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CRYSTAL CHEMISTRY AND SUPERCONDUCTIVITY OF PRESSURE-INDUCED PHASES IN THE In–Te SYSTEM

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Abstract—In the In–Te system, a pressure-induced NaCl-type phase exists in the region $In_{0\cdot80}Te$ to $In_{1\cdot15}Te$. Superconductivity exists in the whole range, with the maximum transition temperature occurring for the stoichiometric InTe. A hypothesis previously given for the metallic behavior of this phase and the decrease of transition temperature on either side of the stoichiometric InTe is further elaborated. It is proposed that the transformation to the NaCl-type structure removes the structural constraint on electron transfer existing in the normal InTe. A method for calculating carrier concentration is given and it is shown that the superconducting transition temperature is a function of carrier concentration.

At least two other pressure-induced In–Te phases exist. One is In_3Te_4 which becomes superconducting at 1·25–1·15°K. In_3Te_4 has the anti-Sn_4As_3 structure with seven atoms in a rhombohedral unit cell, all lying on the threefold axis. The positional parameters of the atoms and interatomic distances are given and the coordination shown to be related to that found in the NaCl-type structure. Pressure–temperature experiments on normal In_2Te_3 indicate that a pressure-induced phase with this (or approximately this) composition cannot be obtained metastably without the presence of the In_3Te_4 and an unidentified phase. The pressure-induced In_2Te_3 phase has the well-known Bi_2Te_3 structure and is closely related to the In_3Te_4 structure. Superconductivity tests and X-ray diffraction investigation lead to the conclusion that the In_3Te_4 phases occurring with the In_2Te_3 phase are sometimes not stoichiometric and in such cases usually contain excess tellurium.

INTRODUCTION

In a recent letter,[(1)] we reported the occurrence and superconducting behavior of pressure-induced vacancy structures of the NaCl-type in the In–Te system. It was proposed that the metallic behavior of the NaCl-type InTe resulted from the removal of the structurally imposed constraint in the normal phase, on electron transfer from In^+ to In^{3+} ions. This proposal has led to successful prediction[(2)] of other superconductors with NaCl-type and a related structure and of existence of solid solution regions in NaCl-type phases of binary systems.

The behavior of the In–Te system at high pressures is quite complex and we shall discuss in this paper only those aspects of it which are fairly clear.

EXPERIMENTAL

Appropriate amounts of the constituent elements in each case were melted together in an evacuated sealed fused silica tube. The resulting product was ground and mixed thoroughly to ensure homogeneity. X-ray powder photographs always showed the mixture of normal compounds expected from the phase diagram reported by Klemm and Vogel.[(3)] Specimens were packed into Ta containers and subjected to pressure and heating as described elsewhere.[(4)] The NaCl-type compounds were obtained usually by using 30 kbar and 400–500°C for various lengths of time not exceeding 4 hr. Pressures and temperatures for other phases will be given in later sections.

X-ray powder photographs (CuK radiation) were taken of all specimens subjected to high pressure and in some cases diffractometer patterns were obtained. Single crystal X-ray data were also obtained in some cases to be discussed later.

Superconductivity tests were made by the method of Schawlow and Devlin.[(5)]

THE NaCl TYPE PHASES

Results

Since our earlier publication[(1)] on the Te-rich NaCl-type compounds, we have obtained In-rich pressure-induced NaCl-type phases to approximately $In_{1\cdot15}Te$. It has also been possible to extend

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the Te solubility to $In_{0 \cdot 80}Te$; previously we reported that it extends to $In_{0 \cdot 82}Te$. The results of superconductivity tests on these specimens are given in Table 1.

The lattice constants of all specimens are listed in Table 1 and plotted vs. composition in Fig. 1.* On the In-rich side, there is practically no change in lattice constant with change in In concentration; this was one of the reasons we thought earlier that solid solution on the In-rich side did not exist. Further, although excess Te enhances the odd-index X-ray reflections, excess In does not appear to do so. In fact, careful examination now shows that although we can just see the {111} reflection of stoichiometric InTe, it can no longer be seen in the photograph of $In_{1 \cdot 15}Te$. Also, the stability at atmospheric pressure of these phases is greater, the greater the Te content; on the In-rich side, the stability is markedly less than that of stoichiometric InTe. Superconductivity tests on the In-rich specimens which had already begun to revert indicate that the composition tends to move toward the stoichiometric InTe with exsolution of In possibly containing dissolved Te.

