

TABLE III. Estimate of reaction constants at 1170°K for Al-doped rutile, anion vacancy model.

K_2' :	$2.4 \times 10^{61} p^{-1/2}$,	$p = \text{pressure in mm Hg}$
K_3 :	$8 \times 10^{20} \text{ cm}^{-3}$	
K_4 :	$3.5 \times 10^{21} \text{ cm}^{-3}$	
K_5 :	$8 \times 10^{21} \text{ cm}^{-3}$	
K_6 :	$3.1 \times 10^{10} \text{ cm}^{-3}$	
K_i :	$2.4 \times 10^{32} \text{ cm}^{-6}$	

(Case 2. Al-doped nonstoichiometric rutile in Sec. III). The constants used in this calculation are grouped together in Table III. The results for $[V_A^-]$ and for $[Ti^{3+}]$ (electron concentration) and $[O^-]$ (hole concentration) are given in Table II. It is found that $[V_A^-] \propto p^{-1/3.2}$. Since $[Ti^{3+}] = (K_2'/K_3)[V_A^-]^{-1}$ it is seen that $[Ti^{3+}] \propto p^{-0.19}$ and that, consequently, $[O^-] \propto p^{+0.19}$.

Superconductivity in the Mercury-Indium Alloy System*

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The superconducting transition temperatures of a large number of Hg-In alloys have been measured and the variation of T_c with composition determined over the entire range. Variation of T_c with number of valence electrons/atom within any particular metallurgical phase is quite strong, T_c in general increasing with decreasing number of valence electrons. The maximum and minimum values of T_c occurring in the system are 4.5 and 3.1°K at approximately 80 and 20 at. % indium, respectively. HgIn, the only stoichiometric compound, has a transition temperature of 3.81°K. The observed composition dependence of T_c is not what one would expect either from Matthias's empirical rules or from the simple BCS formula, assuming a nearly free electron model for the density of states. In one phase a discontinuity in T_c and its composition dependence is found which cannot be correlated with a change in any lattice property and apparently arises from a discontinuous change in electronic structure. In connection with the problem of the effect of one phase upon superconductivity in another with which it is in intimate contact, there is evidence that the transition temperature of HgIn can be lowered a few tenths of a degree if large quantities of a lower transition temperature phase are also present. Electrical conductivity data, which were obtained in the course of the superconductivity measurements by an induced-current method, made possible also the determination of residual resistivity over the entire composition range.

INTRODUCTION

SEVERAL detailed studies of the variation of superconducting transition temperature, T_c , with composition in binary transition metal alloy systems^{1,2} have been made in recent years. Although the dependence of T_c on composition cannot yet be deduced in an unambiguous way from first principles, or even from the BCS model,³ a certain degree of empirical understanding has been achieved. In particular, the rule of Matthias,⁴ connecting T_c with average number of valence electrons per atom, has been remarkably successful in predicting transition temperature variation in a large number of binary and ternary transition metal alloy systems. Experimental work has been concentrated on alloys and intermetallic compounds with at

least one transition metal component, primarily because of the extensive ranges of solid solubility and the sets of isostructural compounds which are associated with transition metals and which are much less common in alloy systems of the nontransition metals. The alloying behavior of the transition elements facilitates comparison of different superconductors since variations in crystal structure can readily be avoided.

Even in binary transition metal systems where several different phases occur, for example Mo-Re, the superconducting transition temperature is found to vary predominately according to the variation of n (average number of valence electrons per atom) following Matthias' rule.⁴ Discontinuous changes in T_c occur at changes of phase but these are usually small compared with the over-all variation.

Data already available indicated that the dependence of T_c on n is less pronounced in alloy systems of the nontransition metals, than in alloy systems with a transition metal component. No comprehensive study had, however, been made over the entire composition range of a nontransition-metal alloy system, and so we decided to investigate the mercury-indium system.

In order to interpret the transition temperature

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¹ J. K. Hulm and R. D. Blaugher, *Phys. Rev.* **123**, 1569 (1961).

² G. F. Hardy and J. K. Hulm, *Phys. Rev.* **93**, 1004 (1954).

³ J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **106**, 162 (1957); **108**, 1175 (1957).

⁴ B. T. Matthias, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. 2.

measurements, it was necessary to establish the phase diagram of this alloy system. The superconductivity measurements were of considerable help in this. A detailed account of the phase diagram work has been published elsewhere.⁵

A preliminary report of the study of the variation of T_c with composition has been published.⁶ This preliminary work emphasized the so-called "quench effect," the discovery that T_c for a sample of given composition is often considerably higher if measured immediately after "quenching from the melt" (casting) into liquid nitrogen, than it is after the sample has been annealed to equilibrium. In this paper we discuss primarily the concentration dependence of the transition temperature in annealed specimens.

It proved possible to use our experimental technique for superconductivity measurements to determine the electrical conductivity of each sample just above the onset of the superconducting transition. These results are discussed below.

