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PHASE TRANSITION IN GERMANIUM TELLURIDE AT HIGH PRESSURES

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The influence of high pressures up to 100 kbar on the crystal structure of GeTe was investigated. It was found that at p = 35 kbar there was a first order phase transition from the rhombohedral phase GeTe I (A7 type) to the cubic phase GeTe II (NaCl type), accompanied by a sudden volume change of 3%. Taking into account the continuous transition GeTe I → GeTe II at T = 400° C, it is suggested that there was a critical point in the phase diagram of GeTe.

THE purpose of our investigation was to determine the influence of high pressure on the structure of germanium telluride, GeTe. The crystal structure of GeTe was first investigated by Schubert and Fricke,[1, 2] who showed that there were two modifications: a high-temperature cubic phase of the NaCl type and a low-temperature rhombohedral phase of the A7 type (As structure type). According to the same authors,[1, 2] the temperature of the transition from the rhombohedral to the cubic phase depended on the composition: in the presence of excess Ge, the transition took place at 460° C, while in the presence of excess Te, it occurred at 390° C; the cubic phase parameter was a = 6.010 Å at 460 °C (excess Ge) and a = 5.992 Å at 390 °C (excess Te). At room temperature, the low-temperature phase had a face-centered rhombohedral cell with the parameters a = 5.986 Å, α = 88.35°, Z = 4. As the temperature was raised, the rhombohedral angle gradually increased, reaching a value of 90° at the transition point; a kink in the temperature dependence of the cell volume was also observed at this point. The results of later investigations[3, 4] were in satisfactory agreement with the data of Schubert and Fricke.[1,2]

The similarity of the structure and the electrical properties of GeTe and of the elements of the subgroup VB (As, Sb, Bi)[5] was not unexpected; a similar relationship has been found between the compounds of groups III–V, II–VI, and I–VII with elements of the group IV. In both cases, the governing factor is evidently the density of valence electrons.

We give below the cell parameters for the elements As, Sb, and Bi and for the compounds GeTe, SnTe:

Substance:	As	Sb	Bi	GeTe	SnTe
a, Å:	5.599	6.226	6,578	5,988	6.319
α:	84°18′	87°24′	87°34′	88°15′	90°
u:	0,226	0,233	0,234	—	0,250

The parameter u for GeTe, which is an important characteristic of the type A7 structure, is missing from the foregoing table. By analogy with the elements As, Sb, Bi, it has been suggested[1–3] that the value of u of GeTe is close to 0.25.

To describe the As-type structure, it is more convenient to use not a face-centered but a primitive rhombohedral cell. For example, the parameters of such a cell are for Bi: a = 4.736 Å, α = 57°14′. Two atoms of Bi occupy the 2(c):000, 2u2u2u position on the ternary axis in the D_{3d}^5 group and have a common center of symmetry. It is quite clear that different atoms in germanium telluride—Ge, Te—can be in the 2(c) position only in the presence of random disorder in the structure. However, in the same group D_{3d}^5[1] two different atom can be placed in two independent positions: 1a (000) and 1b ($^1/_2$, $^1/_2$, $^1/_2$), corresponding to centers of symmetry located on the ternary axis. In the latter case, u = 0.25 and there is no need to assume disorder in the structure of GeTe.

Naturally, before investigating the behavior of GeTe at high pressures, it is necessary to know how atoms are distributed in the structure of this compound. The parameter u of the elements As,

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[1] From the data of Schubert and Fricke [2] and those in the present paper, it follows that the space group of GeTe is D_{3d}^5

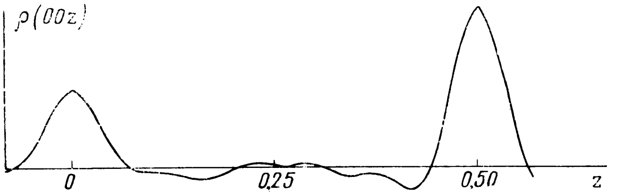

FIG. 1. Linear representation of the electron density in GeTe along the z axis.

