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Artificial Metals: InSb, the Sn Alloys with InSb, and Metallic InTe†

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The metallic forms of indium antimonide, indium telluride, and the metallic alloys InSbSn, InSbSn₂, and InSbSn₄, were prepared at high temperature and high pressure, cooled, and subsequently quenched to -197°C before release of the pressure to one atmosphere. The metastable metallic forms can be retained at one atmosphere pressure at low temperatures indefinitely and studied conveniently. InSb(II) and its metastable alloys with tin have lattice parameters essentially identical with those of metallic tin. The lattice parameter of the cubic form of indium telluride is $6.177 \pm 0.002 \text{ \AA}$ at 25°C . The compressibilities of InSb(II), InSb(I) and of Sn(β) at -197°C are 0.9, 3.6, and $3.1 \times 10^{-6} \text{ bar}^{-1}$, respectively. The compressibilities of InTe(I) and InTe(II) at 25°C are 6.3 and $3.8 \times 10^{-6} \text{ bar}^{-1}$, respectively. The heat of transformation ΔH_{210}° (1 atm) InSb(II) \rightarrow InSb(I) is $-4.77 \pm 0.04 \text{ kcal per mole}$. The resistivity of InSb(II) at 77°K is $77 \times 10^{-6} \Omega\text{-cm}$. The velocity of sound in polycrystalline InSb(II) is approximately 3900 m/sec. The Brinell hardness numbers of InSb(II) and Sn(β) at 77°K are 230 and 46 kg mm^{-2} . InTe(II) is diamagnetic, its susceptibility is -0.14 emu g^{-1} .

I. INTRODUCTION

IT has been demonstrated experimentally¹⁻⁷ by Kennedy and his co-workers, by Drickamer and his co-workers, and by others that diamond-type lattices, when subjected to pressure, suffer a transformation into a denser, more highly coordinated state, which is metallic. The general nature of the phase diagram is that the melting point of the nonmetallic state falls as the pressure is increased until a triple point is reached and the solid-solid transition corresponding to a change from a nonmetallic to a metallic state occurs

after which the melting point rises again with an increase in pressure. It is thought that this general phase diagram applies for all the members of group IV; carbon, silicon, germanium, etc., and to the binary compounds one column removed from group IV in the periodic table such as boron nitride, aluminum phosphide, gallium arsenide, indium antimonide, etc., and even those two removed from group IV (though less work has been done on them) such as zinc selenide, which averages four valence electrons per atom.

It is our purpose here to describe a technique of removing these new materials from the high-pressure apparatus in which they were produced in order that their properties can be studied more completely. The difficulties and limitations of having to work within a high pressure chamber are very great.

II. THE TECHNIQUE

It is very well known in chemistry that a transition from one solid phase to another or from a liquid to a solid or, in some instances, in the opposite direction can be slow and dependent upon nuclei. The transformation of metallic tin to the semiconducting, diamond-type structure at low temperatures well illustrates this.

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¹ A. Jayaraman, R. C. Newton, and G. C. Kennedy, *Nature* **191**, 1288 (1961).

² A. Jayaraman, W. Klement, Jr., and G. C. Kennedy, *Phys. Rev.* **130**, 540 (1963).

³ B. J. Alder and R. H. Christian, *Phys. Rev. Letters* **8**, 367 (1961).

⁴ H. L. Suchan and H. G. Drickamer, *J. Chem. Phys.* **31**, 355 (1959).

⁵ S. Minomura and H. G. Drickamer, *Phys. Chem. Solids* **23**, 451 (1962).

⁶ G. A. Samara and H. G. Drickamer, *Phys. Chem. Solids* **23**, 457 (1962).

⁷ G. A. Samara and H. G. Drickamer, *J. Chem. Phys.* **37**, 408 (1962).

White tin can be kept at temperatures below the temperature at which gray is the stable form (13°C),⁸ if it is free of nucleation centers. White tin, even in the presence of nucleation centers can be kept in the metastable state for long periods of time if the temperature is kept sufficiently low (-196°C).

The technique then is to carry out the transformation from the nonmetallic to the metallic phase, to cook the metallic phase by prolonged heating and compression to rid it of nonmetallic nuclei, then to cool the entire apparatus with liquid nitrogen down to -196°C at which point the pressure is reduced to 1 atm and the sample removed from the apparatus under liquid nitrogen. In those cases in which it is possible to attain sufficiently high pressures and temperatures to obtain the metallic phase directly from the melt, the cooking step is unnecessary and there is little problem in obtaining a solid free of nuclei of the original phase.

