Phase Diagrams of Arsenic, Antimony, and Bismuth at Pressures up to 70 kbars*

W. Klement, Jr.,† A. Jayaraman,‡ and G. C. Kennedy

Institute of Geophysics and Planetary Physics, University of California,
Los Angeles, California

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The meltings under pressure of arsenic, antimony, and bismuth have been determined up to nearly 70 kbar by means of differential thermal analysis (DTA). Arsenic initially melts with a positive dT/dP, the fusion curve flattening out near 940°C at the highest pressures attained. The fusion curve of antimony exhibits practically no change with pressure initially, but takes on a slightly negative slope at higher pressures until a triple point is encountered near 57 kbar and 567°C; the high-pressure polymorph melts with a positive slope of 4.3°C/kbar. For bismuth, a triple point between the liquid and polymorphs IV and V occurs near 38.0 kbar and 296°C, in addition to the well-studied liquid-I-II and liquid-II-IV triple points at lower pressures. DTA was also used to determine the solid-solid phase boundaries in bismuth, triple points occurring between II, III, and IV near 24.0 kbar and 180°C and between III, IV, and V near 53 kbar and 174°C. The III-IV transition occurs at different temperatures upon heating and cooling and this hysteresis interval increases with pressure. No hystereses were observed for the IV-V and III-V transitions. At room temperature and at pressures beyond the well-known I-II and II-III transitions, the III-V transition is next encountered near ∼78–82 kbar (as estimated by extrapolation). Suggestions are made for the structures of the high-pressure Bi polymorphs and analogies are drawn between Bi, Sb, and As for the melting and distortion under pressure of the normal rhombohedral structure.

I. INTRODUCTION

THE elements, bismuth, antimony, and arsenic, all normally crystallize in a rhombohedral (2 atoms/unit cell) structure. In accord with the positions in column V of the periodic table, there are also other similarities in the physical and chemical properties and many further similarities might reasonably be expected to emerge for these elements under high pressure. Bismuth has been investigated more extensively at high pressures than almost all other elements, while antimony and arsenic have commanded much less attention and relatively little is known about their behavior.

The present investigation was undertaken in order to determine the phase diagrams of Bi, Sb, and As at pressures up to 70 kbar and to inquire into the nature of the polymorphic transitions, the crystal structures of the high-pressure polymorphs, and the similarities existing among these elements at high pressure.

II. EXPERIMENTAL PROCEDURES

Pressures up to about 45 kbar were generated in a piston-cylinder apparatus described previously.[1] Higher pressures were obtained with a double-stage device, the details of which have been presented elsewhere.[2,3] Corrections for friction were made in the usual way.[4,5]

Pressures are believed accurate to ±1.0 kbar up to 45 kbar and ±2 kbar at higher pressures.

Phase transformations were detected by means of differential thermal analysis (DTA).[1,5] Temperatures were measured with chromel-alumel thermocouples, using values from the standard tables. Transition temperatures on heating were accepted for the melting experiments, while the values obtained on both heating and cooling were recorded for the solid-solid transformations. Heating and cooling rates were in the range 3–5°C/sec. Transformation temperatures were estimated with a precision of ±2°C.

Elements of semiconductor grade purity (99.999%) were used in the experiments. Tantalum containers were employed throughout, without any visible evidence of contamination with the samples. For melting experiments with As, small volume containers (90-mil diam, 150-mil length) were used; for Bi and Sb, larger containers (150-mil diam, 200 mil long) were employed. In all cases, the melting signals were very distinct; very clear and pronounced thermal arrests were observed for the solid-solid transitions involving Bi III–IV, IV–V, and III–V using the larger sample volume.

One compression run was made for bismuth using a cylindrical column, 0.50 in. in diameter and 1.75 in. long. Previous experience has shown that bismuth under high pressure almost always ruptures carboloy and so a steel linear was introduced to avoid contact between the sample and the pressure chamber. Displacement versus pressure was continuously recorded on an x-y recorder; a slow pump was used for the compression, at a rate of about 1 kbar/min. The use of a long bismuth column enables even small discontinuities to be detected and the gauge is sensitive enough to detect displacements of 3 mil and, hence, volume discontinuities even as small as 0.2%. The displacement for the Bi-I-II-III transition was about 0.15 in.—about an

* Publication No. 263 Institute of Geophysics and Planetary Physics, University of California, Los Angeles, California.

