

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 Gingrich³⁵ showed, in a classic investigation, the existence of P₄ molecules in the melt; a good deal of this molecular species probably

³⁵C. D. Thomas and N. S. Gingrich, *J. Chem. Phys.* **6**, 659 (1938).

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*

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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 is 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 diagram⁷ of the indium-tin system is relatively well known and it seemed experimentally suitable for such a study. Furthermore, the discovery⁵ 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 quenching⁸ 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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¹J. H. Wernick and B. T. Matthias, *J. Chem. Phys.* **34**, 2194 (1961).

²B. R. Coles, *IBM J. Res. Develop.* **6**, 68 (1962); B. R. Coles and S. Wipf (to be published).

³D. P. Seraphim, C. Chiou, and D. J. Quinn, *Acta Met.* **9**, 861 (1961).

⁴R. I. Gayley, E. A. Lynton, and B. Serin, *Phys. Rev.* **126**, 43 (1962).

⁵M. F. Merriam and M. A. Jensen, *Cryogenics* **2**, 301 (1962).

⁶M. F. Merriam, M. A. Jensen, and B. R. Coles, *Phys. Rev.* **130**, 1719 (1963).

⁷M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958), 2nd ed.

⁸In this paper we use the word 'quench' to mean rapid cooling from the *liquid* rather than the solid, state.

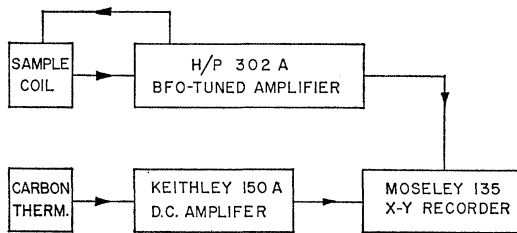


FIG. 1. Block diagram of superconductivity measurement apparatus. Current is fed to the carbon thermometer from a battery with large series resistance.

We describe first the experimental procedures and apparatus, then the results relevant to the 'quench effect,' and finally the other results.

I. EXPERIMENTAL APPARATUS AND PROCEDURE

Samples

The tin and indium used were obtained in the form of 99.999+% pure shot from the Indium Corporation of America. The metals were weighed into thin-walled Teflon capsules (of the proper size to fit into the coils of the measuring apparatus) with tight-fitting caps. The encapsulated samples were then melted in a rocking furnace and quickly plunged into liquid nitrogen. Measurements indicated that the sample temperature dropped below 100°K in about 30 sec. The samples were either kept at 77°K until measurement (an hour or two later) or placed in the annealing furnace, depending on whether the sample was to be measured in the 'quenched' or annealed condition. Oxidation of the samples during furnacing was insignificant.

Superconductivity Measurements

Transitions were followed by monitoring the inductance at 1 kc/sec of a coil containing the specimen. The inductance could be measured directly with a GR 1050A impedance bridge, but was usually detected indirectly by measuring the voltage across the coil when a 1-kc/sec signal was applied. Since the resistance of the copper wire in the coil was temperature-independent below about 25°K any change in coil impedance reflected a change of inductance. The measuring setup is shown in the block diagram of Fig. 1. The key component is the Hewlett-Packard 302A Wave Analyzer. This instrument contains an oscillator (to supply a signal to the coil), a narrow band amplifier (to amplify the voltage developed across the coil), and a rectifier (recorder output). The voltage from the recorder output of the 302A is fed to the y drive of an x-y recorder. Temperature, in the form of a voltage drop across a carbon resistance thermometer, is fed to the x drive. As temperature is varied the superconducting transition is plotted out directly by the recorder. Figure 2 shows such a plot. The great advantage of this setup, aside from the speed and convenience, is the fact that unusual

features in the transition curves, for example double transitions, can be immediately recognized and investigated. Temperature equilibrium is easily checked, as in Fig. 2.

