

Structural and electrical properties of GeSe and GeTe at high pressure

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A combination of x-ray-diffraction measurements, using a diamond-anvil cell, and electrical-resistance measurements, employing an octahedral-anvil press, has been used to elucidate the behavior of GeSe and GeTe at high pressure. In GeSe, x-ray data show that the array of six-membered rings in chair conformation along the a direction is the most compressible. The electrical resistivity decreases with increasing pressure and exhibits an order of magnitude drop at about 25 GPa. GeTe transforms from the rhombohedral to the NaCl-type structure at 3 GPa and, at 18 GPa, transforms into a possibly orthorhombic structure with a space group $Pbcn$, accompanied by a remarkable rise in electrical resistivity. General trends in the pressure-induced structural phase transitions of group-IV and group-VI compounds are discussed in terms of ionicity and covalency. [S0163-1829(97)05337-X]

I. INTRODUCTION

Compounds consisting of group-IV elements (Ge, Sn, and Pb) and group-VI elements (S, Se, and Te) are known as narrow-gap semiconductors or semimetals which have a potential for various optoelectronic applications. At ambient pressure, they (henceforth referred to as $\langle V \rangle$ compounds) fall into three different crystal structures: orthorhombic GeS, cubic NaCl, and rhombohedral GeTe types. The difference is governed by competition between ionicity and covalency of each compound,¹⁻⁴ and structural trends have been delineated by a St. John-Bloch plot^{4,5} or by plotting the average principal quantum number of the compounds against the relative charge transfer.³

It is of great interest to know how the structural trends will change upon application of pressure. Relevant information can be obtained from *in situ* x-ray-diffraction studies under pressure. Indeed, compounds crystallizing in the NaCl-type structure have been studied extensively using diamond-anvil cells.⁵⁻¹⁰ These studies show that lead chalcogenides, initially in the NaCl-type structure, all transform into the CsCl-type structure at high pressure.⁶⁻⁸ Such a pressure-induced NaCl-to-CsCl type transition was also observed in SnTe.^{9,10} In detail, an intermediate phase appears between the NaCl-type and CsCl-type phases.⁶⁻¹⁰ Hence it is obvious that $\langle V \rangle$ compounds in the NaCl-type structure undergo a pressure-induced phase transition into the CsCl-type structure in two steps. This behavior is different from that of the lighter alkali halides in which the NaCl-type phase transforms directly into the CsCl-type phase.¹¹

Relatively little work has been done on the two other structural categories (GeS and GeTe types). Compounds that possess the orthorhombic GeS-type structure at ambient conditions are GeS, GeSe, SnS, and SnSe. Among these, SnS and SnSe undergo a phase transition into the orthorhombic

III-type structure at 905 and 825 K, respectively.¹² High-pressure x-ray-diffraction studies⁶ on GeS and GeSe have shown no indication of phase transition up to 34 GPa, whereas an electrical resistance measurement¹³ on GeSe showed an abrupt drop at 6 GPa and ascribed to a phase transition. This latter study attributed the high-pressure phase to belong to a face-centered-cubic structure.¹³

The third category involves only GeTe. In GeTe, a transition into the NaCl-type structure was discovered by x-ray diffraction at 3.5 GPa and at room temperature.¹⁴ This transition was attributed, by a neutron-scattering study,¹⁵ to originate from the same temperature-induced transition taking place at 720 K at ambient pressure. On the other hand, the 3.5-GPa transition was later questioned by electrical resistance,¹⁶ thermoelectric properties,¹⁷ and x-ray-diffraction studies.^{18,19} There are yet discrepancies among these later studies in the presence or absence of the transition and in the transition pressures. In some cases, the effect of shear stress on the transition has been pointed out.^{16,18,19}

The controversies in the GeSe and GeTe studies might arise from nonhydrostaticity of the applied pressure because the structures of the two compounds are made up of puckered layers²⁰ being basically sensitive to shear stress. In fact the transition pressures in GeTe can be significantly lowered by shear deformation.²¹ Another point to note is a lack of cross checks; multiple probing may be required for a more complete understanding of the high-pressure behavior of GeSe and GeTe.

In the present study we have probed GeSe and GeTe with x-ray diffraction and electrical-resistivity measurement, respectively, using a gasketed diamond-anvil cell and an octahedral-anvil press. The gasketed diamond-anvil cell with fluid pressure-transmitting media is capable of generating hydrostatic pressure. Among the multiple anvil systems, the octahedral-anvil press can provide an environment that ap-

proaches the closest to a hydrostatic condition.^{22,23} A combination of the two measurements has revealed that remarkable changes in structural and electrical properties occur almost concomitantly.

