from semiconducting to metallic forms of Ge were first inferred from resistance measurements of Minomura and Drickamer.[1] Since that time a number of experimental studies have been carried out using several different techniques. Studies on germanium pertaining to the semiconductor transition include those on electrical resistance,[1–6] x-ray diffraction (*in situ*[7–11]) and quenched specimens[12,13] and optical properties.[14,15] The transition has also been detected from studies of dynamically loaded specimens.[16–18] These references are restricted to work on crystalline material and do not include extensive work on amorphous samples.

The present paper reports on x-ray diffraction measurements on Ge taken over a number of years. The initial reason for this study was to ascertain whether there were further phase changes at high pressure. Yin and Cohen[19,20] predicted only the sequence cubic (diamond) $\xrightarrow{9.6\ \mathrm{GPa}}$ body-centered tetragonal (β-Sn) in the pressure range up to 50 GPa. However, similar calculations for Si (Refs. 19–21) failed to include the primitive hexagonal phase which was found experimentally.[11,22] Subsequent calculations[23,24] confirmed this phase theoretically.

Another reason for the study was to carry out x-ray diffraction studies using a modern pressure scale (ruby fluorescence scale[25,26]). Examination of published work indicates a fairly large variation for the transition pressures P_t to the metallic phase (I→II). Early work before about 1975, using fixed points for pressure calibration, tended to overestimate pressures (see Ref. 27). Even after these results for P_t are omitted, the range of values is ~7–11 GPa for Ge. Jamieson[7] and Okai and Yoshimoto[6] suggested that the transition pressure could be affected by the compressing medium, and this has been confirmed by recent studies.[8,10] Qadri *et al.*[10] showed that P_t was as high as 10.5 GPa with hydrostatic stress, and could be initiated at 6.7 GPa with direct compression of the sample without fluid. The present work will report values of P_t using different pressurizing media.

If the metallic phase is formed and the pressure then lowered, a metastable phase results.[2] The structure for the metastable phase (III) was found to be tetragonal ($P4_32_12$) for Ge (2,12) (sometimes called ST-12). The bonding was sp^3 type, and the volume somewhat reduced compared to that of cubic (diamond) phase I at the same (room) pressure. However, Bates *et al.*[13] reported that phase III was found in Ge samples compressed to only 2.5 GPa for long periods of time, while another phase (IV) was produced when phase II was held at pressures between ~11–13 GPa for 10–40 h, then quenched to room pressure in dry ice. Therefore, studies were undertaken to ascertain whether phase III could be produced at such low pressures in a diamond cell with well-characterized pressure, rather than the tungsten carbide anvil system used by Bates *et al.*, with pressure inferred from the load applied to the anvils, calibrated using fixed points.

Qadri *et al.*[10] have reported results on the formation of phase III from phase II, and also reported that they could not form phase III directly from phase I, as reported by Bates *et al.*[13] While the present results overlap with those of Qadri *et al.*, differences are reported between their results and the present. In particular, the effects of both the compressing medium (nonhydrostatic stresses) and the rate of pressure decrease are reported here.

Finally, results are reported on the bulk moduli of phase II and phase III. These data are of interest for comparison with theory. This is of particular importance at the present time because of current theoretical studies of superconductivity in the metallic phases of Ge and Si.[28] Also, the data are of interest for comparison with shock measurements.[29]

Preliminary work on Ge has been published by us.[30,31] The present paper does not use data from Ref. 30, since extra lines which were tentatively identified as phase IV have since been attributed to contamination of x-ray spectra from miscellaneous sources.[32] Data in Ref. 31 have been reanalyzed, and several further experiments have been carried out.