† Present address: Kungl. Tekniska Högskolan, Institutionen för Fasta Tillståndets Fysik, Stockholm 70, Sweden.

‡ Present address: Bell Telephone Laboratories, Murray Hill, New Jersey.

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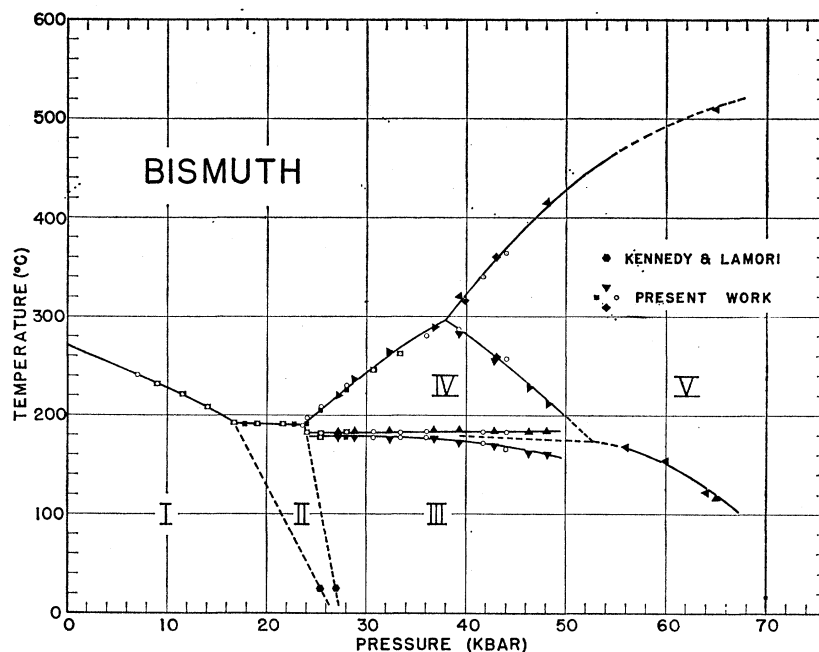
FIG. 1. Phase diagram of bismuth. Temperatures obtained on both heating and cooling are indicated for the III-IV transition. Comparison with previous work is made in the text.

over-all 8% volume change in going from I to III. No volume discontinuity was observed in the range from 30 to 46 kbar, the latter is the pressure at which the piston failed.

III. RESULTS AND DISCUSSION

The experimental data are presented, discussed, and compared with previous work in the sequence—Bi, Sb, As. The similarities apparent among these elements at high pressures are discussed in the final section of this paper.

Bismuth

Data for the melting and polymorphic transformations of Bi, as obtained from several runs in tantalum containers, are plotted in Fig. 1. The definitive coordinates of the first two solid-solid transitions, as established by Kennedy and La Mori,[6] are linearly connected to the appropriate triple points. Temperatures obtained on both heating and cooling for the III–IV transition are also indicated in Fig. 1. The widening of the hysteresis interval with pressure for this transformation was obvious in all runs. No hystereses were detected for the IV–V and III–V transitions.

Due to hysteresis in the III–IV transformation, the "equilibrium" boundary cannot be precisely specified. Although somewhat arbitrary, it is reasonable to take the boundary as lying about midway between the sets of temperatures obtained on heating and cooling, as indicated by the dashed line in Fig. 1. Five triple points have been determined in the present experiments;

these data and also the estimated slopes of the intersecting phase boundaries are presented in Table I.

The slopes are given in cyclic order, around the concerned triple point.

Bridgman[7] carried out the first investigations into the phase boundaries of Bi I through III or IV (all polymorphs labeled in accord with the nomenclature in Fig. 1) and located triple points near 17.0 kbar and 183°C and near 22.0 kbar and 185°C without, however, observing the melting of Bi II and IV or the III–IV transition. Butuzov and Ponyatovskii[8] detected these

TABLE I. Data for the triple-points in bismuth from the present experiments.