II. EXPERIMENTAL PROCEDURE

The GeSe and GeTe samples were grown as single crystals by the Bridgman method and confirmed by powder x-ray diffraction to be in the orthorhombic and rhombohedral structures, respectively. No extra phase was detected. For the high-pressure x-ray-diffraction study on GeSe, pieces scraped from the single crystal by razor blade were used without any further pulverization whereas, in the GeTe study, powder crushed from the crystal was employed. Each sample was pressurized with a gasketed diamond-anvil cell.²⁴ Briefly, the sample was placed inside a 0.25-mm hole drilled in a gasket made of a Ni-based alloy. The culet of each anvil was 0.40 mm across. A mixture of methanol, ethanol, and water (in the volume ratio of 16:3:1) was used as a pressure-transmitting medium. This medium is known to stay liquid up to 14 GPa at room temperature.²⁵ Ruby chips were incorporated to monitor the pressure.²⁶

Molybdenum $K\alpha$ radiation filtered with Zr and collimated to 0.15 mm diameter was used for the GeSe study. The diffracted x rays were recorded by either a flat or a semicircular film with an exposure of about 40 hr. All the films were read by a comparator. Some of the films were read by an image scanner and computer processed. In the GeTe study, Mo $K\alpha$ radiation monochromatized by pyrolytic graphite was employed. The collimation was the same as in the GeSe study. Diffracted x rays were recorded by a position-sensitive detector.²⁷ The exposure time was typically 5 hr.

Electrical-resistance measurements were undertaken by a four-probe method in an octahedral anvil device²² employing a solid pressure-transmitting medium. The pressure generated was estimated from pressure calibration based on resistance changes in several fixed-point standard materials^{22,28,29} and was believed to be quasihydrostatic.^{22,23} The electrical resistance of GeSe was measured on lamellae being parallel to the (002) plane of the crystal. In GeTe, rectangular pieces cleft along the [111] direction of the crystal were used. All the measurements were undertaken at room temperature.

III. RESULTS

A. GeSe

Figure 1 shows x-ray-diffraction patterns of GeSe taken at ambient and high pressures. We note that all the diffraction peaks in the ambient-pressure pattern became significantly weakened unless the procedure described in the experimental section was undertaken. In Fig. 1, every peak in the pattern at 6.4 GPa is broadened to a great extent. This cannot be ascribed to stress because at this pressure the pressure-transmitting medium remains liquid and the pressure is most likely hydrostatic. The broadening was observed in all the patterns taken at high pressure. It leads to larger errors than at ambient pressure in deriving the interplanar spacings, lattice parameters, and volume. The profiles of the x-rayed films remained essentially unchanged to 82 GPa. In Fig. 2 we show pressure dependence of the interplanar spacings.

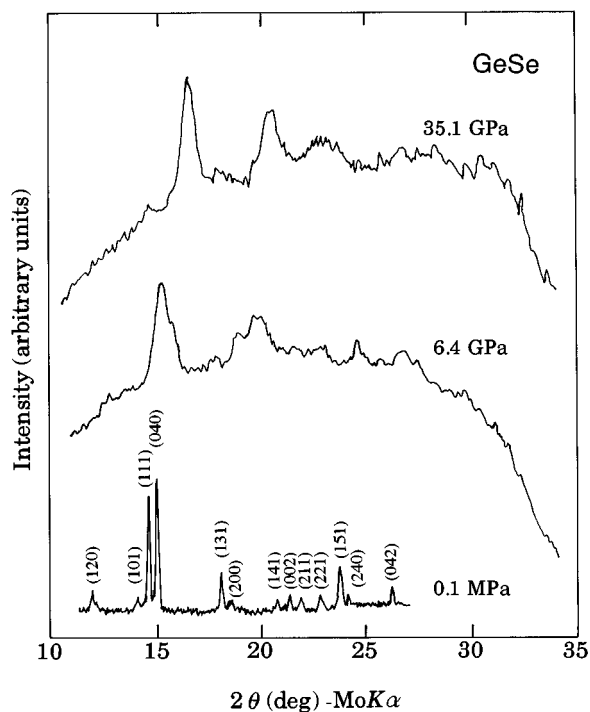


FIG. 1. X-ray-diffraction patterns of GeSe. The ambient-pressure pattern is from diffractometer recording and the patterns at high pressure were obtained after image reading of x-rayed films.

No discontinuity appears over the pressure range studied although some reflections disappear en route. From the persistence of the x-ray-diffraction profiles and the absence of discontinuities in the interplanar spacings, it is reasonable to conclude that GeSe remains in the orthorhombic GeS-type structure to at least 82 GPa.