EXPERIMENTAL TECHNIQUES

The mercury and indium used were both stated to be at least 99.999% pure; the mercury was "Vacumetal" from Metalsalts Corporation, Hawthorne, New Jersey, and the indium (shot) was obtained from the Indium Corporation of America, Utica, New York. The samples were weighed into Teflon capsules with tight fitting caps and heated to 250°C in a rocking furnace. After rocking at this temperature for 30 min or longer, the encapsulated samples were quickly dropped into a bath of liquid nitrogen. This treatment typically cooled a

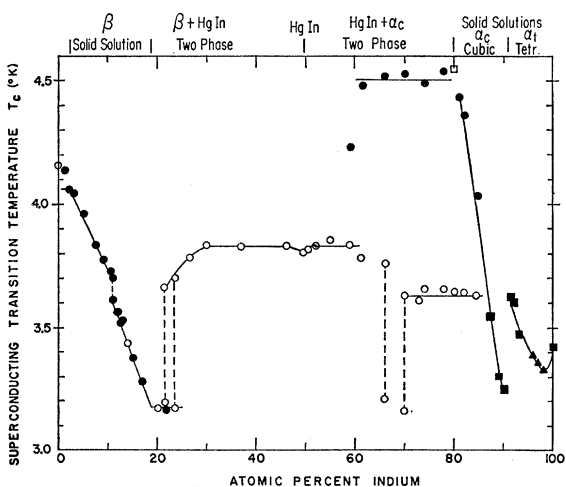


FIG. 1. Superconducting transition temperatures in the mercury-indium system. The temperatures plotted are the upper onset temperatures. Certain samples showed double transitions; these are connected in the figure by a vertical dashed line. Samples were annealed at various temperatures: \circ , 200°K; \bullet , 233°K; \square , 259°K; \blacksquare , 300°K; \blacktriangle , 373°K.

⁵ B. R. Coles, M. F. Merriam, and Z. Fisk (to be published).

⁶ M. F. Merriam and M. A. Jensen, *Cryogenics* 2, 301 (1962).

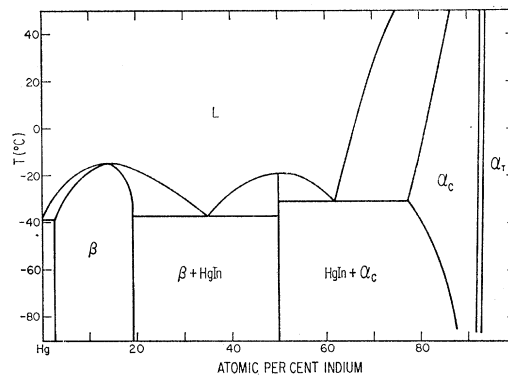


FIG. 2. Phase diagram of the mercury-indium system (taken from reference 5).

sample from above liquidus to well below solidus in less than a minute, as determined by measurements on a dummy sample. Some of the samples having liquidus temperatures well below room temperature were obtained simply by shaking the elements together at room temperature until the melt was homogeneous, then quenching into liquid nitrogen. After preparation the samples were annealed at one of the following temperatures: 100°C (furnace), 27°C (room), -14°C (refrigerator), -40°C (melting heptanone), and -78°C (dry ice-acetone). Annealing times to reach equilibrium varied from a few hours to several months, depending upon annealing temperatures and composition.

The superconducting transitions were observed by using a General Radio 1650-A impedance bridge to monitor the self-inductance of a coil containing the sample. The coil consisted of 4000 turns of AWG No. 38 enamel coated copper magnet wire on a hollow Teflon spool which contained the sample. The coilform had a wall thickness of 0.012 in. and could accommodate a cylindrical sample $\frac{3}{8}$ in. in diameter \times $1\frac{1}{4}$ in. long. The bridge operated at 1 kc and produced a magnetic field at the sample of about 1 G. The sensitivity, i.e., the smallest percentage of the sudden change in inductance defining the superconducting transition which could be reproducibly observed by this technique varied with the normal state electrical conductivity of the sample (in a way which we will discuss below) and with sample geometry, but in all but a very few cases was a few tenths of a percent. In the worst cases (e.g., pure Hg) the sensitivity was a few percent.

Temperatures below 4.2°K were obtained by submerging the coil in a bath of boiling liquid He⁴ the vapor pressure of which was measured with a Wallace and Tiernan FA129 absolute pressure gauge.⁷

To obtain temperatures above 4.2°K the apparatus was placed in the temperature gradient existing in the He vapor above the bath. Calibrated carbon resistors fastened to the outside windings of the coil served to

⁷ The temperature of the He⁴ for a given vapor pressure was taken from the 1958 He⁴ Scale of Temperatures (U. S. National Bureau of Standards, Monograph 10, 1960).