* A reconsideration of the plot of lattice constant vs. $1-x$ for the $In_{1-x}Te$ phases[1] indicated that a straight line could be passed through the points for $x \geqslant 0 \cdot 05$. This line extrapolates to $a = 6 \cdot 175$ Å for stoichiometric InTe (see Fig. 1). The back-reflection lines of the powder photograph of our original InTe were quite broad. We have since made a new specimen for which the back-reflection lines were much sharper and which gave $a = 6 \cdot 177$ Å.

Table 1. *Superconducting transition temperatures,* T_c, *and lattice constants,* a, *and carrier concentrations,* n, *for* $In_{1-x}Te$ *and* $In_{1+x}Te$ *compounds with* NaCl-*type structure*

$1+x$	T_C (°K)	a (Å)	$n \times 10^{-22}/cm^3$
1·15	2·60–2·35	6·179 ± 0·005	1·34
1·10	2·80–2·55	6·182	1·45
1·05	3·41–2·95	6·181	1·58
1·015	3·51–3·25	6·178	1·67
1·00	3·45–3·20	6·177	1·71
$1-x$			
0·95	2·7 –2·5	6·14 ± 0·01	1·47
0·91	2·04–1·87	6·110 ± 0·003	1·28
0·87	1·55–1·40	6·081	1·09
0·83	1·15–1·09	6·055	0·88
0·82	1·06–1·02	6·052	0·83
0·80		6·040	

The X-ray data on the In-rich compounds indicate that the excess In atoms replace Te atoms. If Te vacancies were to occur, the intensity of the {111} reflection should first decrease and at about

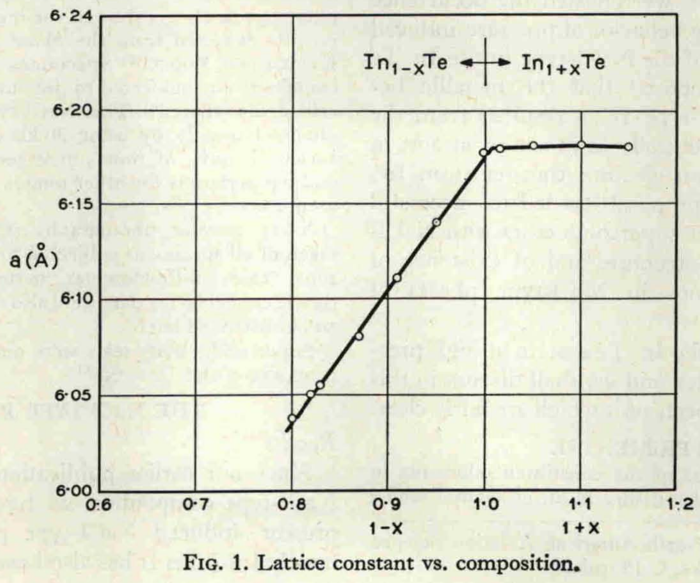

FIG. 1. Lattice constant vs. composition.

the composition $InTe_{0\cdot 94}$ would be identically zero. However, on further dissolution of In, the {111} intensity should increase again and at $InTe_{0\cdot 87}$ (i.e. $In_{1\cdot 15}Te$) it should be relatively more intense than it is for stoichiometric InTe. For increasing replacement of Te by In, there should be a continuous decrease in the intensity of the {111} reflection and, because of its low value for $In_{1\cdot 15}Te$, is not observed.

Discussion

The basis of the explanation proposed for the metallic behavior of the NaCl-type In–Te phases is an extension of the effective ionic model for semiconductors enunciated by GOODMAN.[6] In this model any semiconducting compound can be assigned a plausible ionic formula provided that the arrangement of the atoms in the crystal is known. This can be done because such compounds have saturated ionic-covalent bonds; that is to say, in a pure stoichiometric semiconducting compound the valence electrons are constrained by formation of these bonds.

The InTe phase[7] stable at atmospheric pressure is isostructural with TlSe[8] and therefore has the ionic formula $In^{+}_{0\cdot 5}In^{3+}_{0\cdot 5}Te$. The In^{+} ions have 8- and the In^{3+}, 4-coordination by Te^{2-} ions. The structure therefore stabilizes the valencies, preventing free transfer of electrons from the In^{+} to In^{3+} ions. However, the structural constraint on electron transfer is removed when InTe transforms to the NaCl-type structure; in this structure all cations have 6-coordination by Te^{2-} ions. The ease with which the electron transfer can now occur leads to metallic conductivity. Now the semiconductor $AgSbTe_2$ is isoelectronic with InTe and has[9] a disordered statistical NaCl-type structure at atmospheric pressure. In contrast with the In^{+} ion however, the second ionization potential of the Ag^{+} ion must be very large, thereby inhibiting electron transfer to Sb^{3+} ions.