Table I lists the analysis of the x-ray-diffraction pattern at 69 GPa. Similar analyses of x-ray data recorded at other pressures were used to derive the lattice parameters. Figure 3 shows the pressure dependence of the lattice parameters of GeSe with respect to the ambient-pressure values of $a = 4.414(5)$ Å, $b = 10.862(10)$ Å, and $c = 3.862(6)$ Å. Among the three crystallographic axes, the length along the

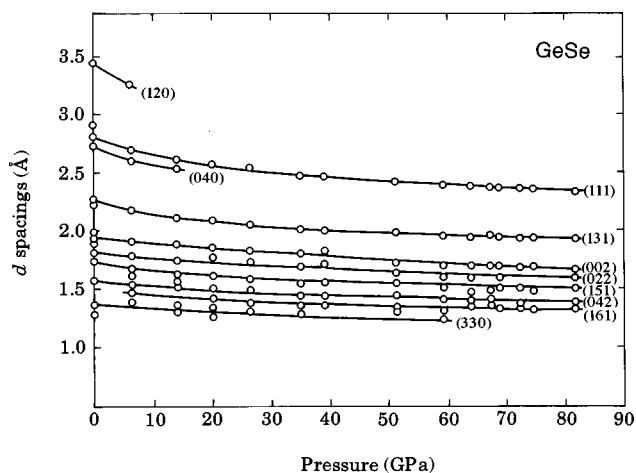


FIG. 2. Interplanar spacings of GeSe as a function of pressure. Solid lines are guides to the eyes.

TABLE I. Analysis of x-ray-diffraction pattern of GeSe taken at 69.0 GPa on the basis of an orthorhombic structure (space group $Pbnm$) with lattice parameters $a=3.49(6)$ Å, $b=9.51(4)$ Å, and $c=3.41(2)$ Å.

$h k l$	d_{obs}	d_{calc}	Error (%)
1 1 1	2.364	2.355	0.37
1 3 1	1.938	1.929	0.47
0 0 2	1.717	1.704	0.78
0 2 2	1.595	1.603	0.55
1 5 1	1.511	1.500	0.73
1 6 1	1.323	1.329	0.47

a -axis direction is more compressible than along the b and c axes. Consequently, the a -axis length becomes comparable to the c -axis length at about 25 GPa. As shown in Fig. 4, GeSe in an orthorhombic structure³⁰ is composed of puckered layers and each layer can be viewed as consisting of six-membered rings in chair conformation. The direction of the array of chairs is taken as the a axis and the chairs form zigzag chains extending along the c axis. Atoms within the layers are covalently bonded to three neighbors, while van der Waals forces along the b axis separate the layers. The bond angles θ_1 and θ_2 , both involved approximately in the a - c plane, are equal to 96.2° , while $\theta_3=91.3^\circ$ and $\theta_4=103.5^\circ$ (Ref. 30). Figure 3 suggests that the zigzag chains are very rigid in GeSe. This behavior is somewhat different from that of black P, which is the monatomic analog of the GeS-type structure. In black P, a neutron diffraction study³¹ has demonstrated that the inherent zigzag chains (along the a axis in this case) are absolutely rigid, exhibiting no contraction upon application of pressure. Axes in the two other directions (b and c axes) in black P were much more compressible. The difference in the compression behavior

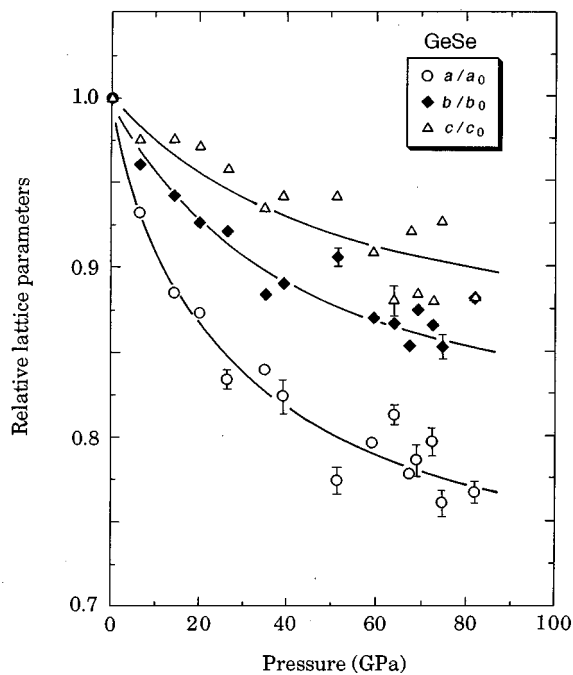


FIG. 3. Relative lattice parameters of GeSe as a function of pressure. Solids lines are guides to the eyes.

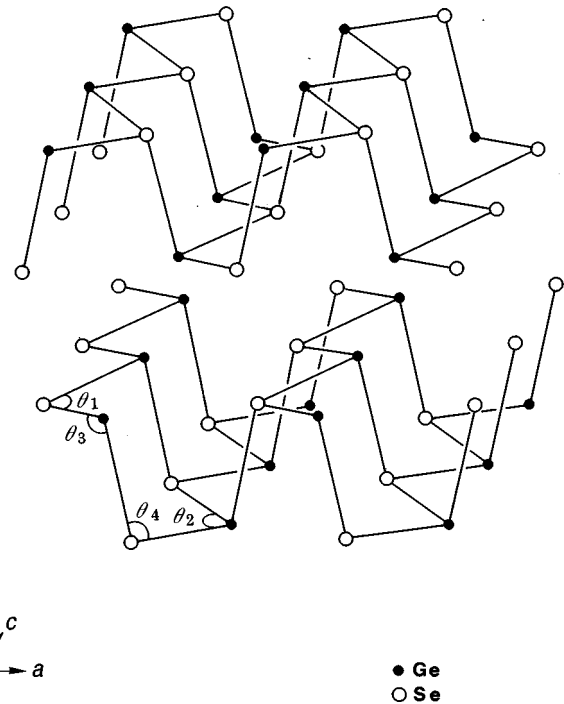


FIG. 4. Crystal structure of GeSe. Solid circles stand for Ge atoms and open circles for Se atoms.