II. EXPERIMENTAL DETAILS

Samples were compressed in a diamond cell whose design has been discussed elsewhere.[33] The hole diameter enclosing the sample in the gasket was normally 150 μm and the gasket thickness ~150 μm at the beginning of the experiment. The powdered sample was typically loaded with a ruby chip, or powdered NaCl, and 4:1 mixture of methanol:ethanol, to maintain quasihydrostatic conditions to ~10 GPa.[34] Pressure was measured using either the ruby fluorescence scale[25,26] or the NaCl equation-of-state scale.[35] The equivalence of the ruby fluorescence and NaCl equation-of-state scales has been demonstrated to 29 GPa.[36]

In early experiments x-ray diffraction information was obtained using photographic detection (wet film) and a conventional fixed-anode x-ray source. Later experiments were carried out with a position sensitive proportional detector[37,38] using this source. Experiments were also carried out at Cornell High Energy Synchrotron Source, Cornell University (Ithaca, NY) (CHESS) using synchrotron radiation and an intrinsic Ge detector (energy dispersive) using techniques[39] similar to those of Baublitz *et al.*[40] It has been pointed out by us[41] that sample heating could be severe in the synchrotron beam under extreme (projected) conditions. Sample heating in our experiments was estimated to be less than 0.2 K, since (i) beam conditions were less severe (5 GeV, 20 mA compared to 8 GeV, 100 mA projected condition used in Ref. 41), (ii) the beam was collimated, so that the photon rate was further reduced by about a factor of 10, and (iii) the sample-fluid geometry discussed above was more conducive to heat dissipation than the case discussed in Ref. 41. All measurements reported here are at room temperature (295±3 K).

Values of lattice spacing d were obtained with an accuracy of ±0.003—0.007 Å, depending on conditions of pressure. When the NaCl equation of state was used, the pressure could be determined with a sensitivity of 1%. The instrumental resolution was ~±0.05 GPa when the shifts of ruby fluorescence peaks were used, but line broadening at pressures above 15 GPa increased this to ~±0.5 GPa. In order to study the influence of nonhydrostatic stress on the transition from the diamond to the metallic phase, selected experiments were carried out with the sample compressed directly between the anvils, in the gasket without a fluid, and also with different compressing media.

It is important to emphasize that the use of a quasihydrostatic compressing medium such as an alcohol mixture does not guarantee that the sample is under hydrostatic stress. "Bridging" of the sample can occur between the anvils, leading to an axial component of stress. It was important to ensure that the volume occupied by the sample was a small fraction (e.g., $\lesssim 20\%$) of the cavity volume at the beginning of the run. Accordingly, high-purity (semiconductor grade) Ge was first powdered, then lightly compressed into thin disklike specimens of thickness ~20 μm, which were then placed within the sample cavity, as suggested by Werner *et al.*[8]

III. RESULTS AND DISCUSSION

Many experiments were carried out on Ge in the pressure range up to 26 GPa. Only phase II (body-centered tetragonal, β-Sn) was found on increase of pressure. Olijnyk *et al.*[11] confirmed this result to ~50 GPa. Phase III (tetragonal) was found on decrease of pressure.[2,10,12] A summary of the volume-pressure relationship under hydrostatic conditions is given in Fig. 1. The results will be presented by considering each phase and transition in turn.

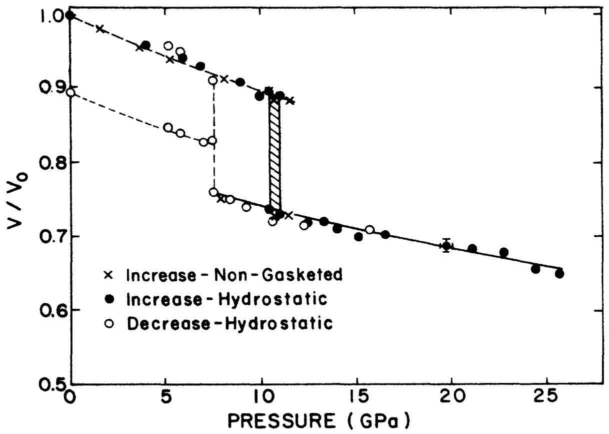

FIG. 1. Relative volume versus pressure for Ge under hydrostatic conditions. (Shaded area is the two-phase region, pressure increasing.)