The solid-solid transformation, however, can be carried out directly in those cases where it is impossible to melt or very difficult to melt under high pressure by the cooking technique using pressures in excess of equilibrium pressure for many hours to affect a complete conversion of the sample. It appears to be helpful to change the pressure and temperature in a somewhat random and arbitrary manner to effect a kind of cruising in the metallic field of the phase diagram.

The metastable materials obtained so far have been found to differ widely in the temperatures to which they can be warmed before they transform back to the normal low-pressure phase. The technique has been applied previously to ice.⁹

III. THE THEORY OF METALLIC DIAMOND

The eight electrons available for bonding in the low-pressure tetrahedral structures just fill the four available orbitals and at the same time establish equivalent bonds to all near neighbors.¹⁰ It is our theory that the forced transformation to a more densely packed structure with more than four neighbors without any increase in the number of bonding electrons or available orbitals causes the system to become metallic.

We suggest that it is not necessary to have vacant orbitals for the metallic state¹¹ but that metallic conduction can result purely from the resonance condition that must exist in a structure which has more truly geometrically equivalent near neighbors than there are possible bonds. Of course, at very high compressions all matter will become metallic¹²⁻¹⁴ since all electron levels

are raised by compression and the ionization potential thus must fall to zero eventually, but before this occurs the new class of resonating metals will occur because the degree of compression necessary to the raising of the coordination number above the bond number probably is less than that for enforced ionization.

The theory can be illustrated in many ways, but the central point is that the condition of geometrical equivalence means that the Franck-Condon principle offers no barrier to electronic resonance with the consequence that resonance occurs throughout the region of geometrical equivalence which may be crystal wide.

Every resonating system can be thought of either in terms of band theory or in terms of alternative dispositions of bonds which are equally likely. In the band theory, for our case of four orbitals and four valence electrons, one sees immediately that the $4N$ electrons of the N equivalent atoms in the macroscopic crystal will lie in the bottom half of the $4N$ levels made by combining the $4N$ orbitals in resonance; and the whole question then becomes one as to whether the splitting of the $4N$ levels is such as to create a gap between the bottom and top sets of $2N$ levels and thus to prevent ready promotion to the conducting levels above the top Fermi level in the ground state. In graphite, which is the two-dimensional case for our system, there are one orbital and one valence electron per atom with three equivalent neighbors. For graphite, it is clear both theoretically¹⁵ and experimentally¹⁶ that the two-dimensional metallic state exists. Thus, we see that for this system, at least, *bond resonance without vacant orbitals can produce the metallic state*. It is our theory that the new metals produced here are the three-dimensional analogs of the two-dimensional metal graphite and that tin itself is such a case (we call these metallic diamonds as a class name). There are four orbitals and four valence electrons with four neighbors in the tetrahedral lattices of diamond, wurzite, and sphalerite which on compression transform, according to Jamieson,¹⁷ into the six-neighbor structure of metallic tin. Thus four bonds have to satisfy six atoms (the central atom contributes 4 valence electrons and each of the surrounding 6 atoms contributes $4/6$ more for a total of 8, just adequate for four full bonds). The resonance state is possible because the Franck-Condon principle has been satisfied by the location of the atoms in equivalent positions, and, as a consequence, the full crystal is set into three-dimensional resonance such that the entire crystal becomes one molecule at least at the absolute zero of temperature. At finite temperatures the principle of strict symmetrical equivalence for neighbors will be violated by the lattice vibrations, and the resonance possibilities will be reduced because of the Franck-Condon principle; or in

⁸ E. Cohen and A. K. W. A. van Lieshout, *Ann. Physik Chem.* **177**, 331 (1936).

⁹ R. L. McFarlan, *J. Chem. Phys.* **4**, 60, 253 (1936).

¹⁰ W. F. Libby, *Phys. Rev.* **130**, 548 (1963).

¹¹ L. C. Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals* (Cornell University Press, Ithaca, New York, 1960), 3rd ed.

¹² E. Wigner and H. B. Huntington, *J. Chem. Phys.* **3**, 764 (1935).

¹³ C. A. ten Seldam, *Proc. Phys. Soc. (London)* **A70**, 97, 529 (1957).

¹⁴ R. E. Behringer, *Phys. Rev.* **113**, 787 (1959).