between GeSe and black P could be ascribed to the difference in the bonding characters; in GeSe, the bonding within the layers is ionic to some extent. The anisotropic compressibility has been reported also for InS from a single-crystal x-ray-diffraction experiment.³² This compound crystallizes in an orthorhombic structure (space group $Pmnn$) and contains puckered layers composed of six-membered rings in chair conformation. Pressure causes a remarkable shortening along the puckered layers and a small compression along the zigzag chains, while an elongation occurs along the direction perpendicular to the layers.³²

Figure 5 shows the pressure dependence of the relative volume of GeSe. Fitting of Birch-Murnaghan equation³³ to the data yields the bulk modulus B_0 to be 40.7 ± 3.5 GPa and

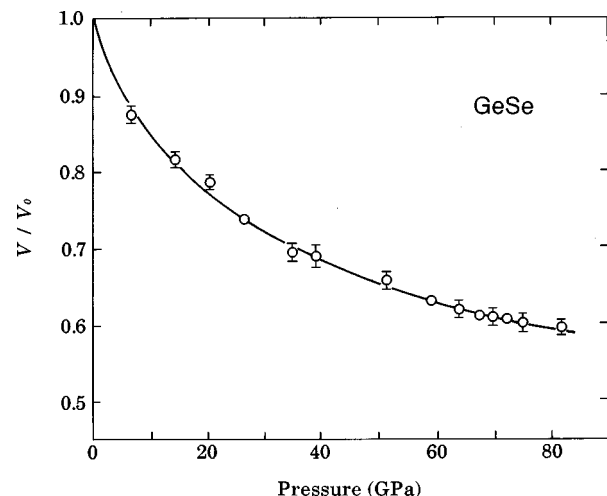


FIG. 5. Pressure dependence of the relative volume of GeSe. Solid line is the fit of Birch-Murnaghan equation to the data. The fitting parameters are given in the text.

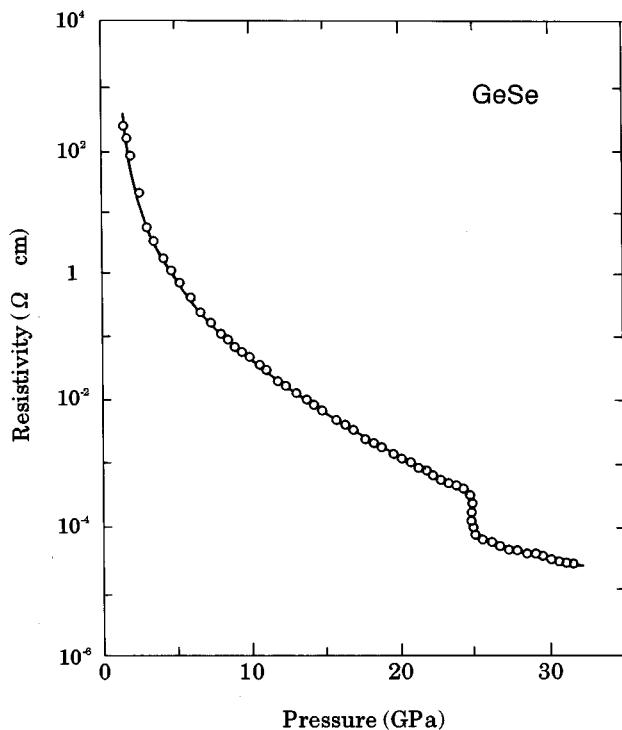


FIG. 6. Electrical resistivity of GeSe as a function of pressure measured along the (002) plane.

its pressure derivative B'_0 to be 5.0 ± 0.4 . These equation-of-state parameters are in reasonable agreement with those ($B_0 = 47.5$ GPa and $B'_0 = 5.1$) of Chattopadhyay *et al.*⁶ who studied GeSe to about 34 GPa also by x-ray diffraction.

In Fig. 6 electrical resistivity of GeSe in the (002) plane is plotted against pressure. The resistivity monotonically decreases with increasing pressure to 25 GPa by about six orders of magnitude. No discontinuity is seen in the vicinity of 6 GPa at which Bhatia *et al.*¹³ observed a drop by five orders of magnitude. Instead, a conspicuous drop by one order of magnitude is observed at about 25 GPa. This pressure corresponds to the point at which the crystallographic a - and c -axis lengths become equal. The resistivity continues to drop up to 32 GPa, the highest pressure reached in this study. The magnitude of the resistivity suggests that GeSe has become metallic at pressures greater than 25 GPa.

