PHASE TRANSITIONS IN TELLURIUM AT HIGH PRESSURES

S. S. KABALKINA, L. F. VERESHCHAGIN, and B. M. SHULENIN

Institute of High-Pressure Physics, Academy of Sciences, U.S.S.R.

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THE behavior of tellurium at high pressures up to 100 kbar was investigated by Bridgman.[1] He discovered two phase transitions at 44 and 69 kbar, the former with a volume change of −5.5% and the latter −0.7%. From measurements of the electrical resistance at various pressures Bridgman concluded that the 44 kbar transition is a transition to the metallic state.[2] Recently evidence has appeared about the possibility of the existence of a phase transition in tellurium at low pressures. According to Tikhomirova and Stishov,[3] the melting curve has a maximum at 10.6 kbar and 482°C, and therefore at p > 10.6 kbar tellurium suffers contraction on melting. To find how the crystal structure of tellurium changes at high pressures we carried out an x-ray diffraction study up to 100 kbar.

We used a special x-ray camera[4,5] for work at high pressures up to 100 kbar; the main part of the camera was an amorphous boron tablet with a channel for the sample, placed between two anvils of the hard alloy VK-6. Pressure calibration was carried out by recording the electrical resistance discontinuities of bismuth at its phase transitions.[1)] Using a similar technique we were able to detect two reversible phase transitions in tellurium: one at 15—20 kbar, and the other at 42—45 kbar.

The data for the first high-pressure phase are given in Table I; they undoubtedly indicate a hexagonal cell with parameters: a = 4.208 Å, c = 12.036 Å, Z = 6 (p = 30 kbar), corresponding to the arsenic structure (A7). The rhombohedral unit cell has: a = 4.69 Å, $\alpha = 53°18'$, Z = 2. The parameter u = 0.230 was calculated from the linear Patterson–Harker section along the z axis. Thus at p = 15 kbar tellurium undergoes a transition from the chain structure A8 to the laminar structure A7. In the new phase each tellurium atom has three nearest neighbors at a distance of 2.87 Å, three neighbors at a distance of 3.48 Å, and six neighbors at a distance of 4.208 Å. The bonds to the nearest neighbors in the same layer are covalent, like the bonds between the neighboring atoms in a chain of the initial phase A8. The distances in both cases are the same: 2.87 Å (A7) and 2.86 Å (A8).

The transition of tellurium to the A7 structure occurs without a change of volume, as is verified by the x-ray diffraction patterns obtained at p = 15 kbar. Under these conditions the transition was incomplete and the x-ray diffraction patterns included lines of both phases. It was found that the unit cell parameters (along the hexagonal axes) are related by: $a_2 = a_1$, $c_2 = 2c_1$; a similar relationship exists between the indices of the corresponding lines $h_2 = h_1$, $k_2 = k_1$, $l_2 = 2l_1$ (the index "1" refers to the initial phase A8, and the index "2" refers to the phase A7). For the phase A7 the condition $h_2 - k_2 + l_2 = 3n$ is satisfied. Since the volume and the number of atoms in a hexagonal cell (Z = 3 in A8, Z = 6 in A7) are both doubled on transition of tellurium from A8 to A7, the density is not affected. Obviously this is why the transition was not detected by Bridgman. According to Bridgman[7] a single crystal of tellurium subjected to hydrostatic pressure up to 12 kbar becomes stretched along the c-axis and compressed along the a-axis ($\Delta c/c_0 > 0$, $\Delta a/a_0 < 0$). Our work has shown that this effect also occurs at higher pressures in the whole region of existence of the phases A8 and A7 (up to 43—45 kbar). Figure 1 shows graphically the results of an x-ray diffraction determination of the linear and volume compressibilities of tellurium up to 40 kbar; it is