Components	Coordinates (kbar,°C)	Slopes of phase boundaries[a] (°C/kbar)
I-II-liq	16.7, 191	(−19); 0; −7.6;
II-IV-liq	23.6, 191	−; +8.9; (<0)
II-III-IV	24.0, 180	−70; (<0); −
IV-V-liq	38.0, 296	−6.5; +12.6; +8.0
III-IV-V	52.6, 174	(−0.6); (−9.3); (−1.6)

[a] Parentheses denote uncertain data.

meltings and agreed exactly with Bridgman on the pressure coordinates of the triple points, although preferring 184°C as the temperature in both cases. Ponyatovskii,[9] in further experiments in a hydrostatic medium, verified the flatness of the Bi II melting curve which was located at 183°C; the II-III-IV triple point was lo-

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[9] E. G. Ponyatovskii, Kristallografiya **5**, 154 (1960) [translation: Soviet Phys.—Cryst. **5**, 147 (1960)].

cated at 22.1 kbar and 174°C, where this temperature was the mean of those obtained upon heating and cooling.

The most serious discrepancies between the present results and the results of these previous investigators involve the temperatures of the Bi II fusion curve and of the II-III-IV triple point. In both cases, the present temperatures were readily and reproducibly determined from clear and distinct DTA signals to be 5–8°C *higher* than those reported by the Russian workers. The sources of the discrepancy are unclear. According to Bundy,[10] the effect of pressure on a chromel-alumel thermocouple at 25 kbar leads to only ~1°C difference from the actual temperature; estimates of the pressure effects on the thermal emf of an iron-nichrome couple, such as that used by Ponyatovskii,[9] are apparently lacking. Also, Ponyatovskii[9] mentioned that "equilibrium" transformation temperatures were taken as the mean of those obtained on heating and cooling. This convention may have some validity for solid-solid transitions but, for melting, the signal obtained on heating is taken since it is possible to overheat a solid only with very high heating rates while the undercooling of a liquid is quite common.

In room-temperature work to higher pressures, Bridgman[11] found several small volume discontinuities, which were ascribed to polymorphic transitions, although no corresponding discontinuities in resistance were detected. The phase diagram[12,13] of Bundy for Bi (to about 75 kbar, revised pressure scale) shows only one of these transformations— that near 44 kbar and 25°C. Bundy's experiments[12] approximately delineated the IV-liquid and V-liquid, IV-V and III-V phase boundaries and suggested that the IV-V-liquid and III-IV-V triple points lie near 38 kbar and 290°C and near 55 kbar and 190°C, respectively.

This determination[13] of the IV-V-liquid triple point is in very good agreement with the present results; the differences between the coordinates for the III-IV-V triple point seem to lie mostly in the interpretation given to the III-IV transformation. The present view of this transition (which is discussed in more detail below) is that no significant difference is indicated over the whole pressure interval for the transformation mechanism and, hence, for the structure of Bi III. The room-temperature compression run for bismuth (Sec. II) did not indicate any volume discontinuity. Thus, there is no support for the existence of the several phase boundaries, as proposed by Bridgman, between the stability fields of Bi II and V; Bundy's data[12] can easily be reinterpreted in accord with this.

The III-V transition at room temperature is widely employed as pressure calibration point. Although a direct determination is beyond the range of the present apparatus, some estimates may be obtained by extrapolation of the III-V phase boundary (Fig. 1). For a linear extrapolation through the 4 experimental points, a pressure of ~82 kbar may be estimated at 25°C; allowing curvature in the phase boundary, such as indicated in Fig. 1, yields an estimate of about 78 kbar. Although these estimates are subject to some uncertainties, they definitely suggest a lower pressure for the Bi III-V transition than the presently accepted value of about 90 kbar. In further support of this contention, the negative curvature indicated in Bundy's diagram[13] for the III-V boundary is relatively uncommon for a phase boundary.