¹⁵ P. R. Wallace, *Phys. Rev.* **71**, 622 (1947).

¹⁶ A. R. Ubbelohde and F. A. Lewis, *Graphite and its Crystal Compounds* (Clarendon Press, Oxford, England, 1960).

¹⁷ J. C. Jamieson, *Abstracts for 1962* (Geological Society of America, New York, 1963), Special Paper 73, p. 178.

band theory language the scattering of conducting electrons will result.

The conduction act itself can be most clearly envisaged as the removal of an electron from the resonating molecule at one edge of the crystal at the cost of the ionization potential, the distribution of the resultant positive charge uniformly over the entire molecule because of the three-dimensional resonance, followed by the neutralization by acquisition of an electron at the opposite side of the crystal with the regaining of the energy corresponding to the ionization potential. In the presence of an electric field the positive charge obviously will not be completely uniformly distributed at any finite temperature because the relaxation time for the molecular lattice will necessarily be the time for the transport act itself, and this limitation in rate will cause a charge gradient to exist across the molecule. At the absolute zero of temperature this electrical resistance would appear to be zero.

Drickamer⁴⁻⁷ and his co-workers have shown that, like true metals, the new compressed phases absorb light down to the lowest frequencies. This can be envisaged as being due to the close-lying states in the crystal (molecule) corresponding to charge displacement from one end of the crystal to the other.

IV. METALLIC InSb

Many of the properties of the normal semiconducting form of indium antimonide are similar to those of gray tin. The lattice constant of the zincblende type of¹⁸ InSb is almost identical with that of gray tin.¹⁹ Gebbie *et al.*²⁰ found that the room-temperature resistivity of InSb drops several orders of magnitude at 30 000-atm pressure. Kennedy *et al.*,^{1,2} Ponyatovskii *et al.*,²¹ and Banus *et al.*²² give pressure-temperature phase diagrams which show a solid-solid transition in InSb at high pressure. Kennedy *et al.*^{1,2} suggested that this solid (I)-solid (II) transition is analogous to the gray-white transition in tin. Smith *et al.*,²³ Jamieson,¹⁷ and Banus *et al.*²² have examined the crystal structure of the high-pressure form of indium antimonide and found it to be analogous in structure to white or metallic tin.

Darnell and Libby,²⁴ Geller *et al.*,²⁵ and Stromberg

¹⁸ H. E. Swanson, R. K. Fuyat, and G. M. Ugrinic, *Standard X-Ray Diffraction Powder Patterns* (National Bureau of Standards, Washington, 1955), Circ. 539, Vol. IV.

¹⁹ H. E. Swanson and R. K. Fuyat, *Standard X-Ray Diffraction Powder Patterns* (National Bureau of Standards, Washington, 1953), Circ. 539, Vol. II.

²⁰ H. A. Gebbie, P. L. Smith, I. G. Austin, and J. H. King, *Nature* 188, 1096 (1960).

²¹ E. G. Ponyatovskii and G. I. Peresada, *Dokl. Akad. Nauk SSSR* 144, 129 (1962) [English transl.: *Soviet Phys.—Doklady* 144, 408 (1962)].

²² M. D. Banus, R. E. Hanneman, A. N. Marino, E. P. Warekois, H. C. Gatos, and J. A. Kafalas, *Appl. Phys. Letters* 2, 35 (1963).

²³ P. L. Smith and J. E. Martin, *Nature* 196, 762 (1962).

²⁴ A. J. Darnell and W. F. Libby, *Science* 139, 1301 (1963).

²⁵ S. Geller, D. B. McWhan and G. W. Hull, Jr., *Science* 140, 62 (1963).

*et al.*²⁶ have obtained the metallic form of indium antimonide at atmospheric pressure by temperature quench of the high-pressure form. Metallic indium antimonide, like tin, readily solidifies into large crystals. Single crystals of InSb(II) from 1–2 mm were obtained when molten indium antimonide was cooled slowly at 25-kbar pressure.

A. Crystal Structure and Spacing

Metallic indium antimonide at atmospheric pressure has lattice spacings and lattice parameters which are essentially identical²⁴ to those of metallic tin²⁷ (Table I). The "average" value of the valence of In and of Sb is equivalent to that of Sn. At present it has not been proven experimentally that the In and Sb atoms occur in the regular alternating order necessary to our understanding of the metallic state.