B. GeTe

X-ray-diffraction patterns of GeTe recorded on compression and decompression are shown in Fig. 7. The pattern at 1.0 GPa on compression, Fig. 7(a), can be unequivocally indexed on the basis of a rhombohedral lattice³⁴ (hereafter denoted as GeTe-I). Upon increasing the pressure to 6.1 GPa, the (220) and (202) reflections merge into a single peak, showing that, at this pressure, GeTe has transformed into the NaCl-type structure (GeTe-II). Some new peaks appear in the diffraction pattern at 18.0 GPa. This suggests an appearance of another high-pressure form (GeTe-III). The reflec-

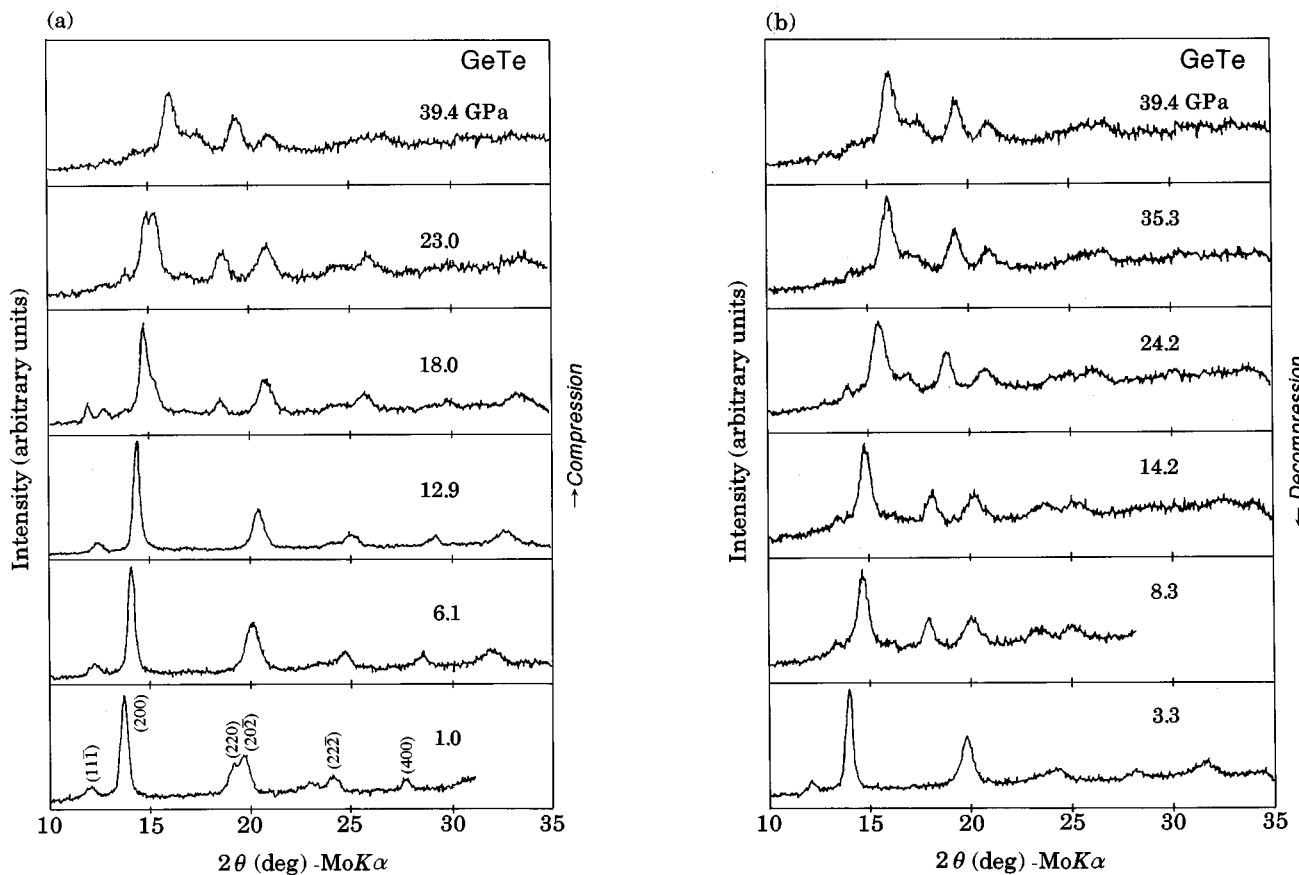


FIG. 7. X-ray-diffraction patterns of GeTe on (a) compression and (b) decompression. The patterns were all recorded by a position-sensitive detector.