Table I

hkl	d_{calc}, Å	d_{meas}, Å	I	*hkl*	d_{calc}, Å	d_{meas}, Å	I
003	4.01	4.15	very weak	025	1.45	1.44	medium
102	3.12	3.11	very strong	116	1.45		
014	2.32	2.31	strong	108	1.39	1.38	medium
110	2.10	2.10	medium	121	1.37		
006	2.01	2.00	weak	212	1.34	1.34	very weak
105	2.01			009	1.34		
022	1.74	1.74	medium	124	1.25	1.25	very weak
204	1.56	1.55	weak	207	1.25		
017	1.56			119	1.13	1.13	very weak

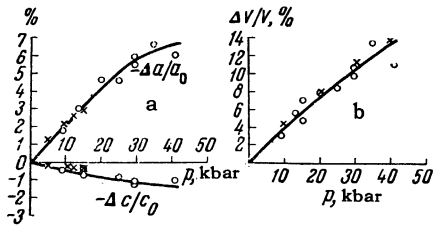

FIG. 1. a) Dependence of the linear compressibility of tellurium on pressure. Circles denote x-ray diffraction data, crosses give Bridgman's data[7]; b) dependence of the volume compressibility of tellurium on pressure. Circles denote x-ray diffraction data, crosses give Bridgman's data.[7]

clear that the data for $\Delta a/a_0$, $\Delta c/c_0$ and $\Delta V/V_0$ (Fig. 1a and 1b) agree to within the experimental error with the Bridgman data.[7,1] The dependence of c/a on pressure, given in Fig. 2, is not continuous: it shows clearly the presence of a phase transition in tellurium at k = 15 kbar, although in calculating c/a for p > 15 kbar the change of symmetry was not allowed for and consequently c was not doubled. The discontinuities of the curves for $\Delta a/a_0$, $\Delta c/c_0$, and $\Delta V/V_0$ plotted as a function of p were masked by the scatter of the experimental points.

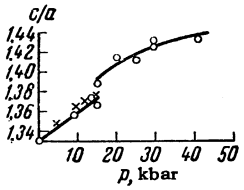

FIG. 2. Dependence of c/a on pressure. Circles denote x-ray diffraction data (for the A7 phase at p = 15 kbar c/2a was used), and crosses denote the values of c/a calculated from Bridgman's data.[7]

This explains the anomaly of the pressure dependence of the melting point of the new phase,[3] characteristic of bismuth and antimony, which belong to the A7 structures.

X-ray diffraction patterns of tellurium at p > 45 kbar indicate a fundamental change of its structure at the second phase transition. Table II gives the interplanar spacings for the new high-pressure phase. We were unable to establish its structure. We merely found that in the pressure range 45—90 kbar the x-ray diffraction patterns of tellurium did not change, and therefore there is some doubt about the existence of the phase transition at 69 kbar detected by Bridgman.[1]

Table II

d_{meas}, Å	I	d_{meas}, Å	I
2.92	strong	1.45	medium
2.43	medium	2.395	weak
2.36	medium	1.33	weak
1.82	strong	1.23	very weak
1.78	medium		

[1)] Pressures corresponding to the phase transitions in bismuth were based on the generalization of the experimental data in Wentorf's book.[6]

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ANISOTROPY OF THE ENERGY GAP IN SUPERCONDUCTING TIN

A. G. SHEPELEV

Physico-technical Institute, Academy of Sciences, Ukr.S.S.R.

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THE anisotropy of the energy gap in superconducting tin, detected by Bezuglyĭ, Galkin, and Korolyuk[1,2] and by Morse et al.[3] in the study of the absorption of ultrasound, amounted to about 30%. The analysis of these experiments carried out by Privorotskiĭ and Pokrovskiĭ[4,5] showed that the minimum energy gap in tin had not yet been observed and that it did not lie on a principal crystallographic axis.

The largest energy gap cannot be detected at all by experiments on the absorption of ultrasound because these give information only about the minimum value of the gap for a Fermi surface strip