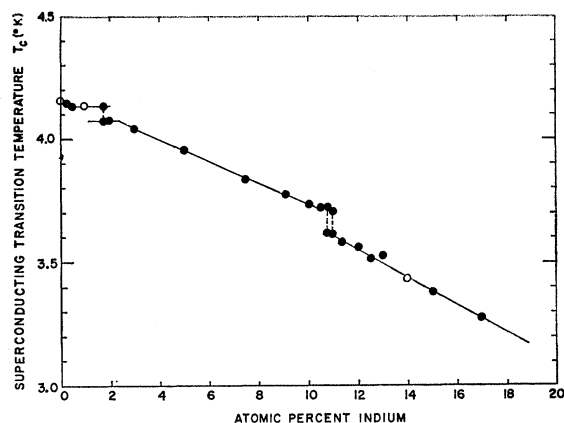


FIG. 3. Superconducting transition temperature for mercury-indium in the 0-20% indium region. The discontinuity in both T_c and its composition dependence at 11 at. % In apparently is not associated with any crystallographic phase change. Annealing temperatures: \circ , 200°K; \bullet , 233°K.

measure the temperature in this region. The calibration was made with Nb, Pb, and liquid He. We estimate the absolute error in our temperature determination in the range above 4.2°K to be $\pm 0.1^\circ\text{K}$ and the relative uncertainty to be not more than 0.05°K . Below 4.2°K these uncertainties are reduced by an order of magnitude.

By using a method similar to that discussed by Zimmerman⁸ and by Chambers and Park⁹ we were able to determine the normal state conductivity of our samples at a temperature T_n just above T_c . This method only required knowing L_0 the inductance of the empty coil at T_n , L_n the inductance of the coil with the sample in it at T_n , and L_s the inductance of the coil with the sample in it below T_c . The parameter which is a function only of sample conductivity (at $T = T_n$) is

$$\frac{\Delta L_n}{\Delta L_s} = \frac{L_0 - L_n}{L_0 - L_s} = F(\sigma).$$

Actually, ΔL_s is just a geometrical factor, and can be dispensed with by properly standardizing the geometry. The calibration of $F(\sigma)$ against σ can, thus, be carried out with any conductor, whether superconducting or not, using a standard four contact technique to measure $\sigma(T_n)$. $F(\sigma)$ depends on the experimental coil and its geometry and on the measuring frequency. Calibration is, therefore, specific to the apparatus and frequency used.

The advantages of this change of inductance method are (1) no leads need be attached to the sample, and (2) the electrical conductivity data are obtained automatically in the course of superconductivity measurements. Although the latter feature can also be obtained by using the resistance criterion for superconductivity,

inductive superconductivity measurements are often more reliable.

Although the absolute accuracy of the electrical conductivities is not as high as with the four-contact method, it is good enough for most purposes. The deviations in $\sigma(T_n)$ determined for the same material in radically different sample geometries imply a possible accuracy of a few percent. We feel that the calibration of our apparatus gives an uncertainty in absolute conductivity values of about 10%.

RESULTS

Annealed Samples

In Fig. 1, we show the transition temperature as a function of composition for annealed samples. The temperature plotted is the upper onset temperature. Our transitions were, in general, rather sharp, and none of the conclusions drawn from the data in this figure are changed if midpoint temperatures are used instead. The data of Reeber,¹⁰ obtained by resistivity measurements on annealed wires, are consistent with our more extensive induction measurements.

Included in Fig. 1 are results for samples annealed at several temperatures. Since one boundary of the close-

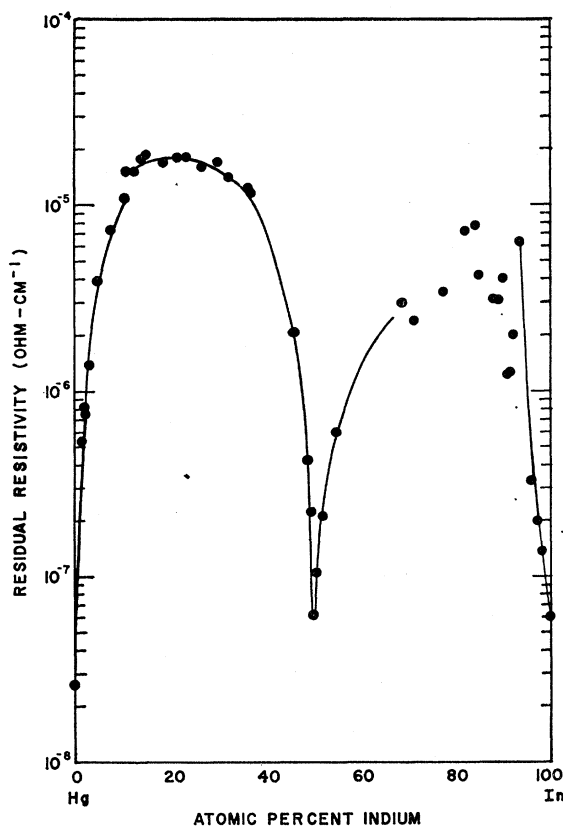


FIG. 4. Residual resistivity of mercury-indium alloys.