A. Ge I

Table I and Fig. 2 summarize the results obtained on the compression of the Ge I, cubic, diamond structure. The solid line in Fig. 2 corresponds to the Murnaghan

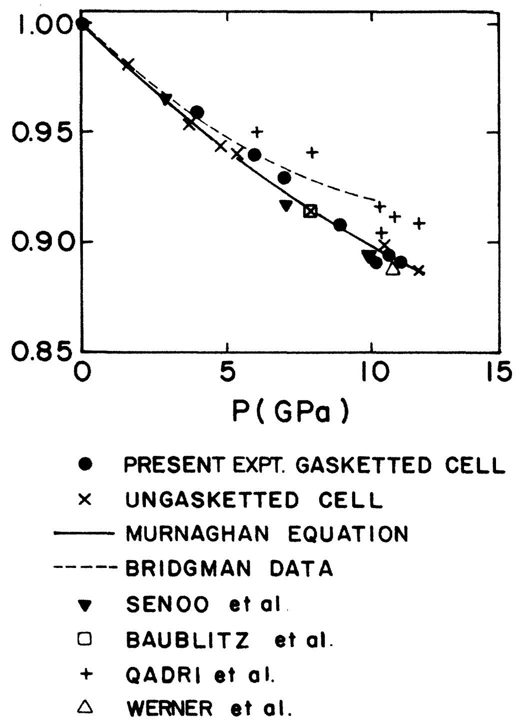

FIG. 2. Pressure-volume relation for Ge I. The present data are compared with previous measurements.

TABLE I. Comparison of experimental and theoretical data for phases I and II, and the I-II transition (Ge).

Parameter	Medium	Present experiment	Other experiments	Theory
P_t (GPa)	No pressure-transmitting medium	8.1±0.3	6.7,[a] 8.0[b]	9.2[c]
			8.0[d] (ice)	9.6[e]
	4:1 methanol:ethanol	10.6±0.05	10.3,[f] 10.7[b]	
			10.5[a]	
	NaCl	9.8±0.1		
$V(P_t)/V_0$,	No pressure-transmitting medium	0.916+0.003 (8.1 GPa)	0.915[d]	0.895[e]
phase I	4:1 methanol:ethanol	0.903±0.003 (10.6 GPa)	0.915[a]	
			0.895[f]	
	NaCl	0.910+0.003 (9.8 GPa)	0.88[b]	
$V(P_t)/V_0$,	No pressure-transmitting medium	0.740±0.007 (8.1 GPa)	0.74[d]	
			0.75[a]	0.73[e]
phase II	4:1 methanol:ethanol	0.732±0.007 (10.6 GPa)	0.74[f]	
			0.72[b]	
	NaCl	0.760±0.008 (9.8 GPa)		
c/a ratio at	No pressure-transmitting medium	0.552±0.002	0.551[d]	
P_t for phase II	4:1 methanol:ethanol	0.548±0.002 (10.6)		0.55±0.002[e]
	NaCl	0.554±0.006 (9.8)		
$\frac{V_{\text{I}}-V_{\text{II}}}{V_{\text{I}}}(P_t)$	No pressure-transmitting medium	0.192±0.007 (8.1 GPa)	0.194±0.009[d]	0.187[e]
				0.209[c]
	4:1 methanol:ethanol	0.189±0.007 (10.6 GPa)	0.182[b]	
			0.173[f]	
	NaCl	0.165±0.008 (9.8 GPa)		
Bulk modulus	No pressure-transmitting medium	90±10 GPa		
phase II pressure derivative	4:1 methanol:ethanol	4.0±1		

[a] Reference 10.
[b] Reference 8.
[c] Reference 42.
[d] Reference 9.
[e] Reference 20.
[f] Reference 11.

TABLE II. Estimates for the pressure of Ge at $V/V_0=0.9$ using different equations and elastic constant data.