Despite considerable interest in bismuth at high pressures, only the structure of the zero-pressure polymorph (Bi I) is known.

Kasper et al.[14] have presented some tentative d spacings for Bi II, as obtained by x-ray diffraction for the sample in a diamond cell. The possibility of Bi III lines in the pattern and uncertainties in the intensities due to the high absorption renders the identification even more difficult and, to date, nothing further has been published. Jamieson and Lawson[15,16] have put forward the suggestion that the structure of Bi II is closely related to bcc—an interpretation believed to be consistent with the ~eightfold coordination in the liquid and the negligible volume change upon fusion. Klement[17] has pointed out that the structure of Bi II may be closely related to the hexagonal (3 atoms/unit cell) phase occurring in Bi-rich Tl alloys.[18–20]

A linear extrapolation to pure bismuth of the volumes/atom determined by Ölander[21] and also Makarov[19] for these ω-phase[22] Bi-Tl alloys suggests a volume/atom of 32.6±0.4 Å³ for ω bismuth. Extrapolations of thermodynamic data,[23] in the manner recently employed by Klement,[24] suggest differences in zero-pressure free energy and in entropy as 0.7±0.4 kcal/mole and −0.1±0.3 entropy units (eu), respec-

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[13] F. P. Bundy and H. M. Strong, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1961), Vol. 13.

[14] J. S. Kasper, J. E. Hilliard, J. W. Cahn, and V. A. Phillips, WADC Tech. Report 59–747, General Electric Company, Schenectady, New York, 1960 (unpublished).

[15] J. C. Jamieson and A. W. Lawson, *Modern Very High Pressure Techniques*, (Butterworths Scientific Publications Ltd., London, 1962).

[16] J. C. Jamieson (private communication).

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[18] M. Hansen and K. Anderko, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958).

[19] W. B. Pearson, *Handbook of Lattice Spacings and Structures of Metals and Alloys*, (Pergamon Press, Inc., New York, 1958).

[20] E. S. Makarov [Soviet Phys.—Cryst. **3**, 3 (1958)] has commented that this structure may be ordered.

[21] A. Ölander, Z. Krist. **89**, 89 (1934).

[22] Herein referred to as such in recognition of the similarity in structure with the ω phases in some Ti- and Zr-base alloys.

[23] R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, *Selected Values for the Thermodynamic Properties of Metals and Alloys* (John Wiley & Sons, Inc., New York, 1963).

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FIG. 2. Melting curves of arsenic and antimony.
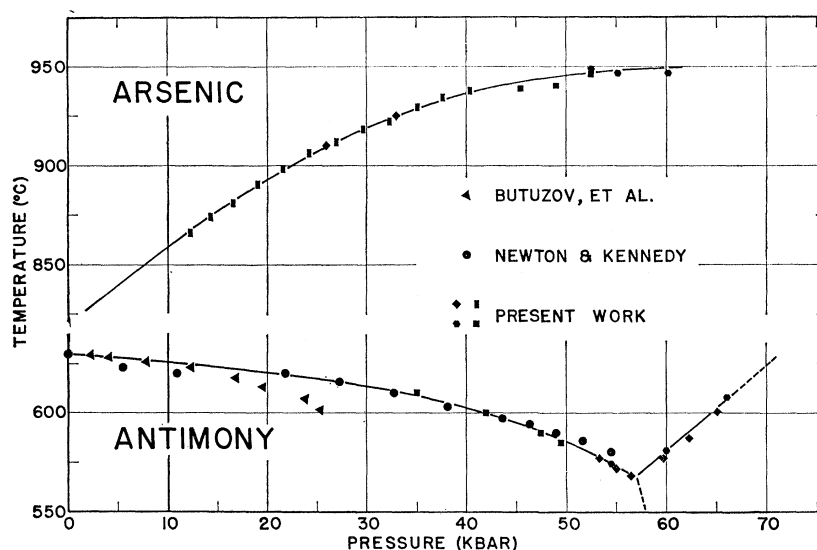
tively, between the ω phase and the stable rhombohedral form at 150°C. The difference in molar volume at zero pressure between these two polymorphs is approximately 3.0 ± 0.4 Å³/atom and, assuming equal compressibilities and neglecting the entropy difference, the transition pressure may be estimated as 18 ± 12 kbar.

