

SUPERCONDUCTIVITY OF INTERMETALLIC COMPOUNDS  
WITH NaCl-TYPE AND RELATED STRUCTURES

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In this Letter, we show that the explanation<sup>1</sup> of the metallic behavior of the high-pressure NaCl-type  $\text{In}_{1-x}\text{Te}$  phases has enabled us to predict successfully that other intermetallic compounds with the NaCl-type and a related structure are superconductors. It is also shown that the superconducting transition temperature,  $T_C$ , is dependent on the carrier concentration,  $n$ , which is calculated on the basis that electrons from a lower valence cation are free to transfer to a higher valence cation. The ionic model of the intermetallic NaCl-type compounds also provides a basis for predicting or accounting for the existence of solid-solution ranges.

The calculated carrier concentrations of the compounds described herein are all low, lying between  $0.47 \times 10^{22}$  and  $2.14 \times 10^{22}/\text{cc}$ . Most of the values are substantially lower than, for example, that of sodium, for which, assuming one free electron per atom,  $n = 2.54 \times 10^{22}/\text{cc}$ . Yet  $T_C$ 's of 0.5-3.5°K are obtained for the compounds and none has yet been observed for sodium.<sup>2</sup> However, the theory recently given by Cohen<sup>3</sup> predicting superconductivity in semiconductors requires not only that the carrier concentration be maximized but that the band structure be favorable. (A high effective electronic mass, as in the case of strontium titanate,<sup>4</sup> is also favorable.) Cohen's theory has already, to an extent, been verified by Hein et al.<sup>5</sup> and by Schooley, Hosler, and Cohen.<sup>4</sup> While it is expected that all the compounds described herein would show metallic conductivity even in the room temperature region, it appears that because of their close structural relation to semiconductors, Cohen's theory might be extended to include them.

In the Letter<sup>1</sup> on the  $\text{In}_{1-x}\text{Te}$  phases, the explanation of the metallic behavior was based on an ionic model in which there was essentially no constraint on transfer of electrons from  $\text{In}^+$  to  $\text{In}^{3+}$  ions. It was shown that  $T_C$  depended on the ratio of monovalent to trivalent ions. This was essentially an indication that  $T_C$  depended on the carrier concentration. In  $\text{In}_{1-x}\text{Te}$ , the number of  $\text{In}^+$  ions per formula unit is  $(1-3x)/2$ ; the number of carriers is then  $(1-3x)$  and because there are four  $\text{In}_{1-x}\text{Te}$  per unit cell,  $n = 4(1-3x)/a^3 \times 10^{-24}$

cc, where  $a$  is the lattice constant in Å. The largest  $n$ ,  $1.71 \times 10^{22}/\text{cc}$ , is obtained when  $x=0$ . When  $x = \frac{1}{3}$ , that is for a hypothetical  $\text{In}_2\text{Te}_3$ , in which all In ions are trivalent,  $n=0$ . A plot of  $T_C$  vs  $n$  for the  $\text{In}_{1-x}\text{Te}$  system is given in Fig. 1; in the region  $0.8 \times 10^{22} \leq n \leq 1.7 \times 10^{22}/\text{cc}$ ,  $T_C$  varies exponentially with  $n$ .

It is also possible to reduce  $n$  by substituting  $\text{Ag}^+$  for  $\text{In}^+$  ions (see reference 1) as in  $(\text{In}_{1-x}\text{Ag}_x)\text{Te}$ , or  $\text{As}^{3-}$  for  $\text{Te}^{2-}$  ions as in  $\text{In}(\text{Te}_{1-x}\text{As}_x)$ . High pressures were required to obtain such specimens. Values of  $a$ ,  $n$ , and  $T_C$  for these specimens are given in Table I. On the basis of carrier concentration alone, higher values of  $T_C$  than observed would have been expected for these specimens. There are at least two ways of accounting for this: (1) In accord with Cohen's theory,<sup>3</sup> changes in band structure caused by changes in ion types might affect  $T_C$ ; (2) reduction of  $T_C$  may be caused by scattering from  $\text{In}^{3+}$  ions which are "inactive" because they are paired with  $\text{Ag}^+$  or  $\text{As}^{3-}$  ions by saturated ionic-covalent bonds.<sup>6,7</sup> In any case, it is clear, and in accord with Cohen's theory, that a decrease in  $n$  in a given system of the type under discussion always results in a decrease of  $T_C$ .