Elastic constants B_0 (GPa)	B_0'	P(Murnaghan) (GPa)	P(Birch first order) (GPa)
74.37	4.76	10.17	10.08
76.0	4.373	10.17	10.09

equation, using precision elastic constant data[43] ($B_0=74.37$ GPa and $B_0'=4.76$). The standard deviation of the experimental points with respect to the Murnaghan equation is 1%. When the experimental points were fitted to the Murnaghan equation, then the best values $B_0=74.9$ GPa and $B_0'=3.0$ were obtained, with a confidence interval of 5×10^{-4}.

Good agreement is obtained with the present experimental results and those of Werner *et al.*,[8] Senoo *et al.*,[44] Baublitz *et al.*,[9] and Olijnik *et al.*[11] However, the data points of Qadri *et al.*[10] lie significantly above the present data, as does the compression curve of Bridgman[45] above ~5 GPa.

There is a body of experimental data for the volume-pressure relationships of solids which shows that the Murnaghan equation fits the data up to reduced pressures $P/B_0\sim0.2$, corresponding to ~15 GPa for Ge. In the absence of elastic constant data giving the second derivative with pressure of the bulk modulus B_0'', equations such as the Rose, Birch second order, or Keane equations cannot be used. Table II compares $P(V)$ values calculated for both the Murnaghan and Birch first order equations using values of B_0 and B_0' from McSkimmin and Andreatch,[43] and Landolt-Börnstein.[46] As can be seen, the values of pressure for $V/V_0\sim0.9$ lie within ~0.01 GPa of each other, well inside the discrepancy with the data of Qadri *et al.*[10] and Bridgman.[45]

B. The I→II transition

The transition from Ge I (cubic-diamond), to Ge II (body-centered tetragonal β-Sn) was observed at different pressures depending on the pressure medium used. This influence of the pressure medium was suggested by Jamieson[7] and Okai and Yoshimoto[6] and later confirmed by the work of Werner *et al.*[8] and Qadri *et al.*[10] The onset pressure for the transition at 10.6±0.06 GPa under quasihydrostatic conditions is in good agreement with Werner *et al.*[8] and Qadri *et al.*[10] In these and subsequent estimates of the transition pressures, the error bars represent an estimate of the accuracy of the pressure measurement at the first indication of the new phase. There may be an overestimate of the pressure, because the advance of the anvils increased pressure beyond the initial onset, but this is minimized for pressure increase by the "auto arrest" of pressure increase due to the volume decrease of the sample.

Figure 3 illustrates the differences in the extent of the two-phase region (I and II) on increase of pressure. The lowering of the onset to 8.1±0.3 GPa when the sample was directly compressed between the anvils is again in good agreement with the result of Werner *et al.*[8] (8 GPa) who compressed Ge in a gasket without a pressurizing medium, and of Qadri *et al.*[10] (7.9 GPa) who compressed a sample with alcohol medium, but applied shear stresses by bridging. The onset pressure of 8 GPa recorded by Baublitz and Ruoff[9] is consistent with a highly nonhydrostatic state. It is difficult to ascertain whether this was from particle bridging between the anvils, or from the medium (ice) used.

An even lower onset pressure of 6–7 GPa was observed by Qadri *et al.* when the sample was compressed in NaCl without a pressurizing medium. This is a surprising result, since the onset should be even lower in this case, since shear stresses on the Ge would be lower. An experiment was carried out by us with a small quantity of alcohol mixture added to a NaCl/Ge mixture, for which the onset pressure was lowered to 9.8±0.1 GPa, presumably due to the presence of shear stress occasioned by the use of too high a fraction of solids (Ge and NaCl) in the cavity.