⁸ J. E. Zimmerman and Rev. Sci. Instr. **32**, 402 (1961).

⁹ R. G. Chambers and J. G. Park, Brit. J. Appl. Phys. **12**, 507 (1961).

¹⁰ M. D. Reeber, Phys. Rev. **117**, 1476 (1960).

packed cubic phase field is strongly temperature dependent (see phase diagram, Fig. 2), the equilibrium transition temperatures reached for certain compositions depend on the annealing temperatures used.

In Fig. 3, we show, to an expanded scale, the variation of T_c with x (x =at. % In) in a region of the β phase. The discontinuity in both T_c and dT_c/dx at 11 at. % In is well outside experimental error.

The depression of T_c with increasing solute concentration in dilute terminal solid solutions, an effect which has been studied extensively by other investigators,^{11,12} occurs in both dilute terminal solid solutions in the Hg-In system. Our data in the terminal solid solutions are shown in Figs. 1 and 3.

The electrical conductivity in the normal state at the superconducting transition temperature, measured by the induction technique described earlier, is given in Fig. 4. These data may also show a discontinuity at 11 at. % In.

"Quench Effect"

The "quench effect" is an increase in T_c arising from rapid cooling from the liquid state of an inhomogeneous specimen. We previously reported⁶ that the effect vanished in pure Hg. It has since been verified that it vanishes also in pure In. We have also determined experimentally that the temperature from which the samples are quenched is unimportant, provided that the samples are liquid when quenched. (By "quenched," we mean "quenched from the melt.")

No thorough study of the annealing of this quench effect was made but, in general, annealing at 200°K proceeded on a time scale of weeks or months, whereas annealing at 233°K required days or weeks. Proximity of the annealing temperature to the solidus temperature was, of course, an important consideration.

DISCUSSION

Superconductivity in Annealed Samples

By an "annealed sample" we mean a sample which has been annealed sufficiently for the superconducting transition to have reached a limiting value of temperature and width.

Terminal Solid Solution

The solid solubility of In in Hg is not extensive, amounting to only a fraction of 1%. In this range T_c decreases with increasing In concentration, the decrease amounting to 0.025°K in the saturated solid solution. Although our data are not extensive enough to apply the analysis of Seraphim *et al.*,¹² there is no reason to doubt that this is simply another case of the nearly

universal rule¹² that the transition temperature of a very dilute alloy decreases with increasing concentration of solute.

The indium-rich solid solution is another example of this rule. Our results here are consistent with those of Reeber,¹⁰ which have been included in the analysis of Seraphim *et al.*¹² Our data extend to somewhat higher Hg concentration than do Reeber's and fit quite well to the two-parameter equation of Seraphim *et al.*, using the parameters they derived from Reeber's data.

Cubic Close Packed Phase

The value of T_c drops discontinuously by about 0.4°K as the solid transforms from tetragonal to fcc at about 91% In; the cubic phase is less favorable for superconductivity. In the tetragonal-cubic transformation two of the several variables affecting T_c , namely, the number of valence electrons/atom and the atomic mass, do not change. Furthermore, the two structures are as nearly alike as two distinct structures can be, although the atomic volume does change slightly. If the change in T_c is ascribed to the change in atomic volume, then, using the x-ray data of Tyzack and Raynor¹³ to compute the volume change,

$$\Delta T_c/\Delta V = 11.6^\circ\text{K}/\text{\AA}^3, \quad (1)$$

where V is the volume *per atom*. A sensitivity of T_c to atomic volume of this order of magnitude is conceivable. For example, in the fcc phase, although high precision lattice data are not available throughout the composition range, it appears that the changes in V and T_c are consistent with the above relation to within a factor of 2. In this case, of course, the electronic concentration is changing also.

The In-Tl system also contains a tetragonal-fcc transformation, at 22.73 at. % Tl. In this case the volume change on going from tetragonal to cubic is positive—the lattice expands.¹³ Stout and Guttman¹⁴ have measured T_c across this phase boundary and they appear to find an *increase* in T_c on going from tetragonal to cubic. Their points are not spaced closely enough in composition to be certain that the increase in T_c is a discontinuity and that it appears at the phase boundary. If these were the only relevant results, we might hope that Eq. (1) has some coarse universal validity and that T_c correlates with atomic volume. In the In-Tl cubic phase, however, we find

$$\Delta T_c/\Delta V \approx -2.2^\circ\text{K}/\text{\AA}^3,$$

for the variations of T_c with atomic volume. In this case the volume is increasing with increasing Tl concentrations while the transition temperature is decreasing. Since all In-Tl compositions have nominally the same number of valence electrons per atom, namely,

¹¹ D. A. Lynton, B. Serin, and M. Zucker, *J. Phys. Chem. Solids* **3**, 165 (1957).