B. Compressibility

The compression $\Delta V/V_0$ for InSb(II), InSb(I), and Sn(β) were measured in a piston-cylinder apparatus at -196°C . The averages of the compression and decompression measurements are given in Fig. 1. The compressibility $(1/V)(dV/dP)_T$ obtained from the initial slopes in Fig. 1 are 0.9, 3.6, and 3.1×10^{-6} bar⁻¹ for InSb(II), InSb(I), and Sn(β), respectively. Thus, the compressibility of InSb(II) is only approximately $\frac{1}{3}$ of that of metallic tin. This, as we shall see, later appears to accompany an increase in hardness as well.

C. Density

The density of InSb(I) is 5.79 g/cm³ from its lattice parameter¹⁸ at 298°K. The density of InSb(II) calculated from its lattice parameters at 77°K (Table I) is 7.28 g/cm³. The directly measured density of InSb(II) is 7.13 ± 0.06 g/cm³.

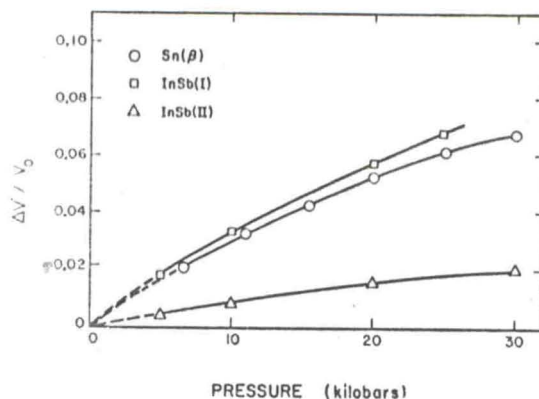


Fig. 1. Compression of InSb(I), InSb(II), and Sn(β) at -197°C .

²⁶ T. F. Stromberg and C. A. Swenson, *Phys. Rev.* 134, A21 (1964).

²⁷ H. E. Swanson and E. Tatge, *Standard X-Ray Diffraction Powder Patterns* (National Bureau of Standards, Washington, 1953), Circ. 539, Vol. I.

TABLE I. Lattice spacings and lattice parameters for Sn(β), InSb(II), and for metallic alloys InSbSn₁, InSbSn₂, and InSbSn₄.

<i>hkl</i>	Sn(β)	InSbSn ₁	InSbSn ₂	InSbSn	InSb(II)	Sn(β)
	25°C	25°C	25°C	-197°C	-197°C	-197°C
	<i>d</i> (Å)	<i>d</i> (Å)	<i>d</i> (Å)	<i>d</i> (Å)	<i>d</i> (Å)	<i>d</i> (Å)
200	2.912	2.918	2.921	2.897	2.910	2.907
101	2.789	2.793	2.794	2.776	2.788	2.778
220	2.062	2.062	2.064	2.057	2.062	2.055
211	2.015	2.015	2.017	2.012	2.030	2.007
301	1.658	1.658	1.660	1.654	1.654	1.651
112	1.483	1.484	1.487	1.476	1.474	1.474
400	1.458	1.458	1.457		1.452	1.453
321	1.442	1.442	1.440	1.438		1.436
420	1.304	1.304	1.303	1.301		1.300
411	1.292	1.294	1.294	1.290		1.287
312	1.205	1.205	1.206	1.201		1.198
501	1.0950	1.096	1.096			1.091
103	1.0437					1.037
332	1.0405	1.041				1.035
440	1.039	1.032				1.028
521	1.0251	1.025				1.022
<i>a</i> ₀	5.8309	5.8356	5.8337	5.8219	5.833	5.8181
(Å)	±0.0006	±0.0007	±0.0027	±0.0024	±0.019	±0.0007
<i>c</i> ₀	3.1824	3.1810	3.1873	3.1665	3.170	3.1634
(Å)	±0.0005	±0.0013	±0.0029	±0.0022	±0.014	±0.0007
<i>c</i> ₀ / <i>a</i> ₀	0.54578	0.54510	0.54636	0.54389	0.5435	0.54372

D. Formation of Metallic InSb from InSb(I)

Neglecting small differences in density due to the temperature coefficient of expansion, then the decrease in volume for the hypothetical transition InSb(I) → InSb(II) at 1-atm pressure is 20.5%. This volume decrease is somewhat greater than would be obtained at a pressure of 25 kbar because of the larger compression of InSb(I). Taking this difference in compression of InSb(I) and InSb(II) into account, then the decrease in volume for this transition is 16.2% at 25-kbar pressure.

