

lattice constant) about $\text{In}_{0.91}\text{Te}$. The In_3Te_4 appears to form peritectically; when it is melted under a pressure of ~ 30 kbar, then cooled and pressure released, a mixture of at least the defect NaCl-type and In_3Te_4 phases is obtained. It is probable that the In_3Te_4 phase, in this case, contains excess Te.

The pressure-induced In_3Te_4 phase is a superconductor. The most nearly stoichiometric one has a transition at $1.25\text{--}1.15^\circ\text{K}$. The superconductivity of this phase has been discussed in the section on the NaCl-type phases and in Ref. 2.

SOME RESULTS OF PRESSURE TEMPERATURE EXPERIMENTS ON In_2Te_3

The pressure-temperature diagram of In_2Te_3 determined by differential thermal analysis will be the subject of a subsequent paper. In this section we discuss the nature of some of the specimens obtained after being subjected to various pressures and temperatures, then cooled and pressure released. The results on the In_2Te_3 are the most difficult to unravel.

It appears that there exists at high pressures an In_2Te_3 phase which is isostructural with the well-known Bi_2Te_3 ,⁽²¹⁾ but it cannot be retained metastably as a single phase. It is not a trivial matter to discern the Bi_2Te_3 -type phase in the powder patterns, because whenever it is present, the In_3Te_4 -type phase is present also and the structures of the two are closely related. Both structures belong to the same space group; both have all atoms on the threefold axis. As shown earlier, In_3Te_4 has the sequence $-\text{In}-\text{Te}-\text{Te}-\text{In}-\text{In}-\text{Te}-\text{Te}-\text{In}-$, dividing the threefold axis body diagonal in approximately sevenths, while the In_2Te_3 must have the sequence $-\text{Te}-\text{Te}-\text{In}-\text{In}-\text{Te}-\text{Te}-$ dividing the threefold axis body diagonal in approximately fifths. The hexagonal a -axes of the two phases are very nearly equal in length and as one would expect the ratio of the hexagonal c -axes (threefold axis body diagonals) of the In_2Te_3 to In_3Te_4 is very nearly 5 : 7 (see below for lattice constants of the former).

The deduction of the existence of a pressure-induced Bi_2Te_3 -type compound was based mainly on the results of 'single crystal' X-ray diffraction photography. In each of two runs, a sizeable crystalline piece of normal form In_2Te_3 was put

into a Teflon cell containing low viscosity silicone oil. One was pressurized at about 32 kbar at 400°C , the other at about 29 kbar and 340°C . What appeared by microscopic examination to be a single crystal was isolated from each. In both cases however, three phases were intimately co-crystallized. One of these phases has not been identified but accounts for 'extra' lines found in the powder photographs of most of the specimens for which 'extra' lines occur. The other two phases were the In_3Te_4 and In_2Te_3 types with their hexagonal a - and c -axes in apparently exact alignment. The In_2Te_3 type phase had hexagonal axes $a = 4.28 \pm 0.01$ and $c = 29.5 \pm 0.1 \text{ \AA}$ in both cases as measured on Buerger precession camera photographs. The In_3Te_4 phase from the higher pressure and temperature experiment had $a = 4.28 \pm 0.01$, $c = 40.2 \pm 0.1 \text{ \AA}$; the other had $a = 4.28 \pm 0.1$, $c = 40.4 \pm 0.1 \text{ \AA}$.

The c -axis lengths of the In_3Te_4 type phases were substantially smaller than found for stoichiometric or near-stoichiometric In_3Te_4 . Further, the 00.9 and 00.21 reflections were no longer observable on the precession camera photographs. It is probable that changes in stoichiometry produce vacancies and shifts in atomic positions.

Unfortunately, we have not been able to obtain metastably a single phase nonstoichiometric In_3Te_4 type. However, superconductivity tests also indicate that some of the In_3Te_4 types phases obtained in the various runs on In_2Te_3 are nonstoichiometric. This conclusion is based on the ideas set forth above on the nonstoichiometric NaCl-type phases. On this basis, excess Te in the In_3Te_4 type phase should result in a decrease of the superconducting transition temperature. For the specimen obtained by pressurizing the In_2Te_3 in the Teflon cell at 32 kbar and 340°C , about 60 per cent was found to be superconducting at $0.96\text{--}0.77^\circ\text{K}$. A specimen that was subjected to 60 kbar and 730°C in a differential thermal analysis experiment was found to contain the NaCl, In_3Te_4 and In_2Te_3 types. This specimen had two transitions, about 20 per cent of it at $1.25\text{--}1.00^\circ\text{K}$ (the NaCl-type phase) and about 20 per cent at $0.5\text{--}0.36^\circ\text{K}$, most likely, the In_3Te_4 -type phase. On the basis of our ideas, it is considered very unlikely that the In_2Te_3 phase is superconducting.

A diffractometer pattern was taken of In_2Te_3 which had been pressurized at about 29 kbar and

Table 4. Powder pattern for In_2Te_3 specimen subjected to 29 kbar and 760°C

Rel. I_{obs}	d_{obs} (Å)	In_3Te_4 -type		Bi_2Te_3 -type	
		d_{calc} (Å)	$hk \cdot l$	d_{calc} (Å)	$hk \cdot l$
23	4.82*				
11	4.685*				
9	4.538	4.533	00.9		
5	3.722*				
3	3.655			3.661	10.1
12	3.579			3.585	01.2
6	3.399	3.400	00.12		
22	3.365	3.366	01.5		
283	3.136	3.120	10.7	3.136	01.5
12	2.999	2.992	01.8		
7	2.906*				
9	2.757	2.739	10.10	2.784	10.7
4	2.627			2.617	01.8
70	2.313			2.312	10.10
26	2.292	2.288	01.14		
13	2.167			2.178	01.11
100	2.133	2.133	11.0	2.133	11.0
19	1.994	2.013	01.17		
18	1.977			1.977	00.15
16	1.944	1.943	00.21	1.941	10.13
8	1.853	1.855	10.19		
37	1.763	1.761	02.7	1.764	20.5
16	1.681	1.683	02.10		
16	1.566			1.567	02.10
13	1.448			1.450	11.15
6	1.436	1.436	11.21	1.436	02.13
		1.360	00.30		
25	1.358	1.358	21.7	1.359	12.5
		1.356	10.28		
4	1.332	1.329	11.24		
6	1.305			1.307	12.8
				1.304	11.18
8	1.262	1.259	12.14	1.263	21.10
9	1.239	1.240	10.31	1.240	12.11
		1.231	30.0		
21	1.229	1.227	30.3	1.231	30.0
		1.225	21.16		

* Unidentified.

melted at 760°C. (About 60 per cent of the specimen became superconducting at 1.3–0.97°K.) The pattern (Table 4) contains four unidentified lines which are rather weak and shows the presence of both the In_3Te_4 and In_2Te_3 pressure-induced phases.* The observed relative intensities given in

Table 4 probably suffer from preferred orientation as the crystallites of all the pressure-induced phases, including the NaCl-type, tend to grow along (110) directions.

* Calculations of spacings in Table 4 are based on the hexagonal lattice constants $a = 4.266$, $c = 40.8$ Å for the In_3Te_4 phase and $a = 4.266$, $c = 29.65$ Å for the In_2Te_3 phase.

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