The above ideas have led to successful prediction[2] of metallic behavior of other intermetallic compounds with NaCl-type and a related structure. Metallic conduction results if the cation is present in two valence states, one of which is less stable than the other. The ionic model also appears to be a basis for predicting or accounting for the existence of solid solution ranges in the intermetallic NaCl-type compounds. If the cation has one stable valence, as for example in the high pressure forms of CdSe and CdTe,[10] no solid solution should be expected.* (Such phases should be semiconductors.) If the cation has two possible valencies and the lower one is numerically equal to that of the anion, solid solution should occur on the anion-rich side because the valence of the anion can be balanced electrostatically by a proper 'mixture' of the higher and lower valence cations; an example is $Sn_{1-x}Te$. However, in this case solid solution rich in the cation should not be attainable.* If the cation has two possible valencies, one of which is numerically lower, the other higher than that of the anion, solid solution rich in either constituent should exist; one example is the Sn–Sb system.[10] Also we have recently reported[2] such occurrence in the Sn–As system, in which case high pressures are required to effect solid solution. It was these ideas that led us to the In-rich NaCl-type In–Te phases which we had at first thought did not exist: while on the Te-rich side, more In^{3+} than In^{+} ions are present, on the In-rich side, more In^{+} than In^{3+} ions are present.

The ionic model also permits the calculation[2] of carrier concentrations. In $In_{1-x}Te$, there are y monovalent and $(1-x-y)$ trivalent In ions per formula unit; then $y+3(1-x-y) = 2\cdot 00$, the total valence which must be electrostatically balanced by In ions. Then $y = (1-3x)/2$ and $(1-x-y) = (1+x)/2$, which except for $x = 0$ is always larger than the number of monovalent ions. Because each In^{+} ions has two electrons, which in the NaCl-type structure are bound to it with nearly zero energy, the number of carriers is $2y$ or $(1-3x)$. The unit cell contains four formula units; thus, the carrier concentration, n, is $4(1-3x)/(a^3 \times 10^{24})$ per cm^3, where a is the lattice constant.

On the In-rich side there will be an excess of In^{+} ions; thus, the number of In^{3+} ions will determine the number of carriers because the latter cannot exceed twice the number of acceptor ions. A comparison of results on SnAs and Sn_4As_3[2] with those on InTe and In_3Te_4 (see following

* We refer here to substantial solid solution. It is possible for very small deviations to occur through, for example, the creation of anion vacancies plus two electrons for each vacancy as proposed by BLOEM[11] for PbS.

section) provides experimental proof of this contention. SnAs with the NaCl-type structure and valence formula $Sn^{2+}_{0\cdot5}Sn^{4+}_{0\cdot5}As^{3-}$, has very nearly the same T_c as InTe with valence formula $In^{+}_{0\cdot5}In^{3+}_{0\cdot5}Te^{2-}$. Each has the same number of carriers per formula unit (although the carrier concentration of SnAs is somewhat higher than that of InTe because its lattice constant is smaller than that of InTe). The pressure-induced phase with stoichiometric formula In_3Te_4 (see following section) has the anti-Sn_4As_3 structure[10] which is related to the NaCl-type structure. The ionic model applied to this phase indicates that $2\frac{1}{2}$ In^{3+} and $\frac{1}{2}$ In^{+} ions are required to balance the 4 Te valencies and there is one carrier per formula unit; for electrostatic balance, Sn_4As_3 requires $3\frac{1}{2}$ Sn^{2+} and $\frac{1}{2}$ Sn^{4+} ions. The superconducting transition temperatures of In_3Te_4 and Sn_4As_3 are respectively 1·25–1·15°K and 1·19–1·16°K. Because SnAs and InTe have about the same carrier concentrations, and the same T_c's, it would be logical to conclude that Sn_4As_3 and In_3Te_4 with very nearly the same T_c's should have very nearly the same carrier concentrations. Thus, In Sn_4As_3 the number of Sn^{4+} ions must determine the number of carriers per formula unit, which is again one. Thus for consistency, when the lower valence ions are in excess, the number of carriers is determined by the number of higher valence cations, and when the higher valence cations are in excess, the number of carriers is determined by the number of lower valence cations.