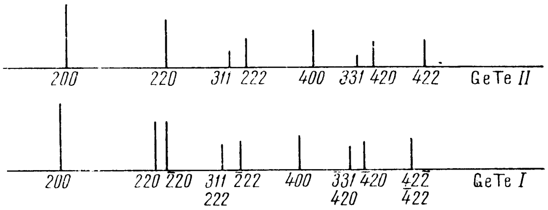

FIG. 2. Schematic representation of GeTe x-ray diffraction patterns (GeTe I is the initial As-type structure; GeTe II is the high-pressure phase with the NaCl-type structure).

Sb, and Bi has been determined by Belov and Mokeeva[6] from a linear Harker–Patterson cross section along the c axis of the hexagonal cell (the diagonal of a primitive rhombohedron) plotted on the basis of Debye diffraction data.

The GeTe used in the present investigation was prepared by S. Karbanov2) by melting together Te (99.94%) and Ge ($\rho = 10\,\Omega$-cm) in the proportions of 1:1. According to the data of a Debye pattern, recorded using apparatus of the RKU-114 type with filtered copper radiation, the structure of this alloy was in full agreement with the published results.[1-3]

To determine the parameter u, we used 33 (hk$l$) reflections in the same Debye pattern. The line intensities were estimated from density marks. We plotted a linear Harker–Patterson cross section and the electron density along the c axis of the hexagonal cell. In the linear cut of the electron density (Fig. 1) there were two clear maxima: at $z = 0$ and at $z = 0.5$; the second maximum was almost twice as high as the first. Thus, we proved that at the point $z = 0$ there was an atom of Ge, and that $z = 0.5$ corresponded to an atom of Te; consequently, $u = 0.250$.

The x-ray diffraction investigation of the structure of GeTe at room temperature at high pressures up to 100 kbar was carried out in a special x-ray camera,[7] the main part of which was a pellet of amorphous boron with a channel to take the sample. The camera was calibrated by x-ray diffraction using the compressibility of NaCl; we used Bridgman's data[8] and molybdenum radiation. To reduce the absorption, the samples under investigation were diluted with amorphous boron in proportions of $\frac{1}{3}$ B + $\frac{2}{3}$ GeTe.

The experiments showed that at high pressures (p = 35 kbar) GeTe underwent a reversible phase transition, which was indicated in the x-ray diffraction patterns (Fig. 2) by the merging of the doublets $220-\bar{2}20$, $222-\bar{2}22$, $420-\bar{4}20$. Consequently, the first doublet was replaced instead by a single line, and in the latter two cases the intensities were redistributed. According to the data obtained, the high-pressure phase had a NaCl-type structure, which was stable up to 100 kbar (which was the upper limit of pressures used in the present investigation). The experimental data obtained are set out in the table.

The transition from the type A7 structure to the NaCl-type structure in GeTe corresponds to a transition in Sb at p = 70 kbar[9] from A7 to the primitive cubic structure.

A detailed x-ray diffraction investigation made it possible to investigate the influence of pressure on the parameters of the rhombohedral (GeTe I) and cubic (GeTe II) phases. The results, shown graphically in Figs. 3–5, indicated that at the transition point, p = 35 kbar, the ratio c/a changed suddenly from $c/a = 1.27$ (GeTe I) to $c/a = \sqrt{3/2} \cong 1.224$ (GeTe II). At the same pressure there was a discontinuity of 3.0% in the dependence of the unit cell volume on p.

Thus, the transition GeTe → GeTe II, detected at high pressures, is undoubtedly a transition of the first kind. As is known,[1-3] the GeTe I → GeTe II transition at T = 400° C is continuous, without a sudden change in volume.

