

SUPERCONDUCTIVITY AND VACANCY STRUCTURES OF THE PRESSURE-INDUCED  
NaCl-TYPE PHASES OF THE In-Te SYSTEM

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We have found that a solid-solution range of Te exists in the pressure-induced NaCl-type InTe. The compounds are actually deficient in In; the formulas may be written  $\text{In}_{1-x}\text{Te}$ , with  $0 \leq x \leq 0.18$ . As far as we know, this is the first time structures with a substantial number of vacancies have been produced at high pressures. Superconductivity exists in the whole range of composition, the transition temperatures  $T_c$  decreasing with In/Te ratio, from 3.45–3.20°K for InTe to 1.06–1.02°K for  $\text{In}_{0.82}\text{Te}$ ; the lattice constant decreases from 6.16 to 6.052 Å (see Table I and Fig. 1). An explanation

of the metallic behavior of these compounds has been deduced and appears also to account for the behavior of  $T_c$  with In/Te ratio.

Normal InTe undergoes transformation at 30 kbar to the NaCl-type phase<sup>1</sup> which is retained metastably at atmospheric pressure and room temperature. This phase was first reported to be superconducting at 2.18°K by Bömmel and others<sup>2</sup> but later Banus and others<sup>1</sup> reported a significantly higher transition temperature 3.7–3.5°K. Our result for InTe is in better agreement with the higher value.

We became interested in the NaCl-type phase when it occurred in some high pressure-high temperature experiments on  $\text{In}_2\text{Te}_3$  and had a lattice constant of 6.052 Å, considerably smaller than that of stoichiometric InTe. Consequently several compositions in the range 33.3 to 55.0 at. % Te were prepared by melting together appropriate amounts of 99.99+ In and Te in sealed evacuated fused silica tubes which were continually agitated to ensure intimate mixing. X-ray powder photographs (CuK radiation) gave the expected patterns for normal  $\text{In}_2\text{Te}_3$  and InTe. For compositions with In/Te  $\leq 1$ , mixtures of InTe and  $\text{In}_2\text{Te}_3$  resulted as would be predicted

CONTENT ANALYSIS

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A. InTe	
B. superconductivity	
B. phase transitions,	
effects of pressure	
on	

Table I. Superconducting Transition Temperatures  $T_c$  and Lattice Constants  $a$  for  $\text{In}_{1-x}\text{Te}$  Compounds with NaCl-like Structure.

$1-x$	$T_c$ (°K)	$a$ (Å)
1.00	3.45 - 3.2	$6.16 \pm 0.01$
0.95	2.7 - 2.5	6.14
0.91	2.04 - 1.87	$6.110 \pm 0.003$
0.87	1.55 - 1.40	6.081
0.83	1.15 - 1.09	6.055
0.82	1.06 - 1.02	6.052

from the reported<sup>3</sup> phase diagram. Pressure was generated in a piston cylinder device. The furnace assembly was the same as that described earlier;<sup>4</sup> the sample container was a tantalum cup with a boron nitride cover. Pressure of about 30 kbar was applied first and the temperature raised to about 800°C. After a few minutes, the temperature was reduced to ambient in about 5 min and the pressure released. In experiments below the melting temperature, the specimens were kept under pressure at 550°C for about one hour.

After being subjected to compression and heating, all specimens yielded metastably retainable NaCl-type phases. In the composition range  $\text{InTe}$  to  $\text{InTe}_{1.22}$ , single phases were obtained;  $\text{In}_2\text{Te}$ , however, transformed to a mixture of  $\text{In}$  and *stoichiometric*  $\text{InTe}$ , indicating (contrary to ref 1) that this phase does not dissolve excess  $\text{In}$ . The same results were obtained whether or not the specimens were melted.

The density of the NaCl-like  $\text{In}_{0.82}\text{Te}$ , determined pycnometrically, was 6.72 g/cc, which implies the formula  $(\text{In}_{0.83}\text{Te}_{0.01}\square_{0.16})\text{Te}$ ; that is, each unit cell contains an average of 3.32  $\text{In}$ , 0.04  $\text{Te}$  and 0.64 vacancies in  $\text{In}$  sites. X-ray diffraction data give a clear corroboration of the vacancy structures. Because the difference in scattering by  $\text{In}$  and  $\text{Te}$  atoms is small, the  $\{111\}$  line of  $\text{InTe}$  is very faint, but, as in the case of  $\text{AgSbTe}_2$ <sup>5</sup> (and contrary to refs 1 and 2), can be seen. As  $\text{In}/\text{Te}$  decreases, the intensities of the odd-index reflections increase relative to the even-index ones. For  $\text{In}_{0.82}\text{Te}$ , the  $\{111\}$ ,  $\{311\}$ , and  $\{331\}$  reflections are readily seen. Weissenberg and Buerger precession camera photographs of a single crystal of  $\text{In}_{0.82}\text{Te}$  corroborate the (statistical<sup>5</sup>) cubicity of this phase.