TABLE II. Analysis of x-ray-diffraction pattern of GeTe-III at 35.3 GPa on the basis of an orthorhombic structure (space group $Pbcn$) with lattice parameters $a=7.441(6)$ Å, $b=7.678(22)$ Å, and $c=5.435(6)$ Å.

$h k l$	d_{obs}	d_{calc}	Error (%)
0 2 1	3.146	3.136	0.32
2 1 1	2.863	2.851	0.42
0 0 2	2.708	2.718	0.35
1 0 2	2.552	2.553	0.03
3 1 0	2.363	2.360	0.11
2 1 2	2.112	2.111	0.09
3 2 1	1.945	1.946	0.02
4 2 1	1.598	1.600	0.13
4 0 2	1.536	1.535	0.06

tions from GeTe-II are coexistent with the GeTe-III reflections and persist to 23.0 GPa. Figure 7(a) demonstrates that GeTe-III remains stable to at least 39.4 GPa. On decompression, Fig. 7(b), GeTe-III is retained to 8.3 GPa and reconverts to GeTe-II at 3.3 GPa, yielding a large hysteresis in the transition between GeTe-II and GeTe-III.

Table II gives the analysis of the diffraction pattern of GeTe-III based on an orthorhombic structure with a space group $Pbcn$, where atomic positions are represented by $8d \pm(x, y, z; x+1/2, y+1/2, -z+1/2; x, -y, z+1/2; x+1/2, -y+1/2, -z)$. Analyses based on other candidates including GeS and TII types gave much worse. We found that a simulated profile with the positional parameters $x=0.13$, $y=0.21$, and $z=0.14$ for Ge; $x=-0.13$, $y=0.09$, and $z=-0.14$ for Te matched with the diffraction patterns for GeTe-III. However, there were some peaks missing in the observed pattern, indicating that the fit was still insufficient. Hence the analysis in Table II remains a proposal. In this proposed structure, the a - and b -axis lengths are nearly equal and both are about $\sqrt{2}$ times of the c -axis length, showing that this structure is pseudotetragonal. Such an assignment has been made by us for the high-pressure phase of SnTe.^{9,10} We note that the GeTe-III-type structure can also be applied to the analysis of the high-pressure phase of PbTe, different from our earlier assignment.^{6,9}

Figure 8 shows the pressure dependence of the interplanar spacings of GeTe recorded during compression and decompression processes. Discontinuities at 3 and 18 GPa on compression represent the GeTe-I to GeTe-II and GeTe-II to GeTe-III transitions, respectively. The 3-GPa transition corresponds to a transition that Kabalkina *et al.* observed at 3.5 GPa.¹⁴ Leger and Redon also observed the same transition at approximately 4 GPa in a solid pressure-transmitting medium.^{18,19} The transition found at 18 GPa is the result obtained in this study.

The equation of state for GeTe is shown in Fig. 9. A volume reduction of about 2% accompanies the GeTe-II to GeTe-III transition. However, no discontinuity in volume is observable at the GeTe-I to GeTe-II transition. This was also mentioned by Leger and Redon,^{18,19} as opposed to the 3% reduction observed by Kabalkina *et al.*¹⁴ Consequently, values of 49.9 ± 3.2 GPa to be B_0 and 3.7 ± 0.8 to be B'_0 are obtained for GeTe-I (rhombohedral structure) and GeTe-II (NaCl-type structure) phases in common. The parameters de-

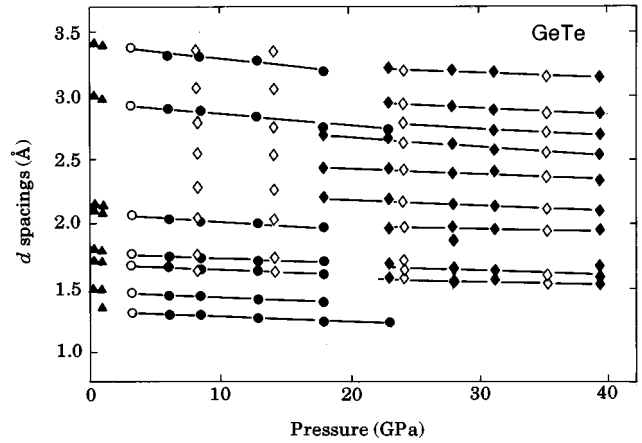


FIG. 8. Interplanar spacings of GeTe as a function of pressure: triangles for GeTe-I, circles for GeTe-II, and diamonds for GeTe-III, solid symbols are on compression and open symbols on decompression. Solid lines are guides to the eyes.

rived for GeTe-III are $B_0=95.1 \pm 5.1$ GPa and $B'_0=5.3 \pm 0.3$. There exists a relevant calculation on GeTe that was performed by Rabe and Joannopoulos using *ab initio* pseudopotential total energy method.³⁵ These authors calculated the bulk modulus of a hypothetical NaCl-type phase of GeTe at 0 K to be 51 GPa although this phase is thermodynamically stable only above 720 K at ambient pressure. The agreement between experiment and calculation appears to be excellent with regards to the bulk modulus of GeTe in the NaCl-type phase.

