

SUPERCONDUCTIVITY OF INTERMETALLIC COMPOUNDS
WITH NaCl-TYPE AND RELATED STRUCTURES

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In this Letter, we show that the explanation¹ of the metallic behavior of the high-pressure NaCl-type In_{1-x}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 0.47×10^{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.² However, the theory recently given by Cohen³ 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,⁴ is also favorable.) Cohen's theory has already, to an extent, been verified by Hein *et al.*⁵ and by Schooley, Hosler, and Cohen.⁴ 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 Letter¹ on the In_{1-x}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 In^+ to 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 In_{1-x}Te , the number of In^+ ions per formula unit is $(1-3x)/2$; the number of carriers is then $(1-3x)$ and because there are four In_{1-x}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 In_2Te_3 , in which all In ions are trivalent, $n = 0$. A plot of T_c vs n for the In_{1-x}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 Ag^+ for In^+ ions (see reference 1) as in $(\text{In}_{1-x}\text{Ag}_x)\text{Te}$, or As^{3-} for 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,³ 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 In^{3+} ions which are "inactive" because they are paired with Ag^+ or As^{3-} ions by saturated ionic-covalent bonds.^{6,7} 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-

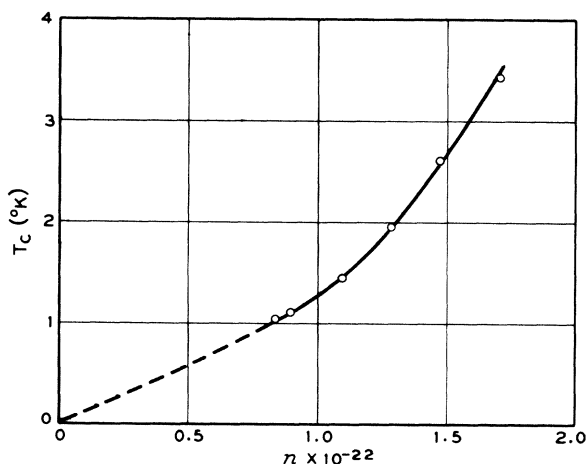


FIG. 1. Superconducting transition temperature vs carrier concentration, n , for the In_{1-x}Te system.

Table I. Data on NaCl-type phases.

Formula	a (Å)	Volume		T_c (°K)
		(Å ³)	$n \times 10^{-22}$	
InTe	6.18 ± 0.01	234	1.71	3.45-3.20
(Ag _{0.1} In _{0.9})Te	6.12	229	1.40	1.89-1.20
(Ag _{0.2} In _{0.8})Te	6.08	225	1.07	1.00-0.77
In(Te _{0.67} As _{0.33})	5.98	214	1.24	1.15-0.85
In(Te _{0.5} As _{0.5})	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_{1-x}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_{0.5}²⁺Sn_{0.5}⁴⁺As³⁻; 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_{0.5}²⁺Sn_{0.5}⁴⁺Sb³⁻. SnSb is reported⁸ 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 test⁹ 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,⁶ a phase with stoichiometric formula In₃Te₄ was discovered. This phase has an anti-Sn₄As₃ structure⁸ which is related to the NaCl-type structure. Both In₃Te₄ and Sn₄As₃¹⁰ are superconductors with nearly the same T_c 's and carrier concentrations¹¹ (Table II).

The occurrence of superconductivity in the Ge_{1-x}Te system, thermodynamically stable at atmospheric pressure, has recently been reported.⁵ 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 Ge₂Te₃, but no single phase has as yet been isolated. Although "single" transitions have been found for "Ge₃Te₄" and "Ge₂Te₃" 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 "Ge₃Te₄" and "Ge₂Te₃" specimens each contain at least two superconducting phases. The predominant phase occurring in both has the anti-Sn₄As₃ structure (see Table II). There is evidence that the In₃Te₄ phase has a solid solution range⁶ and there is some evidence that the Ge₃Te₄ phase does also. For example, a specimen "Ge_{0.85}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 Ge₃Te₄ phase and the lower transition temperature implies a higher Ge content.

It is not surprising that the more nearly stoichiometric Ge₃Te₄ phase has a higher T_c than that of Sn₄As₃ or of In₃Te₄. Stoichiometric Ge₃Te₄ has two carriers per formula unit as opposed to one

Table II. Data on Sn₄As₃ and anti-Sn₄As₃-type phases.

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

^aOf rhombohedral cell containing one formula unit.

^bThese are metastably retained high-pressure phases.

^cThe data are not for a stoichiometric compound (see text).

each for the other two compounds.

The ionic model proposed for the NaCl-type intermetallic compounds allows one to predict when solid solutions will exist and in which of the elements they will be rich. In the Sn-Te system, NaCl-type compounds rich in Te should be expected because in Sn_{1-x}Te the valency of Te may be balanced by both Sn^{2+} and Sn^{4+} ions. It is unlikely, however, that NaCl-type Sn-Te compounds rich in Sn will exist. Similarly compounds of PbS, PbSe, and PbTe rich in the Group-VI element should be attainable, but not those rich in Pb. The high-pressure NaCl-type CdSe and CdTe phases¹² should not have solid solution ranges because of the single stable valences of the atoms involved. In the Sn-Sb system, solid solutions rich in either constituent should occur as has been reported.⁸ Similarly, in the Sn-As system solid solutions rich in either constituent are to be expected. Although Hägg and Hybinette⁸ did not observe this at atmospheric pressure, we have found that compounds Sn_{1+x}As and Sn_{1-x}As can be made at high pressures and retained metastably at atmospheric pressure. However, they begin to revert to the $\text{Sn}_4\text{As}_3 + \text{SnAs}$ and $\text{SnAs} + \text{As}$ phases, respectively, within a few hours after release of pressure. A test for superconductivity on what was later realized to be a partially reverted specimen indicated that again in this system a decrease in n results in decrease in T_c .

The NaCl-type phases in the In-Te system must therefore also have In-rich phases.⁶ Despite our earlier conclusion¹ to the contrary, such phases, to about $\text{In}_{1.15}\text{Te}$, do exist; they cannot be retained metastably very long, but⁶ again for these, T_c decreases with decreasing n .

Finally, it is worth emphasizing that the NaCl-type structure has now been shown to be favorable to both semiconductivity and superconductivity. If

the carrier concentration is high enough, the compound will be a superconductor. This should be true also for the compounds with the Sn_4As_3 structure and for another related structure, the Bi_2Te_3 structure. If it were possible to obtain, for example, a Ge_2Te_3 with the Bi_2Te_3 structure, it would be a superconductor and have a higher transition temperature than that of Ge_3Te_4 .

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¹⁰Hägg and Hybinette (reference 8) reported that the compound Sn_3As_2 was actually the one that existed but had the Sn_4As_3 structure. We have found that " Sn_3As_2 " has two T_c 's, $\sim \frac{1}{3}$ of the specimen at 3.6-3.5°K, $\sim \frac{2}{3}$ at 1.21-1.17°K. The powder photograph indicates that free Sn is present and the T_c 's confirm the presence of Sn and Sn_4As_3 in the right proportions.

¹¹For a discussion of the calculation of these n 's, see reference 6.

¹²C. J. M. Rooymans, *Phys. Letters* **4**, 186 (1963); A. N. Mariano and E. P. Warekois, *Science* **142**, 672 (1963).