Four samples could be measured together in the apparatus of Fig. 3. Temperatures below 4.2°K were obtained and measured by immersion in boiling liquid helium. Temperatures above 4.2°K were obtained by positioning the copper block in the temperature gradient above the bath. The copper tail assists in cooling the block, which remains at uniform temperature so long as the liquid-helium level is below the brass section of the tail. The temperature of the block was measured by a carbon radio resistor calibrated with superconductors of known T_c and with helium vapor pressure data.⁹ Temperature equilibrium between samples and thermometer is essentially complete, as can be seen from the insignificant temperature hysteresis of Fig. 2.

The measuring coils in our apparatus were wound with AWG 38 nylon insulated copper magnet wire on Teflon forms and had an inductance of about 600 μ H empty. The coil inductance fell to about half this value when a sample became superconducting. The magnetic field at the center of the coils was calculated to be about 0.5 G. Power dissipation in the carbon thermometer did not exceed 10 μ W.

QUENCH EFFECT

The increase in T_c in samples quenched from the melt is shown in Fig. 4. As in the Hg-In case, the increase goes to zero at both ends of the composition range (i.e., for pure metals). It is largest in the region 85-95 at. % Sn where several specimens show double transitions. The data reported by Wernick and Matthias¹ are also shown in Fig. 4. In the light of our results it is clear that their samples were not in equilibrium, and were, in some cases, even more severely quenched than ours.

We have taken the upper onset temperature, defined

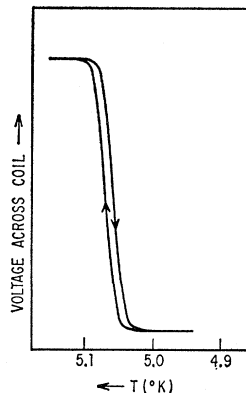


FIG. 2. Typical transition observed with the apparatus of Fig. 1, showing temperature hysteresis. The sample is $\text{In}_{0.876}\text{Sn}_{0.125}$. Hysteresis much smaller than this can be obtained with sufficient care.

⁹ H. von Dijk, M. Durieux, J. R. Clement, and J. K. Logan, Natl. Bur. Std. (U. S.) Monograph 10, Part 2, 12 (1960).

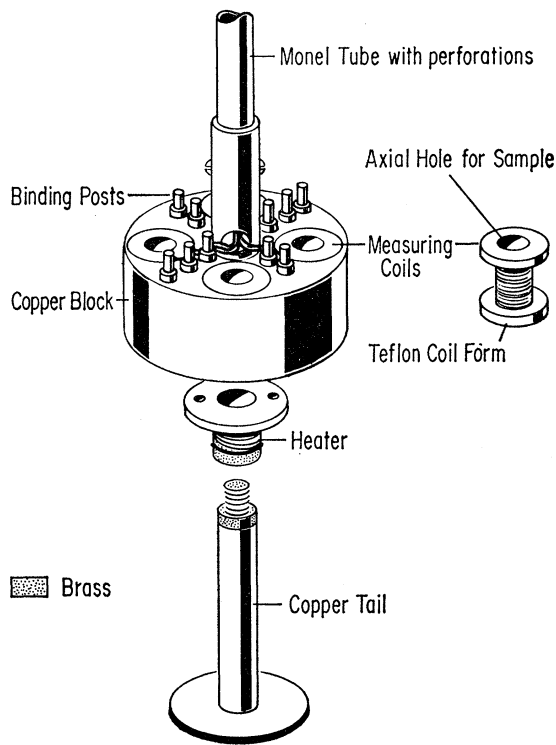


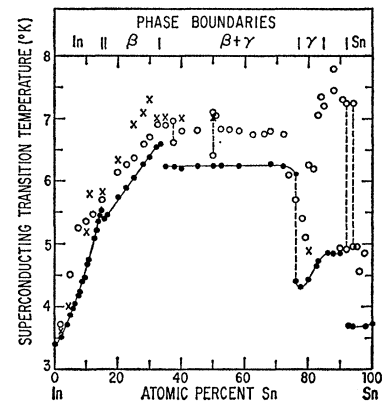
FIG. 3. Apparatus for determining superconducting transition temperatures. Sample capsules are placed in each of the four coils.

as the temperature at which coil inductance first begins to drop steeply, as T_c . Even if midpoint (half the inductance change) temperatures are taken, however, the increase in T_c on quenching is very clearly evident. The data of Wernick and Matthias refer to upper onset temperature. For the annealed samples the transition width is so small that the two criteria give nearly identical curves of T_c (annealed) versus composition (Table I).

