

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 $\text{In}_{0.5}^+\text{In}_{0.5}^{3+}\text{Te}$. 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 $y+3(1-x-y) = 2.00$, 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 .

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