In Fig. 10 electrical resistivity of GeTe in directions parallel and perpendicular to the crystallographic [111] axis is plotted against pressure. A very similar change occurs in both directions. The resistivity (initially in the order of 10^{-2} Ω cm at ambient pressure) decreases monotonically to about 6 GPa and becomes flattened between 6 and 15 GPa. There is no conspicuous change in resistivity between 3 and 6 GPa where the present and earlier^{14,18,19} x-ray-diffraction

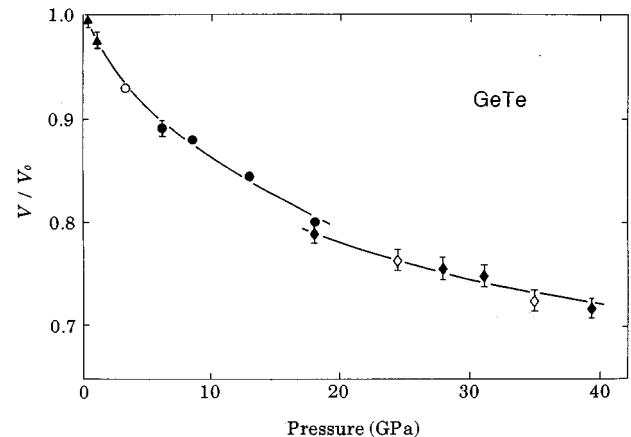


FIG. 9. Pressure dependence of the relative volume of GeTe: triangles for GeTe-I, circles for GeTe-II, and diamonds for GeTe-III; solid symbols are on compression and open symbols on decompression. Solid lines are the fits of Birch-Murnaghan equation to the data. The fitting parameters are given in the text.

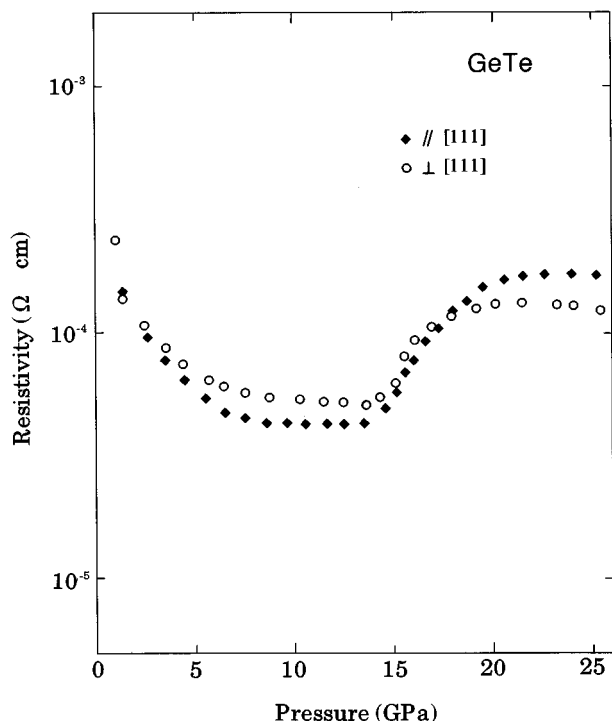


FIG. 10. Electrical resistivity of GeTe measured in directions parallel and perpendicular to the crystallographic [111] axis.

studies observed the GeTe-I to GeTe-II transition. Also, no abrupt change occurs at 9.0 GPa where Khvostantzev *et al.*¹⁶ observed a jump under hydrostatic condition. In our case a discontinuous jump begins at 15 GPa and ends at about 21 GPa. The pressure at the midpoint of the resistivity jump is close to the pressure for the GeTe-II to GeTe-III transition detected by the x-ray diffraction (18 GPa; see Figs. 7–9). These changes in resistivity are quite different from a very recent report of Ignatenko *et al.*³⁶ who observed a sharp drop beginning at 15 GPa and, after a small cusp at 40 GPa, again a sharp drop at about 45 GPa.

IV. DISCUSSION

In Fig. 11 we have plotted $\langle V \rangle$ compounds on a diagram of Littlewood⁴ who categorized the three structures (i.e., GeS, NaCl, and GeTe types, all encased in ellipsoids in the diagram) in terms of ionicity vs covalency. The ionicity and covalency are, respectively, represented by r'_σ and r_π^{-1} , which in turn are derived from orbitally dependent ionic radii of Chelikowsky and Phillips.³⁷ Changes have been made from Littlewood's diagram: (i) The domain of the NaCl-type structure is extended a little bit toward lower ionicity so that SnTe is correctly placed (SnTe crystallizes in the NaCl-type structure at ambient conditions), and (ii) domains for the TII-type, CsCl-type, and GeTe-III structures are provided. The orthorhombic TII-type structure appears at ambient pressure in TII and InI as well as in the high-pressure phase of PbS and PbSe.^{6,8} The CsCl-type structure is obtained at ambient pressure by TlCl and TlBr and has been observed at high pressure in PbS,^{6,8} PbSe,^{5,7} PbTe,^{6–9,10} SnTe,^{9,10} GeTe,²¹ and TII.³⁸ The GeTe-III is a result obtained in the present study. As noted earlier, this structure also ap-