The origin of the 'quench effect,' the enhancement of transition temperature by rapid cooling from the melt, is still uncertain. The present work eliminates the possibility that the effects seen in the Hg-In system arose somehow from peculiarities in the metallurgical constitution of that system. Two possibilities remain: (1) The enhancement of T_c may arise from internal strains in the rapidly cooled samples. Such strains could be expected to develop as a result of differential thermal contraction of two or more phases present. (2) The higher T_c 's could be connected with local crystallographic imperfections frozen in during rapid solidification, leading to substantial short-range disorder. The short-range disorder produced by cold-working metal foils at 4°K increases T_c , as does also the disorder frozen into an evaporated film when it is deposited on a 4°K substrate.¹⁰ We feel the first explanation—that the increase of T_c arises from internal

¹⁰ G. von Minnigerode, Z. Physik. 154, 442 (1959).

FIG. 4. Transition temperature vs composition in the In-Sn system: x—data of Wernick and Matthias; ○—samples quenched from the melt; ●—samples annealed to equilibrium (Table I).



strains—is the more probable one. By 'strains' we mean, of course, plastic strains (i.e., irreversible deformations which remain after the stress is removed); elastic strains (those which disappear reversibly upon removal of stress) can produce only very small changes, of order 0.1 deg at most, in T_c .^{11,12} (The distinction between the plastically strained and short-range disordered conditions lies in the scale of the disorder—i.e., the size of the 'good' regions, relative to a lattice parameter.) Our reasons for preferring the internal strain hypothesis are: (1) The increases in T_c observed in the disordered films and cold worked foils anneal out at temperatures below 77°K, whereas our effect does not. The annealing of short-range disorder should involve only local (on the scale of a lattice parameter) rearrangements, and so would be expected to take place at low temperature. The relief of internal strains, however, may well require diffusion over substantial distances. (2) Our effect does not occur in pure elements, as do the increases in the films and foils, but only in solid solutions or two phase systems. Internal strains depending on differential thermal contraction are, of course, impossible in pure elements. (3) The magnitude of the increase in transition temperature upon quenching varies considerably depending on which phases are present in the sample. For example, in the In-Sn system (Fig. 4), the increase in T_c in samples containing both γ phase and Sn phase (that these samples were, in fact, two phase is shown by the fact that they display two transitions) is substantially greater than in the case of samples consisting of the γ phase and β phase. Similarly, in the Hg-In system⁵ the increase is greater in two phase samples on the In side of HgIn than in two phase samples on the Hg side of this compound. This behavior is exactly what would be expected on the strain hypothesis, since the magnitude of strain effects will depend on the difference in thermal expansion coefficients and yield properties of the two phases involved. On the other hypothesis, since the samples were all quenched at the same rate, we would expect about the same degree of short-range disorder in all samples and

¹¹ A. M. Toxen, Phys. Rev. 124, 1018 (1961).

¹² P. M. Hall, Bull. Am. Phys. Soc. 7, 535 (1962).