Experiments in which shear stresses are present need to be interpreted with care, since mean stress levels may be calculated from the data incorrectly. In the case that NaCl is the pressure transmitting medium there is a finite stress needed to induce plastic flow in the pressurizing medium, resulting in a lower average stress in the sample.[47,48] However, an offsetting effect is the underestimation of the pressure from the x-ray technique used.[49] This arises because the diffracting planes are nearly parallel to the cell axis. As a result, the stress component perpendic-

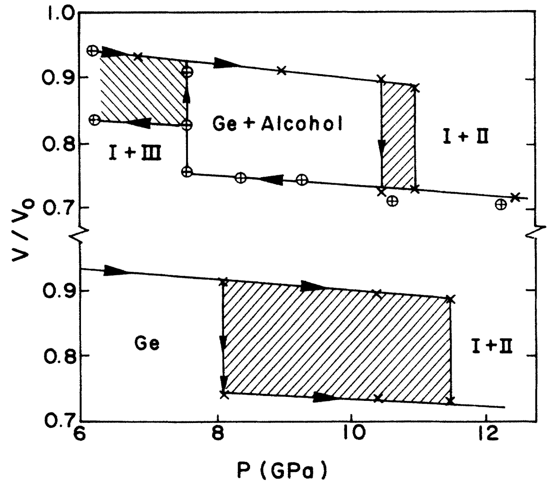

FIG. 3. Two-phase coexistence regions for Ge (increasing pressure) using alcohol (4:1 methanol:ethanol) pressure transmitting medium, and direct compression of Ge between diamond anvils.

ular to these planes is lower than the average stress, and the pressure is underestimated. The two effects are roughly of the same order of magnitude, so roughly cancel each other out.

Figure 3 also includes estimates for the completion of the I-II transition, as monitored by the disappearance of diffraction lines for phase I. It is interesting to note that the presence of shear stresses apparently lowers the onset and increases the completion pressures. This effect was also observed in the experiment with NaCl + Ge + alcohol, since the transition was not complete at 11.7 GPa.

C. Ge II

Data for phase II are given in Table I and compared with other results and theory. For Ge II, an equation of state of the Murnaghan type was fitted using nonlinear regression to determine the values of the bulk modulus $B_{t\text{II}}$ and its pressure derivative $B'_{t\text{II}}$ both, evaluated at the II→I transition pressure, taken to be 7.6±0.05 GPa, since values on decompression were also considered.

The equation obtained, assuming a linear variation with pressure of the bulk modulus, is

$$P = P_t + \frac{B_{t\text{II}}}{B'_{t\text{II}}}\left[\left(\frac{V_i}{V_{\text{II}}}\right)^{B'_{t\text{II}}} - 1\right],$$

where V_{II} is the volume at a given pressure, $V_i = V_{\text{II}}(P_t)$ is the volume at the transition pressure. In our case $V_i/V_0 = 0.76$. The values of $B_{t\text{II}}$ and $B'_{t\text{II}}$ obtained using 5×10^{-4} confidence interval are 90±10 GPa and 4.0±1, respectively.

D. Ge III and the II→III transition

Figure 1 illustrates the behavior of Ge II on release of pressure in a hydrostatic environment. Pressure release steps were $\lesssim 1$ GPa, with periods of days between. At 7.6±0.05 GPa, diffraction lines from both phases I and III appeared. The intensity ratio of the strongest diffractions line of Ge III to Ge I was found to be 0.98 on complete removal of pressure, so that roughly equal amounts of both phases were present.

This result differs from that of Qadri *et al.*[10] who released Ge II from 11 GPa in a hydrostatic environment, finding that Ge II converted completely into phase III. Since Qadri *et al.*[10] did not specify whether pressure was released in small steps, or in one release, an experiment was carried out in which pressure was released rapidly. This and other experiments led us to the following rules for the II-III transition:

(1) Rapid release of pressure under quasihydrostatic conditions (e.g., sudden release of pressure from above the I-II coexistence region to less than 5 GPa, e.g., $\gtrsim 5$ GPa/sec) results in *complete* transformation to phase III.

(2) The presence of shear stress enhances the conversion of II→III.