The reported observations can be interpreted by assuming that the equilibrium boundary between the GeTe I and GeTe II phases in the phase diagram of germanium telluride has a critical point.

Interplanar distances d for GeTe II at p = 40 kbar ($\rho_{\text{x-ray}} = 6.82$ g/cm^3)

No.	Intensity	(hkl)	d, Å	a, Å
1	v. strong	200	2.91	5.82
2	strong	220	2.06	5.82
3	v. weak	311	1.75	5.80
4	moderate	222	1.677	5.81
5	weak	400	1.449	5.80
6	v. weak	331	1.335	5.82
7	mod. weak	420	1.295	5.79
8	mod. weak	422	1.185	5.90

$\bar{a} = 5.80 \pm 0.01$Å

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2)The authors are grateful to S. Karbanov for supplying the alloy.

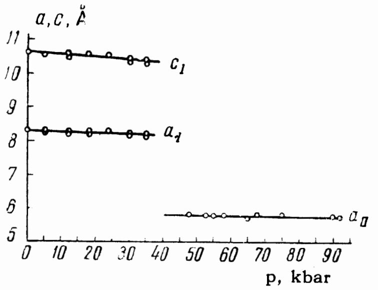

FIG. 3. Pressure dependence of the parameters of GeTe I and GeTe II.

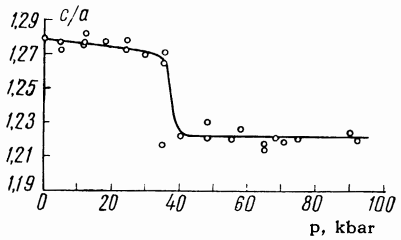

FIG. 4. Pressure dependence of the value of c/a.

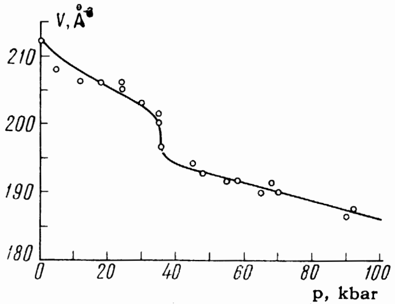

FIG. 5. Pressure dependence of the unit cell volume in GeTe.

Ponyatovskiĭ[10] has suggested the existence of a critical point in the isostructural transition curve of Ce at p = 17.5 kbar and T = 280° C. On the basis of qualitative considerations, Arkhipov[11] has shown that isostructural transitions in metals may be transitions of the first kind or continuous transitions.

Evidently, the structural transition in GeTe is, in this sense, analogous to the transition in Ce. To determine the parameters of the critical point of GeTe, it is intended to carry out later an x-ray diffraction determination of the sudden change in volume at various pressures and temperatures.

Bierly, Muldawer, and Beckman[3] investigated the structure of GeTe–SnTe alloys as a function of the composition in the temperature range from −140° C to +500° C. It is known[12] that GeTe and SnTe form a continuous series of solid solutions. For all alloys (with the exception of pure SnTe), Bierly et al. found a continuous transition of the low-temperature rhombohedral (A7) phase to the cubic (NaCl) phase when the temperature was raised and a reverse transition when the temperature was reduced; according to their data, the temperature of the transition depended on the composition of the GeTe–SnTe alloy: when the percentage content of SnTe was increased, the transition temperature fell.

Comparing these results with the data reported in the present paper, we may conclude that the replacement of Ge atoms with Sn atoms in alloys is qualitatively equivalent to the influence of high pressure on the structure.

We may expect the GeTe–SnTe alloys, having the rhombohedral (A7) structure under normal conditions, to undergo (at high pressures and room temperature) a first-order phase transition to the cubic phase. The transition pressure depends on the composition: as the SnTe content increases the transition pressure decreases. Thus, in addition to pure GeTe, there may exist a whole series of alloys with a critical point in the phase diagram.

The authors are indebted to R. G. Arkhipov for his valuable comments on this investigation.

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