TABLE I. Transition temperatures of annealed In-Sn alloys.

| Composition (at. % Sn) | Superconducting transition (upper and lower limits in °K) | Composition (at. % Sn) | Superconducting transition (upper and lower limits in °K) | Composition (at. % Sn) | Superconducting transition (upper and lower limits in °K) |
|---------------------------|--|---------------------------|--|---------------------------|--|
| 2.0 | 3.515-3.509 | 9.0 | 4.41-4.39 | 37.5 | 6.23-6.18 |
| 3.0 | 3.637-3.623 | 9.25 | 4.44-4.42 | 40.0 | 6.22-6.20 |
| 4.0 | 3.715-3.705 | 9.5 | 4.47-4.44 | 45.0 | 6.23-6.17 |
| 5.0 | 3.869-3.852 | 10.0 | 4.54-4.50 | 50.0 | 6.24-6.20 |
| 6.0 | 3.985-3.960 | 10.5 | 4.67-4.62 | 50.7 | 6.20-6.17 |
| 6.3 | 4.012-4.002 | 11.0 | 4.79-4.74 | 52.5 | 6.24-6.17 |
| 6.5 | 4.041-4.028 | 12.75 | 5.09-5.04 | 58.0 | 6.24-6.20 |
| 6.8 | 4.070-4.056 | 13.25 | 5.21-5.17 | 62.5 | 6.20-6.17 |
| 7.0 | 4.106-4.093 | 14.0 | 5.36-5.30 | 68.0 | 6.27-6.23 |
| 7.25 | 4.144-4.123 | 14.5 | 5.45-5.41 | 72.0 | 6.24-6.20 |
| 7.4 | 4.155-4.141 | 15.0 | 5.53-5.49 | 76.0 | (6.17-5.55) ^a 4.40-4.22 |
| 7.5 | 4.178-4.158 | 15.25 | 5.39-5.37 | 77.2 | 4.31-4.27 |
| 7.6 | 4.180-4.168 | 15.75 | 5.39-5.37 | 80.0 | 4.43-4.38 |
| 7.75 | 4.211-4.195 | 16.5 | 5.45-5.43 | | |
| | | 20.0 | 5.73-5.67 | 82.4 | 4.65-4.57 |
| 8.0 | 4.262-4.229 | 22.5 | 5.88-5.86 | | |
| | | | | 83.0 | 4.73-4.65 |
| 8.25 | 4.295-4.25 | 25.0 | 6.04-6.00 | | |
| | | | | 86.0 | 4.86-4.81 |
| 8.5 | 4.295-4.27 | 28.0 | 6.26-6.19 | | |
| | | | | 87.5 | 4.85-4.77 |
| 8.75 | 4.345-4.325 | 30.0 | 6.38-6.35 | | |
| | | | | 90.0 | 4.87-4.82 |
| | | 32.0 | 6.54-6.50 | | |
| | | 32.5 | (6.55-6.53) ^a 6.50-6.46 | 92.9 | 3.70-3.61 |
| | | | | 94.0 | 3.69-3.64 |
| | | 33.5 | 6.60-6.58 | | |
| | | 35.0 | 6.25-6.22 | 98.0 | 3.69-3.62 |

^a Two transitions observed in this sample.

the increase in T_c should be about the same for all. (4) Finally, consider the following experiment: A 50-50 mixture of Ga and Sn in a sealed tube was heated to above the melting point of Sn, shaken vigorously, and cooled quickly by immersing the tube in liquid nitrogen. Ga and Sn are mutually insoluble in the solid state. The quick frozen alloy, therefore, consisted of small crystals of Ga and Sn with no intermediate phases. The crystals were presumably highly strained internally, since Ga expands on freezing. When measured for superconductivity the sample showed two transitions, one at 4.1°K and the other at 2.0°K. Apparently T_c for both elements (Sn 3.73°K, Ga 1.08°K) was raised by the internal strains. The increase in T_c did not anneal after 30 min at 77°K but did disappear when the sample temperature was raised above the melting point of gallium.

II. EQUILIBRIUM TRANSITION TEMPERATURES

General Features

The lower curve in Fig. 4 and the data of Table I give T_c as a function of composition for indium-tin alloys annealed to equilibrium. As in the Hg-In system, the variation of T_c with composition within a single phase is always of one sign. In the In-Sn system, however, T_c increases with increasing number of valence electrons per atom (increasing Sn content) which is opposite to the situation in the Hg-In alloys.