(3) Rapid depressurization of a mixture of I + II to atmospheric pressure results in a mixture of I + III, consistent with complete conversion of II→III and no conversion of I.

(4) When Ge III is repressurized, phase II is formed. This observation is in agreement with Qadri *et al.*[10]

(5) An experiment was conducted (similar to one reported by Bates, Dachille, and Roy[13]) in which the sample was compressed to 3.6 GPa, and held for one day. Pressure was then released. No trace of phase III could be found, in contrast to the earlier result.[13]

The results are consistent with a model in which phases I and II are stable below and above ~10 GPa, respectively, while phase III is a metastable phase at all pressures, which is produced from II as a result of kinetic factors. The conversion of II→III is favored by the presence of shear stresses and by a larger free-energy difference between the two phases.

The result obtained by Qadri *et al.*[10] on the decompression of phase II in the presence of shear stress differs somewhat from the above result [rule (2)]. Qadri *et al.*[10] reported that "decreasing the pressure from 12 to 10.4 GPa resulted in almost complete loss of phase II and . . . an admixture of Ge I and Ge II." This may be due to slight differences in the quenching procedure.

Data for phase III are listed in Table III. The bulk modulus (102±5 GPa) is reported here for the first time. Data for the lattice parameters at $P=0$ are in good agreement with the data of Kasper and Richards.[12]

TABLE III. Data for phase III (Ge).

Parameter	Present work	Other work
P_t (GPa)	7.6±0.05	
$V(P_t)/V_0$	0.833±0.009	
$V(P=0)/V_0$	0.895±0.01	0.903±0.004[a]
c/a ratio	1.147±0.003 at P_t 1.167±0.0004 at 0	1.16[b] 1.177±0.004[a]
$\frac{V_{\text{III}}-V_{\text{II}}}{V_{\text{II}}}$ at P_t	0.092±0.01	
Bulk modulus (GPa)	102±5	43.6[b] (theory)

[a] Reference 12.

[b] Reference 50.

IV. CONCLUSIONS

An x-ray study of high-pressure phases of Ge has been carried out at room temperature at pressures up to 26 GPa. Data for the variation of volume of the three phases, I (cubic, diamond), II (body-centered tetragonal), and III (tetragonal) as well as the transition pressures for I$\rightleftarrows$II and II$\rightleftarrows$III have been obtained. The studies have been carried out in different stress conditions.

Although several studies have been carried out on Ge in this pressure range, there have been conflicting reports on such fundamental matters as the equation of state of Ge I, the transition pressure of I-II, and the coexistence of I and III on quenching phase II. This paper resolves many of these conflicts:

(1) The compression curve of phase I is found to be in agreement with Murnagham's equation, fitted to precision elastic constant data for the bulk modulus and its pressure derivative.

(2) The transition pressure I$\leftrightarrows$II is found to be sensitive to the pressure of shear stresses. Under quasihydrostatic conditions the onset pressure was found to be 10.6 ± 0.05 GPa, with NaCl as the pressure transmitting medium, at 9.8 ± 0.1 GPa, and with direct compression between the anvils, at 8.1 ± 0.3 GPa. The two-phase region (I-II) was found to exist to higher pressures when shear stresses were present.

(3) The compression curve of phase II was fitted to a modified Murnaghan equation with $B_0=90\pm10$ GPa and $B_0'=4.0\pm1$.

(4) Phase II was found to transform to phase III at 7.6 ± 0.05 GPa on slow release of pressure. Conditions of rapid depressurization and shear stresses favor the conversion to phase III, whereas slow release of pressure in a hydrostatic medium results in partial conversion to phase I as well as III.

(5) The bulk modulus of phase III was found to be 102 ± 5 GPa.

The experimental results have been compared to theoretical predictions. When the complexity of the calculation is taken into account, and the relatively small variation of internal energy over the pressure range ($\sim1\%$), the agreement between theory and experiment is remarkable.

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