The normalized formula for an In-rich compound with NaCl-type structure is

$$In(Te_{2/(2+x)}In_{x/(2+x)}).$$

If it is assumed that all In atoms are ionic, we would have

$$y+3\left(1+\frac{x}{2+x}-y\right) = \frac{4}{2+x},$$

from which

$$y = (1+3x)/(2+x)$$

and

$$1+\frac{x}{2+x}-y = (1-2x)/(2+x)$$

which is the number of trivalent ions per formula unit. A plot of T_c (midpoints) vs. n for both sides is shown in Fig. 2; the agreement is seen to be good. The maximum T_c occurs (within experimental error) for stoichiometric InTe which has maximum n.

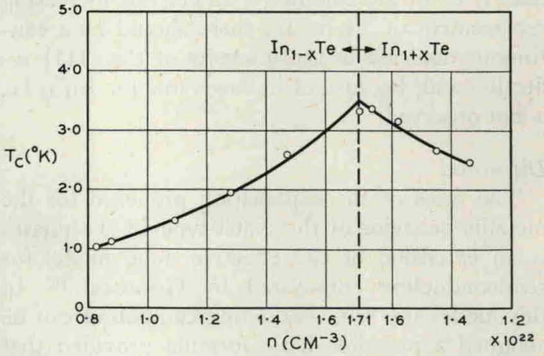

FIG. 2. Superconducting transition temperature, T_c, vs. carrier concentration, n.

We have shown[2] that, as predicted, substitution of Ag^{+} for In^{+} or As^{3-} for Te^{2-} resulted in a decrease of T_c. Both substitutions cause a decrease in n, the Ag^{+} for In^{+} because the Ag 4d electrons are tightly bound to it and As^{3-} for Te^{2-} by increasing the number of In^{3+} (thereby decreasing the number of In^{+} ions) needed for electrostatic balance. However, in these systems, the carrier concentrations required for a given T_c is always somewhat higher than required in the $In_{1-x}Te$ system. It may be speculated that this results from scattering by intervening In^{3+} ions which are 'inactive' because they are paired with Ag^{+} or As^{3-} ions. (See also Ref. 2.)

CRYSTAL STRUCTURE OF THE PRESSURE INDUCED In_3Te_4 PHASE

Weissenberg (CuKα radiation) and Buerger precession camera (MoKα radiation) photographs were taken of a single crystal fragment isolated from a run in which an attempt was made to grow a single crystal of the high pressure In_2Te_3 phase. The diffraction symmetry of the combined photographic data is $R\bar{3}m$; with no systematic absences, the possible space groups are $R\bar{3}m-D^5_{3d}$ and $R3m-C^5_{3v}$. The hexagonal axes as determined from the precession camera photographs are $a = 4{\cdot}27 \pm 0{\cdot}01$, $c = 40{\cdot}9 \pm 0{\cdot}1$ Å; the rhombohedral lattice constants derived from these are $a = 13{\cdot}8_5$ Å, $\alpha = 17{\cdot}7_3$°.

The intensity distribution indicated that all atoms must lie on the threefold axis body diagonal of the rhombohedron (hexagonal *c*-axis) and that ideally, there must be seven atoms in the rhombohedral cell. The ideal formula of the compound appeared to be In_3Te_4. With this formula the most likely space group to which the crystal belongs is $R\bar{3}m$ with one In(1) in 1*a*,000, the other atoms being in 2 *c*, $\pm xxx$ or in the hexagonal description 3*a*,000, $\pm(\frac{1}{3}\frac{2}{3}\frac{2}{3})$ and 6*c*, (000, $\pm\frac{1}{3}\frac{2}{3}\frac{2}{3}$)$\pm 00z$. Later it was found that In_3Te_4 has the anti-Sn_4As_3 structure.[10]

Table 2. Interatomic distances and standard deviations

Atom	Nearest neighbors	Distance (Å)	σ (Å)
In(1)	6Te(2)	3·02	0·03
In(2)	3Te(1)	2·84	0·03
	3Te(2)	3·24	0·05
Te(1)	3In(2)	2·84	0·03
	3Te(1)	3·98	0·03
Te(2)	3In(1)	3·02	0·03
	3In(2)	3·24	0·05
	Next nearest neighbors		
In(1)	6In(1)	4·27	0·01
	6In(2)	4·57	0·03
In(2)	3In(1)	4·57	0·03
	3Te(1)	5·17	0·05
	6In(2)	4·27	0·01
Te(1)	3In(2)	5·17	0·05
	3Te(2)	4·30	0·03
	6Te(1)	4·27	0·01
Te(2)	3Te(1)	4·30	0·03
	3Te(2)	4·25	0·03
	6Te(2)	4·27	0·01