Seraphim *et al.*³ have proposed an empirical formula to describe the variation of T_c with solute concentration in terminal solid solutions based on Sn, Al, and In. If we compare our observations in the In phase (not including compositions containing more than 8.25 at. % Sn, because of the electronic effect we observe at

that composition) with the empirical formula we find a progressively larger difference at the higher Sn concentrations. The difference is, however, not large in absolute terms, and it could perhaps be reduced by adjusting the two parameters in the empirical formula. The numbers are given in Table II. Our results are not in conflict with those of Seraphim *et al.*

We may ask whether the breaks in the T_c versus composition curve can be correlated with any gross chemical parameter such as mass or volume. Mass was effectively eliminated by the choice of In-Sn as the alloy system for study. In Fig. 5, volume per atom and spatial density of valence electrons are plotted as functions of composition. It is apparent by inspection that there is no overriding correlation with T_c from one phase to another, although within a given phase increasing atomic volume usually coincides with increasing T_c (the Sn phase appears to be an exception).

Olsen and Rohrer¹³ have examined the volume dependence of T_c and of the density of states $N(0)$ in those superconducting elements for which the necessary experimental information (pressure dependence of the critical field) is available. They could find no particular correlation between $d \ln T_c / d \ln v$ and $d \ln \gamma / d \ln v$, where γ is the electronic specific heat [proportional to $N(0)$]. They feel that the experimental results from pressure studies imply that the changes in transition temperature with volume are almost independent of the changes in density of states. As they themselves point out, this is not the usual point of view. It is of interest then to (1) compare our values of $d \ln T_c / d \ln v$ obtained directly from measured changes in T_c and v upon alloying with the values quoted by Olsen and Rohrer for pure Sn and In and (2) see to what extent our changes in T_c can be correlated with changes in density of states estimated from a free electron model.

Considering the first question we find from our T_c data and literature data¹⁴ on the lattice parameters that $d \ln T_c / d \ln v$ does not appear to be a significant parameter in our alloys, since it is not composition-independent. Furthermore, it is much larger than the values found by Olsen and Rohrer. For example, they

TABLE II. Our experimental transition temperature data in the In-terminal solid solution compared with the empirical formula of Seraphim *et al.* (Ref. 3). $\delta T_c(\text{calc})$ is equal to $k_1 x + k_2 x \ln x$, where x is the mole fraction of Sn and the k 's are constants.

| at. % Sn | T_c (°K) | $\delta T_c(\text{calc})$ (°K) | $\delta T_c(\text{obs})$ (°K) |
|-------------|---------------|-----------------------------------|----------------------------------|
| 0 | 3.41 | | |
| 2.0 | 3.51 | 0.12 | 0.10 |
| 4.0 | 3.71 | 0.36 | 0.30 |
| 6.0 | 3.98 | 0.65 | 0.57 |
| 8.25 | 4.275 | 0.99 | 0.865 |

¹³ J. L. Olsen and H. Rohrer, *Helv. Phys. Acta* **33**, 872 (1960).

¹⁴ C. G. Fink, E. R. Jette, S. Katz, and F. J. Schnettler, *Trans. Electrochem. Soc.* **88**, 229 (1945).

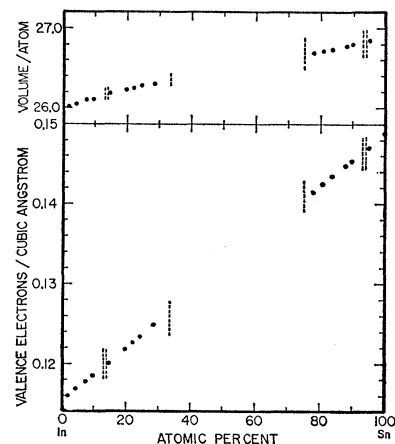


FIG. 5. Volume per atom and spatial density of valence electrons in the In-Sn system, based on the data of Ref. 13.

quote $d \ln T_c / d \ln v = 5.2 \pm 0.4$ for pure polycrystalline In, whereas we obtain approximately 42 for In rich alloys having the In structure. We conclude that transition temperature variation in alloy systems must depend upon a great deal more than volume variation, as might have been expected.