The transformation of metastable InSb(II) back to InSb(I) is apparently very slow at 77°K. No volume change could be detected in an InSb(II) sample kept for one year at 77°K. Dilatometric measurements indicated that the transformation was approximately 50% complete in three months at 195°K. When warmed to 210 ± 2°K metallic indium antimonide transforms rapidly, explosively, back to the semiconducting form, forming a fine powder which frequently is hot enough to start small fires.

The heat of this transformation was measured at 1-atm pressure with a "drop" calorimeter. InSb(II) samples, initially at 195°K were dropped into a calorimeter maintained at a temperature of 297°K. The net amount of heat evolved from the over-all process was determined from the temperature rise of the calorimeter. The indium antimonide samples were weighed before and after the transformation to ascertain that no appreciable oxidation had occurred during the measurement.

The heat necessary to raise the indium antimonide

sample from 195 to 298°K was measured by dropping a weighed sample of InSb(I) into the calorimeter. The change in enthalpy, $H_{195} - H_{298}$, for InSb(I) is in good agreement with the heat capacity data reported by Piesbergen.²⁸ Assuming that the difference in the integrated heat capacity of InSb(I) and InSb(II) is small over the temperature 195 to 210°K, then the heat of transformation:

ΔH_{210}° (1 atm), InSb(II) → InSb(I) = -4.77 ± 0.04 kcal per mole. The corresponding heat of transformation from metallic to semiconducting state is -1.07 kcal per 2-g atoms of tin.²⁹ The PV work of the transition at the transition pressure of 23 000 bar is -3.1 kcal/mole. If the work of compression is included, the total becomes -4.0 kcal/mole in substantial agreement in view of the experimental uncertainties.

E. Electrical Resistance

The electrical resistivity of metallic InSb was measured by the four-probe method at 4.2, 77, and 195°K. The specific resistances are, respectively, 53.0×10^{-6} , 77.0×10^{-6} , and 172×10^{-6} Ω-cm. The specific resistance of InSb(II) is considerably higher than for³⁰ Sn(β) 2.26×10^{-6} Ω-cm at 77°K. The resistance ratio R_{77}/R_{195} for InSb(II) and³⁰ Sn(β) are 0.30 and 0.44, respectively. However, InSb(II) transforms at a slow, but measurable, rate at 195°K. Thus resistance at this temperature had to be obtained by extrapolation to zero time; i.e.,

²⁸ V. Piesbergen, Z. Naturforsch. 18a, 141 (1963).

²⁹ S. L. Jovanovic, Bull. Soc. Chim. Belgrade 12, 51 (1947).

³⁰ K. H. Onnes and W. Tuyn, Proc. Roy. Soc. Amsterdam 25, 443 (1923).

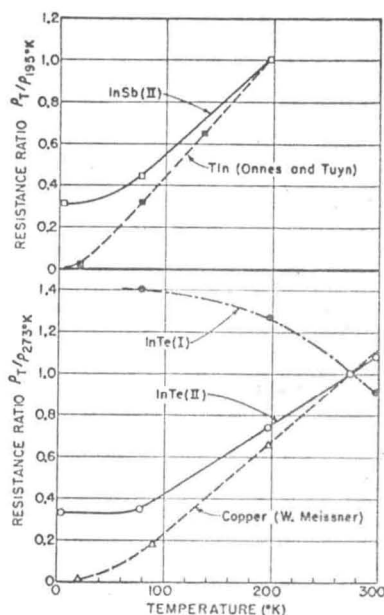


FIG. 2. Resistivity of InSb(II), InTe(I), and InTe(II) as a function of temperature.

the time which the sample was brought to this temperature. No change in resistance with time was detected at 77°K in an interval of two weeks. The resistivities of InSb(II) at 4.2 and 77°K were obtained on samples which were never above 77°K after their preparation at 25-kbar pressure. The resistivity ratio data are given in Fig. 2.

The higher electrical resistivity of InSb(II) in comparison with Sn(β) might be expected by analogy with alloys, notably silver and gold which form substitutional-type solid solutions from atoms of slightly different radii. The electrical resistivities of the intermediate solid solutions of silver and gold are higher than for the pure metals.³¹ This increased resistivity is attributed to imperfection in the periodicity of the lattice of the solid solution.³² The lattice parameters of InSb(II) are essentially identical with those of Sn(β). However, the atomic radii of In and Sb are probably slightly different from Sn. These differences in atomic radii of In and Sb would upset the periodicity in the InSb(II) structure and thus could account for the higher electrical resistivity of InSb(II) in comparison to Sn(β).