¹² D. P. Seraphim, C. Chiou, and D. J. Quinn, *Acta Met.* **9**, 861 (1961).

¹³ C. Tyzack and G. V. Raynor, *Trans. Faraday Soc.* **50**, 675 (1954).

¹⁴ J. W. Stout and L. Guttman, *Phys. Rev.* **88**, 703 (1952).

3, we conclude that our empirical correlation between ΔT_c and ΔV is not satisfied at all—even the sign is wrong. It may still be, however, that some important variable is changing with concentration in the fcc solid solution range and that the discontinuity in T_c accompanying the tetragonal-fcc transformation in Hg-In and Tl-In can be correlated with the discontinuity in atomic volume. Clearly more than two cases are needed to establish this correlation. Electronic specific heat measurements would be quite interesting here.

The variation of T_c with composition within the cubic phase in Hg-In is not what one would expect from the usual BCS formula.³ This point is discussed more fully in Appendix I.

Compound HgIn

It is amusing to note that the transition temperature (3.8°K) of this sharply stoichiometric compound is approximately halfway between pure Hg (4.15°K) and pure In (3.41°K). This compound is the only intermediate phase in the system which resembles the pure metals in absolute value of residual resistivity (Fig. 4). Unfortunately, the structure of HgIn has not been determined.

β Phase

This phase of unknown structure which extends from 2.5 to 19.1 at. % In resembles the two other phases in the system with extended homogeneity ranges in that T_c increases steeply with increasing Hg content. The most interesting feature in this phase is the discontinuity near 11 at. % In (Fig. 3) in both T_c and its derivative with respect to composition. This discontinuity occurs without any thermal arrest or change in x-ray diffraction pattern.⁵ We tentatively conclude that the effect is electronic in nature, such as might be expected, for example, if the Fermi surface, expanding as electron concentration is increased, crossed a Brillouin zone face. The electrical conductivity data (Fig. 4) appear also to show an anomaly near 11 at. % In, though less strikingly. We have not yet studied any of the other electronic properties of this alloy in which an anomaly should also be expected. To our knowledge this is the first time a discontinuity of this sort has been observed in superconductivity measurements within a single phase.

If the discontinuity does in fact arise from an electronic "Brillouin zone effect," it would seem that more consideration should be given to the role of the detailed structure of the Fermi surface in theoretical studies of superconductivity. It may be possible to use superconductivity measurements as a convenient tool for investigating Brillouin zone effects in other systems.

Although we have been regarding the β phase from 2.5 to 19.1 at. % In as a single-phase region, it cannot in fact be one if the electronic structure as revealed by

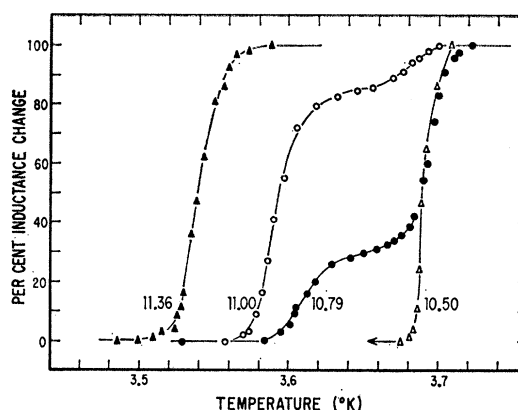


FIG. 5. Superconducting transition for four samples near 11 at. % In region. The numbers beside the curves give the atomic percentage of In.

the superconducting properties changes discontinuously in the region of 11 at. % In as it apparently does, for then the alloys with less than 11 at. % In are qualitatively different from those with more. There should then be a two-phase region near 11 at. % In, separating the two "electronic" phases. In the superconductivity measurements, we do actually find (Fig. 5) that two samples, 10.8 and 11.0 at. % In, show the characteristic double transition associated with a two-phase region. It is hardly surprising that the differential thermal analysis studies⁵ failed to give any hint of this phase boundary, since the heat evolved in an electronic rearrangement will be some orders of magnitude smaller than in usual lattice transformations.

Two-Phase Regions

The question as to what transition temperature will be measured by our magnetic method in a sample containing two superconducting phases with different transition temperatures, has several possible answers:

- (1) The entire sample may appear to become superconducting at the higher T_c .
- (2) The entire sample may appear to become superconducting at the lower T_c .
- (3) A partial transition may be observed at the higher T_c with the remainder of the specimen becoming superconducting at the lower T_c .
- (4) Entirely new transition temperatures may be observed (intermediate between those of the two phases separately).

All four of these possibilities are realized in the mercury-indium system. The first case is illustrated, for example by the alloys with 1, 30, 37, and 78 (annealed 233°K) at. % In. If the higher transition temperature phase is present in the proper grain shape and distribution, and in sufficient quantity, then it can be expected to form a closed shell and shield out the lower transition temperature phase completely.