Tests for superconductivity on powdered specimens were made by the alternating current method of Schawlow and Devlin.<sup>6</sup>

We propose that the crystal structure of the high-pressure form of  $\text{InTe}$  is a disordered one (like that of  $\text{AgSbTe}_2$ <sup>5</sup>) containing equal numbers of  $\text{In}^+$  and  $\text{In}^{3+}$  ions, and that its metallic behavior results from the ease with which electron transfer can occur from  $\text{In}^+$  to  $\text{In}^{3+}$  ions throughout the crystal. Normal  $\text{InTe}$  (ref 7) has the  $\text{TlSe}$  (ref 8) structure and is a semiconductor. The  $\text{TlSe}$  crystal is ordered and contains equal numbers of  $\text{Tl}^+$  and  $\text{Tl}^{3+}$  ions in 8 and 4 coordination respectively; consequently, it is expected that  $\text{In}^+$  and  $\text{In}^{3+}$  ions are arranged similarly in normal  $\text{InTe}$ . The structure stabilizes the  $\text{In}$  valencies because it is energetically unfavorable for an  $\text{In}$  in 8 coordination to be trivalent or one in a tetrahedral site to be monovalent. The compound  $\text{AgSbTe}_2$ <sup>5</sup> is isostructural with the pressure-induced form of  $\text{InTe}$ ;  $\text{Ag}^+$  and  $\text{Sb}^{3+}$  ions have 6 coordination and their average valence is that of  $\text{Te}$ . In  $\text{AgSbTe}_2$  transfer of electrons from  $\text{Ag}$  to  $\text{Sb}$  is also energetically unfavorable because the +1 valence state of  $\text{Ag}$  is highly stable; this compound is also a semiconductor.

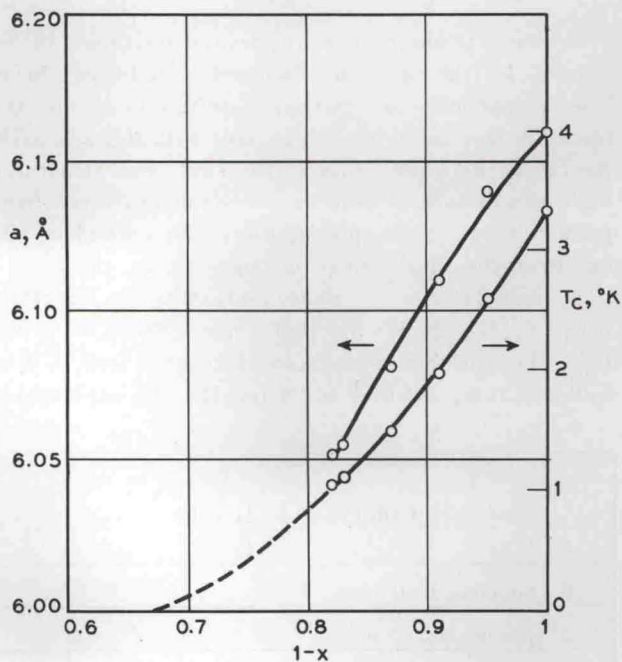


Fig. 1. Lattice constant  $a$  and superconducting transition temperature  $T_c$  vs  $(1-x)$  for the system  $\text{In}_{1-x}\text{Te}$ .

As the ratio of In/Te decreases, the percentage of  $\text{In}^{3+}$  ions in the crystal increases. When  $\text{In/Te} = 0.82$ , the average valence of In is 2.44, implying that 72% of the In atoms are trivalent. It would appear that as the percentage of  $\text{In}^{3+}$  ions increases (with decreasing In/Te), the superconducting transition temperatures should decrease. The curve of  $T_c$  vs  $(1-x)$  in Fig. 1, indicates that  $T_c$  does tend to approach 0 as  $(1-x)$  approaches 0.67 at which point all In atoms would be trivalent.

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<sup>1</sup>M. D. Banus, R. E. Hanneman, M. Strongin, and K. Goen, *Science* **142**, 662 (1963) and pertinent references therein.

<sup>2</sup>H. E. Bömmel, A. J. Darnell, W. F. Libby, B. R. Tittman, and A. J. Yencha, *Ibid.*, **141**, 714 (1963).

<sup>3</sup>W. Klemm and H. U. v. Vogel, *Z. anorg. Chem.* **219**, 45 (1934). See also M. Hansen, *Constitution of Binary Alloys*, (McGraw Hill Book Company, Inc., New York, 1958), p 863.

<sup>4</sup>G. C. Kennedy, A. Jayaraman, and R. C. Newton, *Phys. Rev.* **126**, 1363 (1962).

<sup>5</sup>S. Geller and J. H. Wernick, *Acta Cryst.* **12**, 46 (1959).

<sup>6</sup>A. L. Schawlow and G. E. Devlin, *Phys. Rev.* **113**, 120 (1959).

<sup>7</sup>K. Schubert, E. Dörre, and M. Kluge, *Z. Metallk.* **46**, 216 (1955).

<sup>8</sup>J. A. A. Ketelaar, W. H. t'Hart, M. Moerel, and D. Polder, *Z. Krist.* **A101**, 396 (1939).

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