F. Velocity of Sound

The velocity of sound in polycrystalline InSb(II) is 3850 m/sec as compared to 3320 m/sec for polycrystalline metallic tin.³³

The smaller compressibility and higher velocity of sound would suggest that InSb(II) has a higher Debye

³¹ W. Broniewski and K. Wesolowski, *Compt. Rend.* 194, 2047 (1932).

³² W. Hume-Rothery, *Atomic Theory for Students of Metallurgy* (The Institute of Metals, London, 1960).

³³ *American Institute of Physics Handbook*, edited by D. E. Gray (McGraw-Hill Book Company, Inc., New York, 1963).

temperature than does Sn(β) in keeping with the greater hardness reported later.

V. METALLIC ALLOYS OF TIN AND INDIUM ANTIMONIDE

The similarities in structure of the semiconducting forms and of the metallic forms of indium antimonide and tin suggest that these two substances should be completely soluble in all proportions under conditions where both are in either their (a) semiconducting states or (b) metallic states. It is known that metallic tin is insoluble in InSb(I).³⁴ However, conditions of pressure and temperature at which the metallic and nonmetallic forms of tin and indium antimonide are stable are greatly different.

We now report that tin and indium antimonide form metallic alloys from liquid solutions solidified at pressures where InSb(II) is the thermodynamically favored phase. Such alloys have been obtained in a metastable state at atmospheric pressure by quenching them to -196°C , then reducing the pressure at this low temperature. It appears that a continuous series of solid solutions must exist.

Preparation: Metallic alloys InSbSn, InSbSn₂, and InSbSn₄ were prepared in the following manner: The elements In, Sn, and Sb each of 99.995% purity were melted and thoroughly mixed in an evacuated silica tube. The solution was then cooled rapidly to room temperature. This yielded a finely divided mixture of Sn(β) and InSb(I). This mixture was transferred to a boron nitride container, compressed to 30-kbar pressure at 24°C then heated to 600°C. Each sample was kept at this pressure and temperature for one hour and then cooled slowly to -196°C . The pressure then was reduced to 1 atm and the sample removed from the apparatus—all at a temperature of -196°C .

These metallic alloys show an increase in thermal stability as the tin content is increased. InSb(II) reverts explosively to InSb(I) when the temperature is raised to -65°C . The metallic alloy InSbSn transforms slowly (hours) at room temperature with transformation becoming essentially complete in one minute at 45°C. The rates of conversion of InSbSn₂ and InSbSn₄ are slower and occur at even higher temperatures. (These data in themselves essentially prove that solid solutions have been formed.)

The lattice spacings for Sn(β), InSb(II), and the metallic alloys InSbSn, InSbSn₂, and InSbSn₄ were obtained from x-ray diffraction measurements using the Bragg-Brentano method (Cu K α x radiation) at atmospheric pressure. At 25°C the lattice parameters (of Table I) of InSbSn₄ and InSbSn₂ and Sn(β) at 25°C are in good agreement with those given by Swanson and Tatge.²⁷ Likewise the lattice parameters of InSbSn and InSb(II) are not significantly different from Sn(β) at -196°C .

³⁴ P. Baruch and M. Desse, *Compt. Rend.* 241, 1040 (1955).

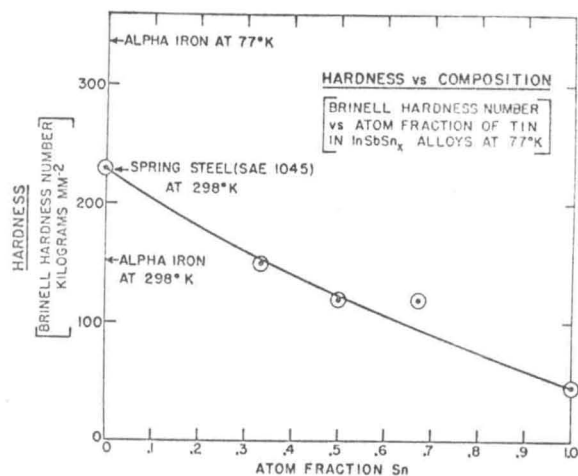


FIG. 3. Brinell hardness numbers of the metallic alloy system InSb-Sn at 197°C.