Considering now question (2), if we attempt to deduce the strong composition dependence of T_c , and in particular the discontinuities at the changes of phase, from the BCS¹⁵ microscopic theory of superconductivity, we are immediately frustrated by our lack of knowledge of $N(0)$, the density of states. Therefore, we cannot reasonably inquire whether the BCS approach is able to account for the jump in T_c at the phase boundaries, but we may reasonably ask whether the usual BCS formula, with a constant or slowly varying electron-phonon interaction parameter, can describe the variation of T_c within a single phase, where the variation of the density of states should, in this alloy system, resemble that calculated from a free electron model.

The BCS formula is

$$T_c = \alpha \theta_D \exp[-(1/N(0)V)], \quad (1)$$

where θ_D is the Debye characteristic temperature of the solid, α is a numerical constant of order unity, $N(0)$ is the density of states in energy at the Fermi energy (at 0°K), and V is a measure of the strength of the electron-phonon coupling which produces the superconductivity. The characteristic temperature is almost certain to be a gentle function of composition in this alloy system, and does not occur in the exponential in any case. Since In-Sn alloys contain no unfilled d band, $N(0)$ should increase smoothly in any given phase as increasing valence electron concentration expands the Fermi surface. We, therefore, expect T_c to increase with increasing Sn concentration in each phase, as observed.

To make a quantitative estimate of $N(0)$ we use a

¹⁵ J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).

TABLE III. In this table the variation of electron-phonon interaction parameter obtained from our experimental transition temperatures in the In terminal solid solution is displayed and compared with the Morel-Anderson parameter ($\lambda - \mu^*$). The values of θ_D (Debye temperature) and $N(0)$ (density of states) have been estimated as described in the text. a^2 and λ are intermediate parameters in the Morel-Anderson theory.

| At. % Sn | T_c (°K) | θ_D (°K) | $N(0)/[N(0)]_{\text{In}}$ | $[N(0)V]^{-1}$ | V/V_{In} | $(m^*/m)a^2$ | λ | $\lambda - \mu^*$ |
|-------------|---------------|--------------------|---------------------------|----------------|-------------------|--------------|-----------|-------------------|
| 0 | 3.410 | 109.0 | 1.0000 | 3.29 | 1 | 0.520 | 0.336 | 0.24 |
| 4.0 | 3.710 | 108.0 | 1.0067 | 3.16 | 1.034 | 0.518 | 0.337 | 0.24 |
| 8.25 | 4.275 | 106.9 | 1.0125 | 3.04 | 1.069 | 0.516 | 0.338 | 0.24 |

free electron model, assuming that the problem is simply one of free electrons in a box, and that the only effect of changing concentration is to change the number of electrons. The density of states is given by¹⁶

$$N(0) = C(N_a)^{1/3}(v_a)^{2/3}, \quad (2)$$

where N_a is the number of valence electrons/atom (equal to $3+x$ where x is the Sn concentration), v_a stands for volume per atom, and C is a constant. This model certainly has its limitations, but should be at its best in an alloy system such as ours. It is known to describe specific-heat data within experimental error in the Sn phase of the Sn-In system.⁴

Either the unknown parameter V or the density of states must change discontinuously at phase boundaries, since T_c does. Comparison of our data with Eq. (1) is, therefore, best made in the terminal solid solutions, where $N(0)$ can be normalized to the pure element and any changes in V or $N(0)$ arising from structure changes are absent.