The thermodynamic sanctions for such a transformation having been established, it is now necessary to consider the x-ray diffraction results of Kasper, et al.[14] The d spacings and intensities of the 9 lines presented can be fairly well accounted for by a hexagonal structure with atoms at $(0,0,0)$, $(\frac{1}{3},\frac{2}{3},u)$, and $(\frac{2}{3},\frac{1}{3},\bar{u})$, and $c=3.16\pm3$ Å, $a=5.77\pm4$ Å, and $c/a=0.55\pm1$. The positional parameter, u, is uncertain, but must lie between $\frac{1}{2}$ and $\frac{1}{3}$. For $u=\frac{1}{2}$, an extinction of the (20.0) line would be required, but this is not observed. For $u=\frac{1}{3}$ and $c/a=\sqrt{\frac{3}{8}}=0.612$, the ω structure is equivalent to bcc $([01.0]_\omega\|[1\bar{1}0_{bcc}, [00.1]_\omega\|[111]_{bcc}; a_\omega=\sqrt{2}a_{bcc}, c_\omega=\frac{1}{2}\sqrt{3}a_{bcc})$.

The volume/atom for Bi II computed from the above lattice parameters is 29.4 ± 0.7 Å³. According to Bridgman,[11] the volume/atom of Bi II near 25 kbar is ~0.85 of the volume/atom of Bi I at zero pressure, or about 30.1 Å³—which is in modest agreement with the calculation for the hypothesized structure.

The present experiments conclusively demonstrate that there are only 5 polymorphs of bismuth in the pressure range explored. The III–IV transformation has been carefully investigated and the hysteresis interval firmly established. Although hystereses are known in many transformations (e.g., α–β and β–γ uranium,[25] α–β mercury[5]), the widening of the hysteresis interval with pressure has been observed in only one elemental transformation—the bcc-hcp transformation in thallium.[2] By analogy with the thallium transition, it is suggested that Bi III is hcp and Bi IV is bcc. The ab-

sence of hysteresis in the IV–V transition is analogous to the behavior of the bcc-fcc transition in thallium,[2] although the temperature stabilities are inverted. This analogy can hardly be considered as decisive, but it is quite plausible to suggest that the structure of Bi V is fcc.

Arsenic

Data for the melting of As, from several runs in tantalum containers, are presented in Fig. 2. These data connect satisfactorily with the liquid-gas-solid triple point, which lies near[26] 817–818°C or 822°C and about 37 bar. Depending on the precise temperature of the triple point, the present data suggest an initial dT/dP for the melting curve, of 3.5–4.5°C/kbar. As readily seen from Fig. 2, the slope of the fusion curve decreases rapidly at the higher pressures. The possibility of a maximum could not be verified in these experiments and it an only be concluded that the melting curve is flattening out at the highest pressures and a triple point may be expected at pressures somewhat above the explored range.

Bridgman failed to detect any discontinuity, suggestive of a phase transformation, in room-temperature resistance[27] and volume[11] measurements to about 75 and 100 kbar, respectively.

Antimony

Results for the melting of Sb, from 3 separate runs in tantalum containers, are plotted in Fig. 2, together with the data of Butuzov, Ponyatovskii, and Shakhovski[8] and of Newton and Kennedy.[1] The determinations of Butuzov et al.[8] are most compatible with a normal melting point of 630°C, but inexplicably fall too low in temperature above 15 kbar. The results of Newton and Kennedy[1] are the most reliable up to about 45 kbar,

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above which the friction corrections were slightly underestimated.

The present results are in good agreement among themselves and with the Newton-Kennedy data below 45 kbar. A triple point occurs near 57 kbar and 567°C. In the vicinity of the triple point, the slopes of the phase boundaries are (in °C/kbar): Sb I-liquid, -2.6; Sb II-liquid, $+4.3$; Sb I-Sb II, -21. The latter slope is obtained by linear interpolation between the triple point and the discontinuity[11] in volume found by Bridgman near 83.3 kbar and room temperature.