The intermetallic compounds with NaCl-type and related structures will be metallic and apparently superconductors, provided there are pres-

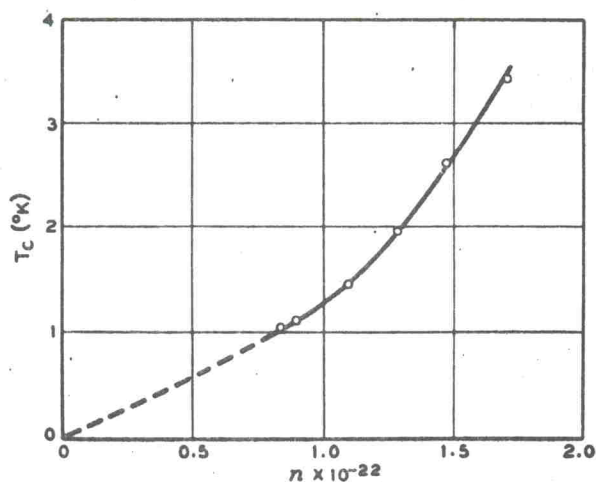


FIG. 1. Superconducting transition temperature vs carrier concentration,  $n$ , for the  $\text{In}_{1-x}\text{Te}$  system.

Table I. Data on NaCl-type phases.

Formula	$a$ (Å)	Volume		$T_c$ (°K)
		(Å <sup>3</sup> )	$n \times 10^{-22}$	
InTe	6.18 ± 0.01	234	1.71	3.45-3.20
(Ag <sub>0.1</sub> In <sub>0.9</sub> )Te	6.12	229	1.40	1.89-1.20
(Ag <sub>0.2</sub> In <sub>0.8</sub> )Te	6.08	225	1.07	1.00-0.77
In(Te <sub>0.67</sub> As <sub>0.33</sub> )	5.98	214	1.24	1.15-0.85
In(Te <sub>0.5</sub> As <sub>0.5</sub> )	5.91	206	0.97	0.62-0.44
SnAs	5.72	187	2.14	3.65-3.41
SnSb	See text			

ent in them cations in two valence states, the lower of which is less stable than the higher. The ions of different valence must each be present in sufficient number to give adequate carrier concentration. Some examples are the In<sub>1-x</sub>Te system (Fig. 1) and those discussed above. Another example is SnAs which has a thermodynamically stable NaCl-type structure at atmospheric pressure; its valence formula is Sn<sub>0.5</sub><sup>2+</sup>Sn<sub>0.5</sub><sup>4+</sup>As<sub>1</sub><sup>3-</sup>; SnAs has a  $T_c$  of 3.65-3.41°K (see also Table I).

Another compound which we predicted should be a superconductor is SnSb with valence formula Sn<sub>0.5</sub><sup>2+</sup>Sn<sub>0.5</sub><sup>4+</sup>Sb<sub>1</sub><sup>3-</sup>. SnSb is reported<sup>8</sup> to have a rhombohedrally distorted NaCl-type structure at atmospheric pressure. Our specimen was prepared by melting appropriate proportions of Sn and Sb in an evacuated, sealed, fused-silica tube, mixing thoroughly in the molten condition, and then annealing for 184 hours at 250°C. The test<sup>9</sup> for superconductivity, as usual on the powdered specimen, showed that 88% of the specimen was superconducting in the range 1.42-1.30°K, the remainder in the range 2.37-1.42°K. The powder photograph, however, though having broad back-reflection lines, showed no phase other than that of NaCl or distorted NaCl-type structure. Thus, although we do not as yet understand the origin of

the two (or more) transitions, there is no doubt that an NaCl-like SnSb is a superconductor.