The physical basis for case 2, which we observe in

the alloys from 73 to 85 (annealed 200°K) at. % In, is less clear. The most probable explanation is that the result arises from a (hypothetical) metallurgical tendency of the alloys in this composition range to consist of isolated precipitates of HgIn, each completely surrounded by cubic phase material. Since our measurement depends upon infinite conductivity in a shell enclosing the bulk of the sample, the superconducting transition of the HgIn would be hard to detect, and the sample would appear to become superconducting only at the transition temperature of the cubic phase material. This *ad hoc* conjecture could be verified by ordinary metallographic methods, provided the metallography were carried out below room temperature.

Case 3, two transitions, is observed whenever the amount or distribution of the phase with higher T_c is such that a completely closed shell is not formed, and the lower T_c phase is not completely shielded out. Some typical inductance vs temperature curves showing two transitions are reproduced in Fig. 5. Similar double transitions have been observed at the compositions corresponding to the vertical dashed lines in Fig. 1.

In the compositions of 21.5, 23.5, and 26.5 at. % In and in those of 66.0 and 70.0 at. % In, we observe a combination of Cases 3 and 4. The upper transitions in the first three samples have been depressed below the value which would have been expected, namely, the HgIn value of 3.83°K. Apparently, in this two-phase region (near 20% In) the intimate mixture of β material and HgIn material results in a modification of the T_c of the latter. This effect is not an artifact introduced by the method of handling the data; in particular, the selection of upper onset temperatures as a criterion for T_c is not essential. It is, of course, well known¹⁵ that T_c of a film of, for example, Sn may be progressively lowered by depositing increasing amounts of a nonsuperconducting metal (e.g., Ag) on top of it, provided only that all film thicknesses are small compared to a superconducting coherence length (10^{-5} cm). The presence of a degree of superconducting order in a superconductor above its transition temperature when it is in close physical contact with another (higher T_c) superconductor has also been observed.¹⁶ We are probably observing a similar situation here.

Two samples, at 66 and 70 at. % In, showed double transitions, with the lower T_c occurring well below that of either neighboring phase. The samples were measured after one month's, and again after three months', annealing (200°K), and it seems unlikely that the lower transition can be attributed to a nonequilibrium phenomenon. It could be suggested that it arises from a compound, not shown in Fig. 2, which decomposes between 200 and 233°K. However, we would not

propose such a compound on the basis of the superconductivity evidence alone.

General Considerations on the Hg-In System

Looking at the Hg-In system as a whole, the only consistent feature which stands out is the smooth and rapid increase in T_c with decreasing Hg concentration which occurs in every phase having an extended composition range. (The minimum in T_c in the indium rich terminal solid solutions is an exception not peculiar to Hg-In.) The variation of electrical conductivity with composition in these composition ranges is less consistent. The simple BCS formula and a nearly free electron model of the type Harrison¹⁷ has shown to be a very good description of most Group II and III metals would predict a decrease in T_c with decreasing x rather than the increase observed. (This is demonstrated in Appendix I.) The Matthias regularities, which describe rather well the variation of T_c with composition in the transition metals, seem inappropriate here, since T_c is a monotonic rather than a periodic function of electron concentration in our alloys. Evidence on other nontransition-metal alloy systems is needed to settle this point conclusively.

Looking at other indium-rich alloys one finds, after the initial mean free path effect, that Pb raises T_c of¹⁸ In as rapidly as does Hg, but that¹⁴ Tl has only a small and predominantly decreasing effect. If the difference between In-Tl and In-Pb is ascribed simply to an increase in number of electrons in the latter, one is left again with the In-Hg system as a complete aberration. It is perhaps conceivable that the tendency of mercury in chemical combination to form an "inert pair" of $6s^2$ electrons results, in its alloys, in a narrow, high density-of-states band arising from these levels. Such a band would favor superconductivity. It may be remarked that in pure Hg the density of states greatly exceeds the free electron value. In Tl and Pb this band would be full and play no part.

This concept might also help in the discussion of the β -phase behavior, for it is clearly shown by transition-metal alloys that abrupt changes of $N(E)$ with composition in a high density-of-states band overlapped by a more normal one need not lead to phase changes. The discontinuity in T_c and dT_c/dx at about 11 at. % indium appears to be the only example yet discovered of such a change in superconducting properties not associated with a change in crystal structure.

This is, however, highly speculative and serious consideration of such possibilities need only be given if band structure calculations for mercury show clearly that the nearly free electron picture with two conduction electrons is seriously inadequate.

¹⁵ W. A. Simmons and D. H. Douglass, Jr., Phys. Rev. Letters **9**, 153 (1962).

¹⁶ D. P. Seraphim, F. M. d'Heurle, and W. R. Heller, Appl. Phys. Letters **1**, 93 (1962).

¹⁷ W. A. Harrison, in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960), page 28.