Similarities Among the Group VB Elements

The rhombohedral structure in which bismuth, antimony, and arsenic normally[19] crystallize is characterized by atoms at (x,x,x) and $(\bar{x},\bar{x},\bar{x})$. These positional parameters, together with the lattice parameters and rhombohedral angles for the elements at zero pressure and room temperature, are

	Bi[28,29]	Sb[19]	As[19]
x	0.234	0.233	0.226
$a(\text{Å})$	4.746	4.507	4.131
α	57.24°	57.1°	54.2°

It is readily seen that there are monotonic sequences, with increasing Z, for all three of the parameters. The coordination is increased from 3+3 to exactly 6 for $x=0.250$ and a recent survey[5] of the data for other anisotropic structures suggests that such deformation may very well occur with increasing pressure. The elastic moduli data[30] indicate that $[(C_{33}-C_{13})/(C_{11}+C_{12}-2C_{13})]$ is about 0.35 or 0.41 for Bi, 0.32 for Sb, which suggests that the rhombohedral angle, α, increases with increasing pressure. There apparently are no data, but it may be expected that $(C_{33}-C_{13}) < (C_{11}+C_{12}-2C_{13})$ for As also. For $\alpha=60°$ exactly, the packing efficiency[31] for this rhombohedral structure is a maximum. The structure, in fact, is now identical with simple cubic (one atom/unit cell) for $\alpha=60°$ and $x=\frac{1}{4}$.

For bismuth,[28,29] the positional parameter and rhombohedral angle decrease with increasing temperature—the effect being opposite to that of pressure. Sufficiently reliable data are not available for antimony and arsenic, but similar variations in the structural parameters may be expected.[5]

According to Bridgman,[11] the volume changes at the room temperature polymorphic transitions are

Bi I–II,	4.6%,	0.98 cm³/mole,
Bi II–III,	3%,	0.64 cm³/mole,
Bi III–V,	1.2%,	0.25 cm³/mole,
Sb I–II,	3.7%,	0.67 cm³/mole,

the other "transitions" reported by Bridgman[11] having been ignored in this compilation. Much similarity is not particularly obvious between the Sb and the Bi transitions and the general ignorance concerning the polymorphism of antimony and also arsenic at higher pressures would seem to preclude the drawing of any analogies at present. However, the most reasonable suggestion for the structure of Sb II would be that it is closely related to bcc.

Only x-ray or neutron diffraction *at pressure* can definitely establish the structure of a given high-pressure polymorph. Although these techniques are presently being extended to very high pressures, they promise to be limited to relatively low temperatures. The problem of disentangling liquid structures at high pressures appears to be quite formidable, since even the zero-pressure experimental requirements are quite stringent. It seems worthwhile then to attempt to infer as much as possible about the structures of the liquids from the fusion curve determinations.

For the sequence of elements presently investigated, attention is directed primarily to the melting curves for the rhombohedral (2 atoms/unit cell) structure. It may be readily appreciated from Figs. 1 and 2 that there is no characteristic slope, dT/dP, to be associated with the melting of this structure. The melting curve of bismuth decreases rapidly with increasing temperature, with little curvature. For antimony, the melting curve is only slightly negative, with somewhat more curvature. The fusion curve for arsenic is positive and exhibits a great deal of curvature and, at higher pressures, may even go through a maximum. Nothing is known at present of the melting curve of phosphorus, but the slope[8] established for the black, orthorhombic form strongly suggests that the rhombohedral[16] form would melt with a steep, positive slope and much curvature may be manifested, in addition. Since the entropies of fusion are apparently not too dissimilar $(4.77\pm0.18$ [23] eu for Bi, ~5.25[32] eu for Sb, others unknown), the answer to the sequence of melting slopes must be sought primarily from a consideration of the volume changes of fusion.

