

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  $\text{InTe}$ . 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.<sup>(6)</sup> 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  $\text{InTe}$  phase<sup>(7)</sup> stable at atmospheric pressure is isostructural with  $\text{TlSe}$ <sup>(8)</sup> and therefore has the ionic formula  $\text{In}_{0.5}^+\text{In}_{0.5}^{3+}\text{Te}$ . The  $\text{In}^+$  ions have 8- and the  $\text{In}^{3+}$ , 4-coordination by  $\text{Te}^{2-}$  ions. The structure therefore stabilizes the valencies, preventing free transfer of electrons from the  $\text{In}^+$  to  $\text{In}^{3+}$  ions. However, the structural constraint on electron transfer is removed when  $\text{InTe}$  transforms to the NaCl-type structure; in this structure all cations have 6-coordination by  $\text{Te}^{2-}$  ions. The ease with which the electron transfer can now occur leads to metallic conductivity. Now the semiconductor  $\text{AgSbTe}_2$  is isoelectronic with  $\text{InTe}$  and has<sup>(9)</sup> a disordered statistical NaCl-type structure at atmospheric pressure. In contrast with the  $\text{In}^+$  ion however, the second ionization potential of the  $\text{Ag}^+$  ion must be very large, thereby inhibiting electron transfer to  $\text{Sb}^{3+}$  ions.

The above ideas have led to successful prediction<sup>(2)</sup> 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  $\text{CdSe}$  and  $\text{CdTe}$ ,<sup>(10)</sup> 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  $\text{Sn}_{1-x}\text{Te}$ . 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.<sup>(10)</sup> Also we have recently reported<sup>(2)</sup> 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  $\text{In}^{3+}$  than  $\text{In}^+$  ions are present, on the In-rich side, more  $\text{In}^+$  than  $\text{In}^{3+}$  ions are present.

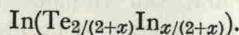
The ionic model also permits the calculation<sup>(2)</sup> of carrier concentrations. In  $\text{In}_{1-x}\text{Te}$ , there are  $y$  monovalent and  $(1-x-y)$  trivalent In ions per formula unit; then  $y+3(1-x-y)=2.00$ , the total valence which must be electrostatically balanced by In ions. Then  $y=(1-3x)/2$  and  $(1-x-y)=(1+x)/2$ , which except for  $x=0$  is always larger than the number of monovalent ions. Because each  $\text{In}^+$  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  $\text{cm}^3$ , where  $a$  is the lattice constant.

On the In-rich side there will be an excess of  $\text{In}^+$  ions; thus, the number of  $\text{In}^{3+}$  ions will determine the number of carriers because the latter cannot exceed twice the number of acceptor ions. A comparison of results on  $\text{SnAs}$  and  $\text{Sn}_4\text{As}_3$ <sup>(2)</sup> with those on  $\text{InTe}$  and  $\text{In}_3\text{Te}_4$  (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<sup>(11)</sup> 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  $\text{In}_3\text{Te}_4$  (see following section) has the anti- $\text{Sn}_4\text{As}_3$  structure<sup>(10)</sup> which is related to the NaCl-type structure. The ionic model applied to this phase indicates that  $2\frac{1}{2}$   $\text{In}^{3+}$  and  $\frac{1}{2}$   $\text{In}^+$  ions are required to balance the 4 Te valencies and there is one carrier per formula unit; for electrostatic balance,  $\text{Sn}_4\text{As}_3$  requires  $3\frac{1}{2}$   $\text{Sn}^{2+}$  and  $\frac{1}{2}$   $\text{Sn}^{4+}$  ions. The superconducting transition temperatures of  $\text{In}_3\text{Te}_4$  and  $\text{Sn}_4\text{As}_3$  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  $\text{Sn}_4\text{As}_3$  and  $\text{In}_3\text{Te}_4$  with very nearly the same  $T_c$ 's should have very nearly the same carrier concentrations. Thus, in  $\text{Sn}_4\text{As}_3$  the number of  $\text{Sn}^{4+}$  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



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  $n$ .

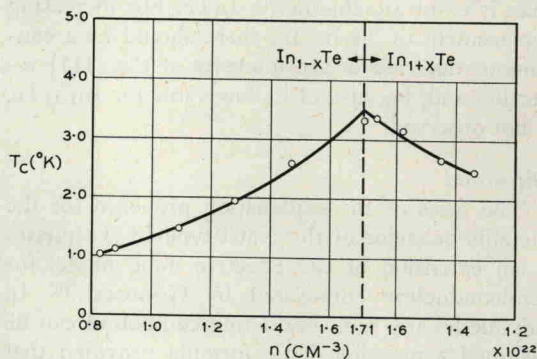


Fig. 2. Superconducting transition temperature,  $T_c$ , vs. carrier concentration,  $n$ .

We have shown<sup>(2)</sup> that, as predicted, substitution of  $\text{Ag}^+$  for  $\text{In}^+$  or  $\text{As}^{3-}$  for  $\text{Te}^{2-}$  resulted in a decrease of  $T_c$ . Both substitutions cause a decrease in  $n$ , the  $\text{Ag}^+$  for  $\text{In}^+$  because the  $\text{Ag } 4d$  electrons are tightly bound to it and  $\text{As}^{3-}$  for  $\text{Te}^{2-}$  by increasing the number of  $\text{In}^{3+}$  (thereby decreasing the number of  $\text{In}^+$  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  $\text{In}_{1-x}\text{Te}$  system. It may be speculated that this results from scattering by intervening  $\text{In}^{3+}$  ions which are 'inactive' because they are paired with  $\text{Ag}^+$  or  $\text{As}^{3-}$  ions. (See also Ref. 2.)

#### CRYSTAL STRUCTURE OF THE PRESSURE INDUCED $\text{In}_3\text{Te}_4$ PHASE

Weissenberg ( $\text{CuK}\alpha$  radiation) and Buerger precession camera ( $\text{MoK}\alpha$  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  $\text{In}_2\text{Te}_3$  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  $R\bar{3}m - C_{3v}^5$ . 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,  $\alpha = 17.73^\circ$ .