Metallic indium antimonide is physically much harder than metallic tin.²⁴ Brinell hardness numbers for InSb(II) and Sn(β) at -196°C are 230 ± 30 and 46 ± 10 kg mm⁻², respectively. The Brinell hardness numbers (at -196°C) for the metallic alloys InSbSn₄, InSbSn₂, and InSbSn lie between those of Sn(β) and InSb(II) (Fig. 3). Since Sn(β) and InSb(II) have essentially identical lattice parameters (Table I), the x-ray data alone are not sufficient proof that solid solution exists in these metastable tin-indium antimonide alloys. However, the variation of thermal stability cited above, the variation of the Brinell hardness number (Fig. 3), and of the superconducting transition temperature³⁵ with the composition all indicate that solid solutions were formed.

VI. METALLIC INDIUM TELLURIDE

Our techniques for the preparation of metallic indium telluride, InTe(II), were similar to those used for the preparation of InSb(II). InTe(II) has been prepared (a) directly from solid InTe(I),³⁶⁻⁴¹ and (b) from samples cooled from 850°C at 30-kbar pressure.⁴² The latter method should, according to the phase diagram of Banus *et al.*,⁴⁰ yield InTe(II) directly from

³⁶ B. R. Tittmann, A. J. Darnell, H. E. Bömmel, and W. F. Libby, *Science* 139, 1301 (1963).

³⁷ M. D. Banus, J. A. Kafalas, R. E. Hanneman, and H. C. Gatos, Solid State Research Report, Lincoln Laboratory, MIT, No. 3, 1962 (unpublished).

³⁸ M. D. Banus, R. E. Hanneman, and J. A. Kafalas, Solid State Research Report, Lincoln Laboratory, MIT, No. 4, 1962 (unpublished).

³⁹ M. D. Banus, R. E. Hanneman and J. A. Kafalas, Solid State Research Report, Lincoln Laboratory, MIT, No. 1, 1963 (unpublished).

⁴⁰ A. J. Darnell, A. J. Yencha, and W. F. Libby, *Science* 141, 713 (1963).

⁴¹ M. D. Banus, R. E. Hanneman, M. Strongin, and K. Goen, *Science* 142, 662 (1963).

⁴² C. B. Sclar, L. C. Carrison, and C. M. Schwartz, *Science* 143, 352 (1964).

⁴³ H. E. Bömmel, *Bull. Am. Phys. Soc.* 8, 623 (1963).

liquid indium telluride. Moreover, it would seem less likely to contain InTe(I) as an impurity in view of the difficulty experienced in carrying the solid (I) \rightarrow solid (II) reaction to completion. In both methods of preparation InTe(I), once obtained, was cooled to -196°C then brought to atmospheric pressure. Metallic InTe(II) was stored at -196°C since it reverts slowly to InTe(I) at room temperature.⁴⁰ All other elements, detectable by spectrographic analysis, amounted to less than 0.03%.

A. Properties

1. Structure

The tetragonal form of normal InTe collapses at high pressure and temperature to a NaCl (B_1)-type structure⁴⁰ which by suitable quenching can be brought to atmospheric pressure in a metastable state. Subsequent to our first report³⁹ we have been able to obtain reflections for the first three odd $[hkl]$ indices of InTe(II). Only the first of the odd indices, hkl [111], was observed by the Bragg-Brentano technique at 25°C . However, reflections attributed to hkl (311) and (331) were observed at -196°C due to enhancement of the intensity of the diffracted beam at this lower temperature. Geller *et al.*⁴³ report odd-index reflected for [111], [311], and [311] in NaCl-like In_{0.82}Te.

The lattice constants for InTe(II) are given in

TABLE II. Lattice spacings and lattice parameters of InTe(II) at atmospheric pressure.

hkl	25°C $d_{hkl}(\text{\AA})$	-196°C $d_{hkl}(\text{\AA})$
111	3.570	3.549
200	3.091	3.086
220	2.185	2.177
311	...	1.856
222	1.784	1.776
400	1.544	1.538
331	...	1.411
420	1.381	1.375
422	1.261	1.256
511
440	1.093	1.087
531
600	1.0295	1.0244
620	0.97626	0.97192
543
622	0.93134	0.92642
441	0.89188	0.88762
711
640*	0.85633	0.85253
$a_0(\text{\AA})$	6.177 ± 0.002	6.147 ± 0.002
(Calculated from last 5 lines)		

Table II. The diffraction angles (2θ) of InTe(II) were measured relative to the diffraction angles of NaCl yielded by a small quantity of NaCl added to the

⁴³ S. Geller, A. Jayaraman, and G. W. Hull, Jr., *Appl. Phys. Letters* 4, 35 (1964).

