

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 In_{1-x}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 phase¹ 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 others² but later Banus and others¹ 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 In_2Te_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 In_2Te_3 and InTe. For compositions with In/Te ≤ 1 , mixtures of InTe and In_2Te_3 resulted as would be predicted

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Table I. Superconducting Transition Temperatures T_c and Lattice Constants a for In_{1-x}Te Compounds with NaCl-like Structure.

$1-x$	T_c ($^{\circ}\text{K}$)	a (\AA)
1.00	3.45 - 3.2	6.16 ± 0.01
0.95	2.7 - 2.5	6.14
0.91	2.04 - 1.87	6.110 ± 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 reported³ phase diagram. Pressure was generated in a piston cylinder device. The furnace assembly was the same as that described earlier;⁴ 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 $^{\circ}\text{C}$. 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 $^{\circ}\text{C}$ for about one hour.

After being subjected to compression and heating, all specimens yielded metastably retainable NaCl-type phases. In the composition range InTe to $\text{InTe}_{1.22}$, single phases were obtained; In_2Te , however, transformed to a mixture of In and *stoichiometric* InTe , indicating (contrary to ref 1) that this phase does not dissolve excess 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 In, 0.04 Te and 0.64 vacancies in In sites. X-ray diffraction data give a clear corroboration of the vacancy structures. Because the difference in scattering by In and Te atoms is small, the $\{111\}$ line of InTe is very faint, but, as in the case of AgSbTe_2 ⁵ (and contrary to refs 1 and 2), can be seen. As In/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 (statistical⁵) cubicity of this phase.

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

We propose that the crystal structure of the high-pressure form of InTe is a disordered one (like that of AgSbTe_2 ⁵) containing equal numbers of In^+ and In^{3+} ions, and that its metallic behavior results from the ease with which electron transfer can occur from In^+ to In^{3+} ions throughout the crystal. Normal InTe (ref 7) has the TlSe (ref 8) structure and is a semiconductor. The TlSe crystal is ordered and contains equal numbers of Tl^+ and Tl^{3+} ions in 8 and 4 coordination respectively; consequently, it is expected that In^+ and In^{3+} ions are arranged similarly in normal InTe . The structure stabilizes the In valencies because it is energetically unfavorable for an In in 8 coordination to be trivalent or one in a tetrahedral site to be monovalent. The compound AgSbTe_2 ⁵ is isostructural with the pressure-induced form of InTe ; Ag^+ and Sb^{3+} ions have 6 coordination and their average valence is that of Te. In AgSbTe_2 transfer of electrons from Ag to Sb is also energetically unfavorable because the +1 valence state of Ag is highly stable; this compound is also a semiconductor.

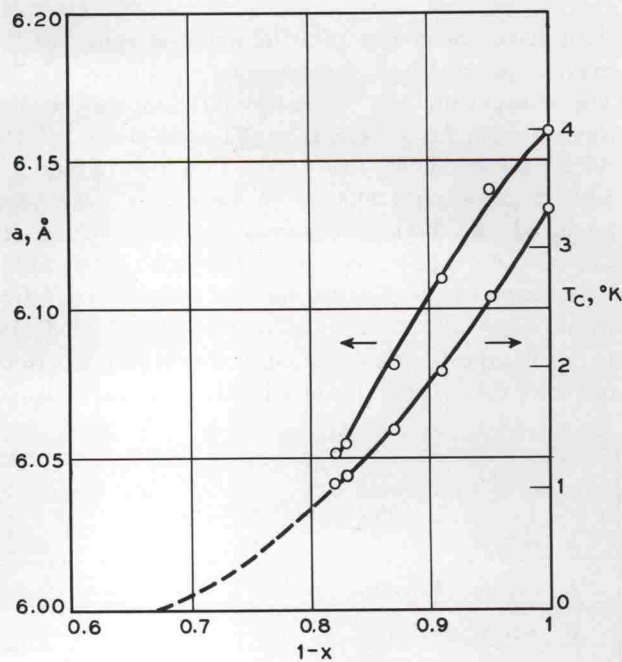


Fig. 1. Lattice constant a and superconducting transition temperature T_c vs $(1-x)$ for the system In_{1-x}Te .