

the composition $\text{InTe}_{0.94}$ would be identically zero. However, on further dissolution of In, the $\{111\}$ intensity should increase again and at $\text{InTe}_{0.87}$ (i.e. $\text{In}_{1.15}\text{Te}$) 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 $\text{In}_{1.15}\text{Te}$, 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 $\text{In}_{0.5}^{3+}\text{In}_{0.5}^{+}\text{Te}^{2-}$. 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 $y+3(1-x-y)=2.00$, 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 $\text{Sn}_{0.5}^{2+}\text{Sn}_{0.5}^{4+}\text{As}^{3-}$, has very nearly the same T_c as InTe with valence formula $\text{In}_{0.5}^{+}\text{In}_{0.5}^{3+}\text{Te}^{2-}$. 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

$$\text{In}(\text{Te}_{2/(2+x)}\text{In}_{x/(2+x)}).$$

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 .

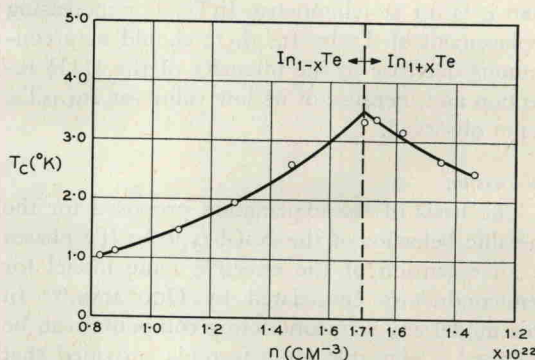


FIG. 2. Superconducting transition temperature, T_c , vs. carrier concentration, n .

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 (CuK α radiation) and Buerger precession camera (MoK α 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 $R\bar{3}m-D_{3d}^5$ and $R3m-C_{3v}^5$. The hexagonal axes as determined from the precession camera photographs are $a = 4.27 \pm 0.01$, $c = 40.9 \pm 0.1$ Å; the rhombohedral lattice constants derived from these are $a = 13.85$ Å, $\alpha = 17.73^\circ$.