Intensities of selected reflections from the precession camera photographs were estimated visually by comparison with a calibrated intensity strip. Lorentz-polarization corrections were applied by means of the WASER[13] and GRENVILLE-WELLS–ABRAHAMS[14] charts. No correction was made for absorption. As in the case of the isostructural Sn_4As_3, the atoms must be disposed along the hexagonal *c*-axis near multiples of 1/7. Thus using the relative observed structure amplitudes and the BUERGER tables,[15] adjustments around multiples of 1/7 were made. The BUSING–MARTIN–LEVY[16] least squares program modified by Cetlin for the present Bell System IBM 7094 monitor program was then used to refine the parameters. The atomic scattering factors used were from THOMAS and UMEDA,[17] corrected for the real part of the dispersion.[18]

The values of the *z*-parameters obtained were: for In(2), 0·4273; Te(1), 0·1284; and Te(2), 0·2908. Standard errors were 0·0008, 0·0006 and 0·0009 respectively. Except for β_{33}, all other thermal parameters β_{ii} and β_{ij} are zero. β_{33} parameters were also refined, but the standard errors on them indicate that they are essentially indeterminate from the data used. However, because the correlation matrix indicated insignificant interaction[19] with positional parameters, the latter may be considered to be virtually unaffected by the indeterminacy of the thermal parameters.

Interatomic distances and their standard deviations are given in Table 2. In most cases the standard deviations are large. The nearest neighbor coordination of all atoms is octahedral and next nearest neighbor coordination is 12. The In_3Te_4 structure* is related to the NaCl-type structure, but it will be noted (Table 2) that Te(1) has 3In and 3Te (instead of all In) nearest neighbors, In(2) has 9In and 3Te (instead of all Te) and Te(1) has 9Te and 3In (instead of all Te) next nearest neighbors. The In(2)–Te(1) next nearest neighbor distances are rather large because of the large Te(1)–Te(1) contact distances.

The average nearest neighbor In–Te distance is $3{\cdot}03 \pm 0{\cdot}11$ Å. If for the moment, the large limits of error are overlooked, we may compare the average In–Te distance, 3·03 Å with 3·09 Å in the stoichiometric InTe. Because the ratio of trivalent to monovalent In ions in the In_3Te_4 is 5 : 1 as compared with 1 : 1 in InTe, one would expect a substantial decrease in the average size of the In atom; 0·06 Å is substantial, but the large limits of error preclude any assertion regarding the comparison of distances.

FURTHER CHARACTERIZATION OF THE PRESSURE INDUCED In_3Te_4 PHASE

A specimen of In_3Te_4 prepared at $\sim$35 kbar and 550°C for 1 hr was very nearly single phase. A slight trace of the NaCl-type phase was seen in

* The reader is referred to Ref. 10 for excellent diagrams of the structure.

Table 3. *Powder pattern for* In_3Te_4 (CuK*α radiation*)

hk·l	d (Å) obs.	d (Å) calc.	Rel. I obs.	Rel. I calc.
00·3	13·5	13·53	*VW*	60
00·6	6·78	6·79	*VVW*	20
00·9	4·50	4·51	*VW*	65
00·12	3·386	3·382	*VW*	71
10·7	3·093	3·110	*VVS*	1250
01·8	3·006	2·992	*VW*	39
10·10	2·729	2·732	*W*	76
01·14	2·272	2·278	*M–S*	342
11·0	2·128	2·128	*S*	463
11·3	2·098	2·109	*W*	35
10·16		2·097		65
01·17	2·003	2·004	*W–M*	97
00·21	1·934	1·932	*W–M*	34
11·9		1·935		37
10·19	1·860	1·848	*VVW*	15
11·12	1·800	1·801	*VW*	32
20·5		1·797		6
02·7	1·754	1·756	*M–S*	215
00·24	1·691	1·691	*VW*	33
01·23	1·587	1·591	*VW*	35
20·14	1·555	1·555	*W–M*	93
20·17	1·458	1·459	*VW*	32
11·21	1·431	1·431	*W*	69
21·7	1·355	1·354	*M–S*	166
00·30		1·353		5
10·28		1·349		10
12·14	1·255	1·256	*W–M*	83
10·31	1·231	1·234	*M**	38
00·33		1·230		3
30·0		1·229		66
11·27		1·228		8