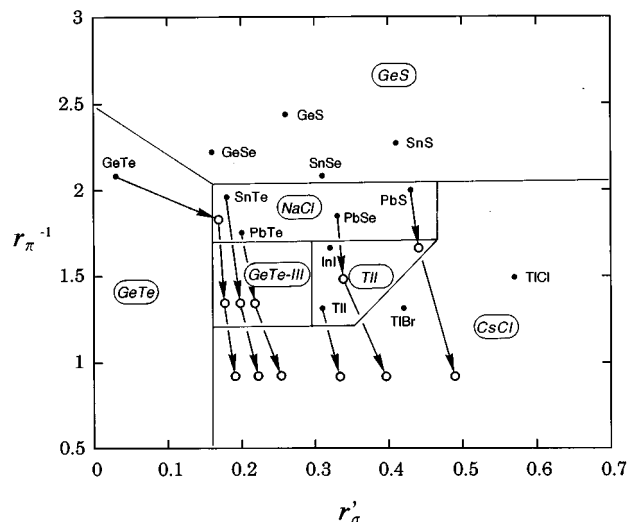


FIG. 11. Trends in the $\langle V \rangle$ compounds after Littlewood (Ref. 4) with some changes made by the present authors (see text). The parameters for the plotting are $r'_\sigma = r_p^A - r_p^B$ and $r_\pi = \{(r_p^A - r_s^A) + (r_p^B - r_s^B)\}$, where r_s and r_p are the ionic radii of s and p orbitals of components A and B (Ref. 37). Encased in ellipsoids are structure types. Solid circles stand for the structures possessed at ambient pressure and open circles at high pressure. Arrows follow the structural sequences driven by pressure.

pears in the high-pressure phases of PbTe (Refs. 9 and 10) and SnTe.^{9,10} In plotting the compounds in the domains of TII- and CsCl-type structures (limited to the ambient pressure), we have, as Littlewood did,⁴ referred to the orbitally dependent ionic radii of Chelikowsky and Phillips.³⁶ The resultant map places the domains of the TII- and CsCl-type structures at regimes essentially less covalent than the domain of the NaCl-type structure. On the other hand, there are no available data for the GeTe-III structure because no compound crystallizes in this structure at ambient pressure. Our placement of the GeTe-III domain right to the domain of the GeTe-I structure rests simply on an assumption that anionic p -orbital radii would be much more compressible than the cationic radii, leading to an increase of r'_σ with pressure.

Arrows in Fig. 11 indicate sequences of pressure-induced transitions in $\langle V \rangle$ compounds. In GeTe, for example, an arrow originating from the GeTe-type structure (GeTe-I) is oriented towards the NaCl-type structure (GeTe-II). Past the NaCl-type structure and after experiencing GeTe-III, the arrow reaches the CsCl-type structure. Likewise, PbTe and SnTe follow the same sequence, skipping of course the transition to the NaCl-type structure (because the atmospheric phase of these compounds is the NaCl-type structure). In the cases of PbS and PbSe, a pressure-induced transition occurs from the NaCl-type via the TII-type structure to the CsCl-type structure.

In Fig. 11, arrows are all directed downward and to the right (i.e., “down-right”). Therefore, an apparent trend upon application of pressure to $\langle V \rangle$ compounds is the sequential change towards the down-right direction. If there was the second pressure-induced transition in GeTe from the NaCl-type to the GeS-type structure,²¹ the arrow should have pointed up-right. This is against the general trend. In the

down-right extremity, the bonding of $\langle V \rangle$ compounds becomes much more ionic and less covalent.

V. CONCLUSION

The present *in situ* x-ray-diffraction measurements at high pressure have revealed that GeSe remains in the orthorhombic structure to at least 82 GPa, whereas GeTe transforms at 3 GPa from the rhombohedral structure to the NaCl-type phase (GeTe-II) and into another high-pressure phase (GeTe-III) at 18 GPa. Assignment of an orthorhombic structure with a space group *Pbcn* is proposed to GeTe-III. The electrical resistance of GeSe exhibits a sharp drop at 25 GPa, which corresponds to the pressure where the *a* and *c* axes attain similar lengths in the orthorhombic structure. In GeTe, a

remarkable jump in the resistance begins at 15 GPa and ends at 21 GPa, the midpoint corresponding to the phase transition from GeTe-II to GeTe-III as seen in the x-ray-diffraction experiment. These pressure-induced structural changes apparently fall on the general trends in $\langle V \rangle$ compounds.

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