Since the coordinations in the rhombohedral (2 atoms/unit cell) structures do not differ appreciably, the coordinations in the liquid must then be examined, as emphasized repeatedly[2,5] by the present authors. For Bi, the best estimate of the coordination is ~7.7[33] at zero pressure. This lends some insight into the negative melting slope and, at higher pressures, the coordination probably increases only slowly, since there is only slight curvature in the fusion curve. For Sb, the zero-pressure coordination in the liquid is ~6,[34] slightly greater than for the solid; a more rapid increase in coordination with

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[29] C. S. Barrett, Australian J. Phys. 13, 209 (1960).
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[31] E. Parthé, Z. Krist. 115, 52 (1961).

[32] A. Schneider and G. Heymer, *The Physical Chemistry of Metallic Solutions and Intermetallic Compounds* (Her Majesty's Stationery Office, London, 1959).
[33] P. C. Sharrah and G. P. Smith, J. Chem. Phys. 21, 228 (1953); P. C. Sharrah, J. I. Petz, and R. F. Kruh, *ibid.* 32, 241 (1960).
[34] H. Hendus and H. K. F. Muller, Z. Naturforsch. 10a, 254 (1955); 12a 102 (1957).

pressure is expected and, thus, greater curvature in the fusion curve. No data are apparently available for As, but molecular associations and, hence, lesser coordination are probably present in the liquid and this can account for the positive melting slope and the greater curvature. For P, Thomas and Gingrich[35] showed, in a classic investigation, the existence of P_4 molecules in the melt; a good deal of this molecular species probably

exists at higher pressures. The trajectories of the fusion curves for these isostructural elements are, thus, considered to be dependent mostly upon the relative coordinations in the liquid.

ACKNOWLEDGMENTS

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Superconductivity in the Indium-Tin System*

M. F. Merriam and M. Von Herzen†

University of California, San Diego, La Jolla, California

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Transition temperatures as a function of composition have been measured throughout the In-Sn binary system. Samples 'quenched' from the liquid state had higher transition temperatures than well-annealed samples, confirming the effect reported earlier for Hg-In compositions. The enhancement in T_c was 2–3°K for the most favorable compositions. It is argued that the effect arises from internal strains in the samples and not from short-range disorder. The equilibrium T_c values vary from 3.4°K (near pure In) to 6.6°K (β phase, 33.5 at.% Sn). Transition temperature within any particular phase is a strong function of valence electron concentration, but not a function of the type found in transition metal superconductors. In all phases T_c increases with increasing valence electron concentration. The data in the In terminal solid solution are compared with the BCS formula, and with the theory of Morel and Anderson. A substantial variation of the electron-phonon interaction parameter with alloying is required if the data are to be described with the BCS formula. The variation in this parameter computed from the theory of Morel and Anderson is very much less than the observed variation in our case. In the tetragonal In phase a discontinuity in dT_c/dx is found at $x=8$ at.% Sn. A crystallographic phase change at this composition in unlikely, and the discontinuity is thought to be an electronic effect. An apparatus for rapid and convenient measurement of transition temperatures is described.

TRANSITION temperatures for several In-Sn compositions were measured several years ago by Wernick and Matthias,[1] but only the dilute primary solid solutions in this alloy system have been thoroughly investigated.[2–4] We thought it advisable to repeat and extend the measurements of Wernick and Matthias for several reasons. Study of superconducting transition temperature (T_c) versus composition in In-Sn alloys formed a logical continuation of our earlier work on

Hg-In,[5,6] allowing us to extend the range of measurement to four electrons per atom. The constitution diagram[7] of the indium-tin system is relatively well known and it seemed experimentally suitable for such a study. Furthermore, the discovery[5] that the superconducting transition temperature (T_c) of Hg-In alloys could be raised as much as 30% above the value for samples in metallurgical phase equilibrium by quenching[8] from the melt required verification in another alloy system. Finally, the discovery of the 'quench effect' raised doubts about the T_c values reported by Wernick and Matthias, since their samples were not carefully annealed.

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[7] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958), 2nd ed.
[8] In this paper we use the word 'quench' to mean rapid cooling from the *liquid* rather than the solid, state.