hk·l	d (Å) obs.	d (Å) calc.	Rel. I obs.	Rel. I calc.
12·17	1·205	1·203	*VW*	32
11·30	1·142	1·142	*VVW*	23
02·31	1·066	1·068	*W–M**	24
22·0		1·065		42
11·33		1·065		1
30·21	1·039	1·037	*VW*	11
03·21		1·037		11
22·9		1·036		5
13·7	1·008	1·008	*W–M*	65
11·36	0·9955	0·9963	*W**	18
30·24		0·9945		34
03·24		0·9945		34
31·14	0·9648	0·9649	*W*	40
21·31	0·9554	0·9544	*W*	40
10·43	0·9127	0·9143	*VW**	12
31·20		0·9136		5
40·7		0·9109		30
30·30		0·9100		6
03·30		0·9100		6
00·45	0·9021	0·9018	*VW**	3
22·24		0·9011		32
04·14	0·8785	0·8789	*VW**	19
12·38	0·8491	0·8478	*W**	38
01·47	0·8388	0·8407	*M**	24
02·43		0·8402		27
04·20		0·8396		3
32·7		0·8375		69
22·30		0·8368		14
23·14	0·8130	0·8125	*W**	54
13·31	0·8064	0·8062	*M**	60
41·0		0·8051		105

* Broad line.

the powder photograph. The lattice constants determined from the powder photograph (CuKα radiation) are $a = 4{\cdot}26 \pm 0{\cdot}01$, $c = 40{\cdot}6 \pm 0{\cdot}1$ Å or in the rhombohedral description $\alpha = 13{\cdot}7_5$ Å, $\alpha = 17{\cdot}8_0°$. The powder pattern indexed on the hexagonal basis is given in Table 3. Shown also are qualitatively estimated intensities and those calculated* from

$$I_{\text{rel}} = p|F|^2 \times 10^{-5} L{\cdot}P$$

where p is the multiplicity, F, the structure factor and $L{\cdot}P$ the Lorentz-polarization factor. The positional parameters were those obtained from the single crystal analysis, and because the program* allows only individual isotropic temperature factors, In(1) and Te(2) were assigned values of 0·5 $Å^2$ and In(2) and Te(1) values of 1·0 $Å^2$.†

When this pressure-induced In_3Te_4 phase was heated at 200°C in an evacuated sealed fused silica tube for 67 hr, it decomposed into a mixture of the atmospheric pressure In_2Te_3 phase and an NaCl-type phase with composition (determined from the

* The program used was originally derived by TREUTING[20] for the IBM 704 and modified for the IBM 7094 by N. V. Vaughan and A. R. Storm.

† Differences in vibration amplitudes of the atoms were indicated by the results from the single crystal analysis.

lattice constant) about $In_{0\cdot 91}Te$. The In_3Te_4 appears to form peritectically; when it is melted under a pressure of $\sim$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 1·25–1·15°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 –In–Te–Te–In–In–Te–Te–In–, dividing the threefold axis body diagonal in approximately sevenths, while the In_2Te_3 must have the sequence –Te–Te–In–In–Te–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 $a = 4\cdot 28 \pm 0\cdot 01$ and $c = 29\cdot 5 \pm 0\cdot 1$ Å in both cases as measured on Buerger precession camera photographs. The In_3Te_4 phase from the higher pressure and temperature experiment had $a = 4\cdot 28 \pm 0\cdot 01$, $c = 40\cdot 2 \pm 0\cdot 1$ Å; the other had $a = 4\cdot 28 \pm 0\cdot 1$, $c = 40\cdot 4 \pm 0\cdot 1$ Å.

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 0·96–0·77°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 1·25–1·00°K (the NaCl-type phase) and about 20 per cent at 0·5–0·36°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 d_{calc} (Å)	In_3Te_4-type $hk{\cdot}l$	Bi_2Te_3-type d_{calc} (Å)	Bi_2Te_3-type $hk{\cdot}l$
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
25	1·358	1·360 1·358 1·356	00·30 21·7 10·28	1·359	12·5
4	1·332	1·329	11·24		
6	1·305			1·307 1·304	12·8 11·18
8	1·262	1·259	12·14	1·263	21·10
9	1·239	1·240	10·31	1·240	12·11
21	1·229	1·231 1·227 1·225	30·0 30·3 21·16	1·231	30·0

* 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 $a = 4{\cdot}266$, $c = 40{\cdot}8$ Å for the In_3Te_4 phase and $a = 4{\cdot}266$, $c = 29{\cdot}65$ Å for the In_2Te_3 phase.

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