We have compared our data for the In solid solution, 0–8.25 at. % Sn, with Eq. (1), and also with the theory of Morel and Anderson.¹⁷ The comparison, which is summarized in Table III, was accomplished as follows: The constant α in Eq. (1) was chosen to be 0.84.^{18,19} Debye temperatures were estimated from the known solidus temperatures with the Lindemann melting rule,²⁰ using the experimental value for pure In²¹ (109°K) to fix the adjustable constant in the Lindemann formula. The Debye temperature estimated in this way for the 8.25 at. % Sn composition differs by only 2% from the value for pure In. We, therefore, need not consider in detail the limitations of this method of estimating θ_D , since even a 100% error in estimating the change in θ_D would not seriously affect our conclusions about the composition dependence of T_c . The density of states we obtain from Eq. (2), again normalizing to the value

for pure In in order to fix the constant. This amounts to describing all compositions up to 8.25 at. % Sn by a free electron model with the same effective mass. The experimental electronic specific data for pure In²¹ ($\gamma = 1.60$ mJ/mole-°K) yields an effective mass ratio m^*/m of 1.3. The variation of $N(0)$ calculated on this model is not large, amounting only to a little over 1%, over the 8.25% composition range. Consequently, we find (Table III) that the observed variation in T_c with composition implies a large variation in V , approximately 7% over the 8.25% composition range. We, therefore, conclude that Eq. (1) with a constant or slowly varying V does not describe our data.

Morel and Anderson¹⁷ have attempted to calculate $N(0)V$ in terms of experimentally accessible parameters, primarily crystallographic data, with the aid of a number of simplifying assumptions. In particular, they disregard the details of crystal structure, approximating metals to a nearly free electron model (this may not be too unreasonable, see, e.g., Harrison,²²) and they also assume that the electron-ion interaction and the direct Coulomb interaction between electrons are characterized by the same screening radius, which is calculated with the Thomas-Fermi model. We have computed their parameter ($\lambda - \mu^*$), which is equivalent to $N(0)V$, for several compositions, with the results shown in the last column of Table III. No change at all is found over the composition range being considered. Apparently the factors causing the variation in T_c have been left out of the Morel-Anderson calculation.

Since the conclusions of each of the two preceding paragraphs depend upon the approximate validity of a free electron model, careful specific heat measurements would certainly be desirable.

In the other terminal solid solution, based on Sn, the variation of T_c with composition is not as strong as in the case we have considered. However, careful specific heat measurements have been made in this case, and the comparison of experiment with Eq. (1) can, therefore, be made with precision and confidence. Gayley *et al.*⁴ have established that a varying V is required if Eq. (1) is used to describe the data. They also point out that the variation required is about an order of magnitude larger than that arising from

¹⁶ D. H. Parkinson, Rept. Progr. Phys. **21**, 226 (1958).

¹⁷ P. Morel and P. W. Anderson, Phys. Rev. **125**, 1263 (1962).

¹⁸ J. K. Hulm and R. D. Blaugher, Phys. Rev. **123**, 1569 (1961).

¹⁹ B. B. Goodman, J. Hillairet, J. J. Veyssié, and L. Weil, in *Proceedings of the Seventh International Conference on Low-Temperature Physics, 1960*, edited by G. M. Graham and A. C. Hollis Hallet (University of Toronto Press, Toronto, 1961), p. 354.

²⁰ F. Lindemann, Physik. Z. **11**, 609 (1910); cited in J. M. Ziman, *Electrons and Phonons* (Oxford University Press, New York, 1960), p. 57.

²¹ C. A. Bryant and P. H. Keesom, Phys. Rev. **123**, 491 (1961).

²² W. A. Harrison, in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960), p. 28.