In the high-pressure-high-temperature study of the In-Te system,<sup>6</sup> a phase with stoichiometric formula In<sub>3</sub>Te<sub>4</sub> was discovered. This phase has an anti-Sn<sub>4</sub>As<sub>3</sub> structure<sup>8</sup> which is related to the NaCl-type structure. Both In<sub>3</sub>Te<sub>4</sub> and Sn<sub>4</sub>As<sub>3</sub><sup>10</sup> are superconductors with nearly the same  $T_c$ 's and carrier concentrations<sup>11</sup> (Table II).

The occurrence of superconductivity in the Ge<sub>1-x</sub>Te system, thermodynamically stable at atmospheric pressure, has recently been reported.<sup>5</sup> We have induced new high-pressure phases in the Ge-Te system which can be metastably retained at atmospheric pressure. The system is a complex one, containing at least three superconductors in the composition range between GeTe and Ge<sub>2</sub>Te<sub>3</sub>, but no single phase has as yet been isolated. Although "single" transitions have been found for "Ge<sub>3</sub>Te<sub>4</sub>" and "Ge<sub>2</sub>Te<sub>3</sub>" at 1.80-1.55 and 1.83-1.56°K, respectively, x-ray diffraction investigation and tests for superconductivity of several specimens including some with higher Ge content indicate that the "Ge<sub>3</sub>Te<sub>4</sub>" and "Ge<sub>2</sub>Te<sub>3</sub>" specimens each contain at least two superconducting phases. The predominant phase occurring in both has the anti-Sn<sub>4</sub>As<sub>3</sub> structure (see Table II). There is evidence that the In<sub>3</sub>Te<sub>4</sub> phase has a solid solution range<sup>6</sup> and there is some evidence that the Ge<sub>3</sub>Te<sub>4</sub> phase does also. For example, a specimen "Ge<sub>0.85</sub>Te" eventually became 80% superconducting above 0.3°K: 16% at 1.44-1.31°K and 64% at 1.21-0.87°K. The specimen appeared to contain predominantly the Ge<sub>3</sub>Te<sub>4</sub> phase and the lower transition temperature implies a higher Ge content.

It is not surprising that the more nearly stoichiometric Ge<sub>3</sub>Te<sub>4</sub> phase has a higher  $T_c$  than that of Sn<sub>4</sub>As<sub>3</sub> or of In<sub>3</sub>Te<sub>4</sub>. Stoichiometric Ge<sub>3</sub>Te<sub>4</sub> has two carriers per formula unit as opposed to one

Table II. Data on Sn<sub>4</sub>As<sub>3</sub> and anti-Sn<sub>4</sub>As<sub>3</sub>-type phases.

Formula	$a_{rh}$ (Å)	$\alpha_{rh}$ (deg)	$a_{hex}$ (Å)	$c_{hex}$ (Å)	Volume <sup>a</sup>		$T_c$ (°K)
					(Å <sup>3</sup> )	$n \times 10^{-22}$	
Sn <sub>4</sub> As <sub>3</sub>	12.23	19.23	4.09	36.01	174	0.56	1.19-1.16
In <sub>3</sub> Te <sub>4</sub> <sup>b</sup>	13.75	17.80	4.26	40.58	212	0.47	1.25-1.15
Ge <sub>3</sub> Te <sub>4</sub> <sup>b,c</sup>	13.11	17.93	4.11	38.68	189	1.06	1.80-1.55

<sup>a</sup>Of rhombohedral cell containing one formula unit.

<sup>b</sup>These are metastably retained high-pressure phases.

<sup>c</sup>The data are not for a stoichiometric compound (see text).