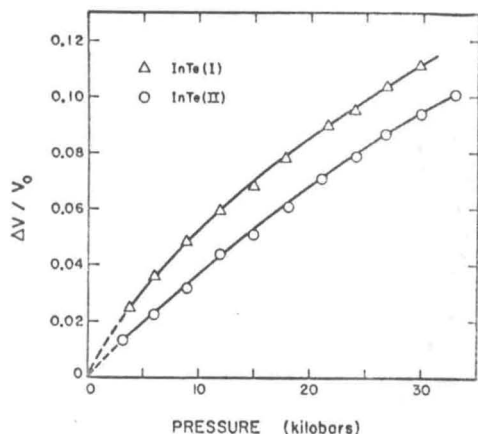


Fig. 4. Compression of InTe(I) and InTe(II) at 25°C.

powdered InTe(II). The lattice parameter a_0 calculated from the five smallest values of d_{hkl} is $6.177 \pm 0.002 \text{ \AA}$ at 25°C. This is in agreement with the lattice parameters reported by Banus *et al.*,⁴⁰ Sclar *et al.*,⁴¹ and Geller *et al.*⁴³

2. Expansion Coefficient; Density

The average coefficient of linear expansion between 25 and -196°C calculated from the different lattice constants at these temperatures is $22 \pm 2 \times 10^{-6} \text{ deg}^{-1}$. The density of InTe(II) calculated from a_0 in Table II is $6.83 \pm 0.01 \text{ g/cm}^3$. The density measured pycnometrically is $6.68 \pm 0.06 \text{ g/cm}^3$. The theoretical density of InTe(I) calculated from lattice constants given by Schubert *et al.*⁴⁴ is 6.34 g/cm^3 . Thus, the decrease in volume for the hypothetical case InTe(I) \rightarrow InTe at 1-atm pressure and 25°C is 7.2%, much smaller than for InSb.

3. Compressibility

The relative volumes of InTe(I) and InTe(II) were determined up to 30-kbar pressure at 25°C. The compressibility of InTe(I) and InTe(II), calculated from the initial slopes (Fig. 4) is 6.3×10^{-6} and $3.8 \times 10^{-6} \text{ bar}^{-1}$, respectively. Using the densities and compressions given above, then the volume

⁴⁴ K. Schubert, E. Dörre, and M. Kluge, *Z. Metallk.* 46, 216 (1955).

decrease at the equilibrium pressure for the transition InTe \rightarrow InTe(II) at 25°C should be about 5.5%. Use of this volume change and the slope (dT/dP) of the InTe(I) \rightleftharpoons InTe(II) transition given by Banus *et al.*⁴⁰ gives 0.4 kcal/mole for this transition at 25°C.

4. Electrical Resistivity

The electrical conductivity of the InTe(II) is metallic in behavior in contrast to that of InTe(I) which is a semiconductor. Figure 2 shows the resistance as a function of temperature at 1-atm pressure. In Te(II) has a somewhat lower temperature coefficient of resistance (77 to 300°K) than does copper. The electrical resistivity between 77 and 4.2°K is essentially constant. This is probably due to the impurity, InTe(I) since the samples for these measurements were made by direct conversion of InTe(I) to InTe(II). No pieces of InTe(II) large enough for electrical measurements by the 4-probe method could be obtained by using the liquid \rightarrow InTe(II) method of synthesis.

5. Magnetic Susceptibility

The susceptibility of the tetragonal and cubic forms of indium telluride were measured by the Gouy balance technique. Both forms of indium telluride were diamagnetic. The susceptibilities of InTe(I) and InTe(II) are -0.22×10^{-6} and $-0.14 \times 10^{-6} \text{ emu/g}$. Borg *et al.*⁴⁵ reports a susceptibility of $-0.17 \times 10^{-6} \text{ emu/g}$ for InTe(II) from nuclear magnetic resonance studies.

VII. CONCLUSION

A new family of artificial metals has been produced which should have most revealing properties.

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⁴⁵ K. C. Borg, W. H. Jones, Jr., and F. J. Milford, *Bull. Am. Phys. Soc.* 8, 261 (1964).