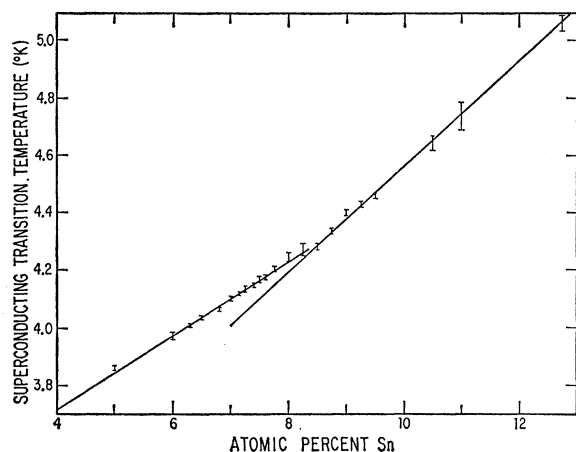


FIG. 6. Variation of transition temperature within the In phase, showing apparent electronic effect at about 8.25 at. % Sn. The spread shown on each point represents total transition width and is not to be interpreted as experimental error.

variations in lattice spacing according to the theory of Morel.²³

We, thus, come to the same conclusion reached by Gayley *et al.*, namely, that Eq. (1) is valid only with a variable V , and that the variation of V with composition which is required to fit the data is much larger than can be calculated from existing theory. As they point out, the work of Seraphim *et al.*³ in several nontransition metal alloy systems indicates a certain universality in the variation of V with alloying. In Sn, In, and Al based terminal solid solutions the effect of alloying on V is always such as to result in an increasing T_c once the electronic mean free path becomes less than the range of coherence.

Markowitz and Kadanoff²⁴ have recently calculated the effect of impurities upon T_c of a pure superconductor. They consider both the very dilute region (mean free path greater than coherence length) which need not concern us here, and the 'valence' region, up to impurity concentrations of order ten percent. They conclude that in this latter region, which is the region of our data, T_c should vary linearly with impurity concentration, at a rate determined by the gross properties of the solvent metal. Our observations in the In terminal solid solution are in agreement with this conclusion.

²³ P. Morel, *J. Phys. Chem. Solids* **10**, 277 (1959).

²⁴ D. Markowitz and L. P. Kadanoff, *Phys. Rev.* **131**, 563 (1963).

Electronic Effect

The curve of transition temperature versus composition changes slope at about 8 at. % Sn (Fig. 6). The data shown in Fig. 6 were obtained from samples annealed with considerable care, and the change of slope is felt to be real. It is very unlikely that a crystallographic phase change occurs in this composition, for the following reasons: (1) All evidence from the literature^{7,25} indicates otherwise; (2) the superconductivity discontinuity is small, unlike those associated with the known changes of phase, and (3) x-ray powder diffraction studies,²⁶ for samples, on both sides of the 8% discontinuity, for example on a sample containing 6.0 and one containing 12.75 at. % Sn, yielded similar patterns (In phase). The feature in the T_c versus composition curve is, therefore, probably an electronic effect, presumably arising from an interaction of the Fermi surface with a Brillouin zone boundary. Such an electronic effect should be reflected in a variety of other properties of the solid²⁷ and we are pursuing investigations along this line.

Phase Diagram

Although the refinement of the metallurgical equilibrium diagram of the In-Sn system was not the primary purpose of this investigation, a certain amount of information appeared automatically in the course of the transition temperature measurements. Superconductivity measurements have not traditionally been employed to any great extent in phase diagram work, but can be very helpful in determining phase boundaries, as, for example, in the mercury-indium system.²⁸ We will discuss the detailed findings in a later paper. For the present we note only that no evidence was found for the two compounds of indium and tin discussed by Meissner.²⁹

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²⁵ W. B. Pearson, *Lattice Spacings and Structures of Metals and Alloys* (Pergamon Press, Inc., New York, 1958), p. 699.

²⁶ We are indebted to Professor G. O. S. Arrhenius for the use of the diffractometer.

²⁷ W. J. Tomasch and J. R. Reitz, *Phys. Rev.* **111**, 757 (1958).

²⁸ B. R. Coles, M. F. Merriam, and Z. Fisk, *J. Less-Common Metals* (to be published).

²⁹ H. Meissner, *Phys. Rev.* **109**, 686 (1958).