¹⁸ W. Meissner, H. Franz, and H. Westerhoff, Ann. Physik **13**, 505 (1932). Also M. F. Merriam (unpublished).

*General Considerations on Superconductivity in
Nontransition-Metal Alloy Systems*

Even with a more complete theory of superconductivity than we at present possess, the calculation of the critical temperatures of the superconducting elements will still present great difficulties, difficulties of the sort that face the calculation of the normal-state conductivities. Such a calculation of the conductivity involves not only that of the strength of the electron-lattice interaction, but also a detailed consideration of the electronic structure of the particular metal; for it is obviously wrong to treat the carriers as identical or as being divided into a small number of sets, and integrals over at present unknown Fermi surfaces are involved. Both these aspects will still bedevil the fitting of experiment to theory in superconductivity, even if all questions about the role of Coulomb interaction and the cutoff of the phonon excitation spectrum are answered.

The properties of alloys would seem at first sight to present even greater difficulties, but it may be hoped that regularities of superconducting behavior as a function of electron concentration, residual resistivity, or other variables will help to focus attention on features of importance.

In contrast to the success of empirical rules put forward by Matthias⁴ for transition group superconductors, the full *d*-shell superconductors seem to show no consistent features, with the exception of the paucity of superconductors with fewer than two conduction electrons per atom; and even this has recently¹⁹ appeared in a different light. Where extensive ranges of solid solution exist, the critical temperature is a monotonic function of composition except for certain minima close to pure metals,¹² which may be associated with the transition to impurity-dominated scattering in the "dirty superconductor" region.²⁰ This is not surprising, however, since significant changes in electronic structure in alloys (Brillouin zone overlaps, etc.) are likely to be the source of the phase changes; and it is, therefore, probable that within most single phase regions θ_D and $N(E)$ will be smooth functions of composition.

ACKNOWLEDGMENTS

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APPENDIX I

BCS Formula in Hg-In Alloys

In the composition range $\text{Hg}_{0.20}\text{In}_{0.80}$ – $\text{Hg}_{0.10}\text{In}_{0.90}$ there exists a single phase—fcc solid solution—without change of lattice parameter. The superconducting transition temperatures of alloys in this composition

range change monotonically from 4.5°K (80% In) to 3.2°K (90% In). The existence of this phase, located far enough from pure In so that mean free path effects do not influence T_c , makes possible a test of the BCS relation

$$kT_c = 1.14\hbar\omega_{av} \exp(-1/NV),$$

which we approximate as

$$T_c = 1.14\theta_D \exp(-1/NV), \quad (\text{A1})$$

where N is the density of states in energy at the Fermi energy at 0°K, ω_{av} is some average phonon frequency, θ_D is the Debye characteristic temperature, and V is a measure of the strength of the electron-phonon interaction which produces the superconductivity. Since N , the density of states per unit volume, can be approximately computed from the free electron model and θ_D can be estimated from the Lindemann melting rule, we can make a rough check of the validity of Eq. (2) assuming a constant V . Values of N and θ_D so obtained will both be somewhat approximate, but the conclusions we draw will not be seriously affected by small inaccuracies. It is a feature of the BCS theory that V should be only weakly dependent upon composition. Since V cannot be independently determined, the theory is not very useful if this is not so.

Considering just the pure elements Hg and In, for example, Eq. (A1) works quite well; $V_{\text{Hg}}/V_{\text{In}} = 0.98$, which is essentially unity considering that Hg and In have radically different crystal structures, atomic weights, etc. We shall see that the fcc solid solutions, for which T_c varies approximately linearly, from 80–90% In do not satisfy the BCS relation nearly so well in spite of the fact that we might expect them to satisfy it better (identical unit cell dimensions, etc.).

The Lindemann melting rule for estimating θ_D of a substance from its melting temperature can be written in the form²¹

$$\theta_D = 120T_m^{1/2}\bar{A}^{-5/6}D^{1/3}, \quad (\text{A2})$$

where T_m is the melting (solidus) temperature, \bar{A} is the mean atomic weight, and D is the density. The solidus temperatures of the 80 and 90% In alloys have been measured in this laboratory⁵ and are 271 and 370°K, respectively. The densities are easily computed from the x-ray data.¹⁸ Computing θ_D we obtain 69.0 and 83.5°K for the 80 and 90% In compositions, respectively. For comparison, Eq. (A2) gives $\theta_D = 93$ °K for pure In.

To compute N we use the free electron formula²²

$$N = \frac{4\pi m^*}{h^2} \left(\frac{3n}{\pi V_a} \right)^{1/3}, \quad (\text{A3})$$

²¹ J. M. Ziman, *Electrons and Phonons* (Oxford University Press, New York, 1960), p. 58.

²² J. M. Ziman, *Electrons and Phonons* (Oxford University Press, New York, 1960), p. 107.

¹⁹ M. F. Merriam, *Bull. Am. Phys. Soc.* **7**, 474 (1962).

²⁰ P. W. Anderson, *J. Phys. Chem. Solids* **11**, 26 (1959).

TABLE I. Summary of data for the Hg-In alloys.

Metal	T_c	θ_D	γ (cal/mole-deg ²)	m^*/m
Hg	4.15	73 ^a	4.57×10^{-4}	1.9
Hg _{0.20} In _{0.80}	4.6	69.0 ^b	3.85 ^d	1.4
Hg _{0.10} In _{0.90}	3.2	83.5 ^b	3.89 ^d	1.4
In	3.4	111 ^c	3.94 ^e	1.4

^a R. L. Douglass, R. G. Petersen, and N. E. Phillips, in *Proceedings of the Seventh International Conference on Low Temperature Physics*, edited by G. M. Graham and A. C. Hollis Hallett (University of Toronto Press, Toronto, Canada, 1961), p. 403.

^b Lindemann melting rule. See text.

^c B. S. Chandrasekar and J. A. Rayne, *Phys. Rev.* **124**, 1011 (1961).

^d Estimated on modified free-electron model. See text.

^e J. E. Schirber and C. A. Swenson, *Phys. Rev.* **123**, 1115 (1961).

with an effective mass m^* . In Eq. (A3), V_a is atomic volume and n the number of electrons/atom. For In, $n=3$, and the 80 and 90% In alloys $n=2.8$ and 2.9, respectively. Since N is related to the electronic specific heat, it can be determined calorimetrically. If this is done for In,²³ the value obtained satisfies Eq. (A3) for $m^*/m=1.4$. Consequently, we will use this value of m^* for the fcc solid solutions, obtaining the values of γ ($C_e=\gamma T$) shown in Table I.

We observe that, in going from 80 to 90% In, both γ , which is directly proportional to N ($\gamma=\frac{1}{3}\pi^2k^2N$), and

²³ J. M. Ziman, *Electrons and Phonons* (Oxford University Press, New York, 1960), p. 117.

θ_D increase with increasing indium content in the range 80–90% In, but that T_c decreases. Equation (1), therefore, does not give even a qualitative description of the situation, since it predicts an increase in T_c if θ_D and N both increase and V is approximately constant.

If we ask what variation in V is necessary to fit the data for T_c , we find

$$V(80\% \text{ In})/V(90\% \text{ In})=1.15. \quad (\text{A4})$$

Since use of the Lindemann rule to calculate θ_D is probably the least certain assumption in the above calculation, we verify the insensitivity of the conclusion to this result. If we assume, as an extreme case, $\theta_D(80\% \text{ In})=\theta_D(90\% \text{ In})=83.5^\circ\text{K}$, we calculate the ratio (A4) to be 1.10 instead of 1.15.

It is difficult to understand a 15% variation in V over a 10% composition range in a single phase solid solution alloy where the lattice parameter does not change appreciably and the density of states presumably reflects only a 3% change in number of conduction electrons/atom.

We conclude that our results for compositions Hg_{0.20}In_{0.80} to Hg_{0.10}In_{0.90} are not well described by Eq. (A1).

Neutron Diffraction Study of Short-Range Order in β -CuZn*

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Neutron diffuse scattering measurements have been made on an isotopically enriched single crystal of β CuZn at a series of temperatures above T_c . The observed short-range order scattering exhibited the general characteristics of critical scattering, quite unlike the diffuse scattering reported for any other ordering alloy, and confirmed that the order-disorder transformation in this alloy is a phase transformation of second (or higher) order. No quantitative evaluation of the short-range order parameters from the measured scattering was possible. A comparison of the measured scattering with calculations based on the theories of Zernike, Cowley, and Elliott and Marshall showed rather good agreement, suggesting that these simple theories give a reasonable approximation to the actual short-range order correlations above T_c . From a consideration of the discrepancies between these theories and the experimental data, it appears that at temperatures above T_c the Ising model forms a surprisingly good model for this alloy.

INTRODUCTION

X-RAY diffuse scattering studies of short-range order in binary alloys have centered primarily on alloys with face-centered cubic lattices,¹ such as the well-

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¹ See, for example, the review by B. E. Warren and B. L. Averbach, in *Modern Research Techniques in Physical Metallurgy* (American Society for Metals, Cleveland, 1953).

known Cu₃Au. Only three such studies have been made on alloys of an equally interesting type, the equiatomic body-centered cubic alloys, and in two of these (LiMg² and MoTi³) the alloys do not order at any temperature, while in the third⁴ (β -AgZn) a complex hexagonal

² F. H. Herbstein and B. L. Averbach, *Acta Met.* **4**, 414 (1956).

³ J. Dupouy and B. L. Averbach, *Acta Met.* **9**, 755 (1961).

⁴ E. Suoninen and B. E. Warren, *Acta Met.* **6**, 172 (1958).