corresponds with the 0.7-ev level determined earlier by the post-bombardment conductivity method.[3]

Finally, it is seen in Fig. 3 that an additional peak is present at 0.74 ev following neutron irradiation. This has not been reported previously. This peak is not observed in annealed unirradiated crystals. Furthermore, it is enhanced by subsequent electron bombardment, and is observed to decay afterward.

V. ACKNOWLEDGMENT

It is a pleasure to express our appreciation to Dr. J. F. Marshall for many helpful discussions.

PHYSICAL REVIEW VOLUME 117, NUMBER 6 MARCH 15, 1960

Superconductivity of Dilute Indium-Mercury Alloys*

Morton D. Reeber
International Business Machines Corporation, Research Laboratory, Poughkeepsie, New York

(Received October 12, 1959)

Measurements were made of the critical magnetic field for the transition from the superconducting to the normal state in polycrystalline rods of the substitutional solid solution In-Hg, containing 0–7 atomic percent Hg. The treatment given these alloys was designed to assure homogeneity in composition in which case the transitions to the normal state were found to be similar to those for pure elemental superconductors. It was, moreover, possible to distinguish between properties that are characteristic of the ideal alloy system and properties which arise from structure within the specimen. T_c, the transition temperature at zero field, was measured as a function of composition and was found initially to decrease (up to a concentration of 1.75 atomic percent Hg) after which it began to increase with added Hg concentration. The width of the transition to the normal state, as measured by the variation of specimen resistance in a longitudinal magnetic field, was found to show a regular dependence upon composition, and also reached a minimum value at 1.75 atomic percent Hg. The superconducting properties of pure indium were measured and used as a standard. For indium it was found that:

$$T_c=3.407\pm0.002^\circ\text{K};\quad H_0=293\pm2\%\text{ oersted};$$

and $(dH_c/dT)|T_c=-155.5\pm3\%$ oersted/°K.

INTRODUCTION

THE characteristic properties of a pure elemental superconductor, relatively free from strains and inhomogeneities, are usually found to embody a discontinuous change in resistance at the critical temperature, a well-defined, reproducible, and unique critical field, and exclusion of magnetic flux upon entering the superconducting state.[1] Experiments with alloys, impure or strained elements, and compounds frequently reveal, in contrast to pure elemental materials, strikingly different properties.[1–4] For example, high magnetic fields may be required for the restoration of the full normal state resistance, the Meissner-Ochsenfeld effect is often incomplete and does not coincide with the loss of electrical resistance, the transition between states frequently takes place only over large field and/or temperature intervals, and currents flowing in the specimen often affect the transition, as measured by resistance techniques, in a manner which suggests that the supercurrent is localized in small regions of the specimen. Such behavior has, more often than not, been inferred to be the normal inherent behavior of alloys.[1]

On the other hand, not all alloys are found to behave in the manner described above. Stoichiometric compounds and certain alloys,[5–7] when prepared with great care have occasionally exhibited transition characteristics similar to those of pure elemental superconductors. This suggests the possibility that homogeneity of the system might be a significant factor in making a solid solution alloy behave like a pure elemental superconductor.

We have attempted to investigate this possibility by a careful study of the indium-mercury alloy system, chosen because of its convenient critical temperature and critical field range, and the ease with which the material could be cold worked and annealed. Moreover, both elements are available in extremely pure form and it was therefore hoped that detrimental effects due to the presence of unknown impurities would thereby be avoided.

EXPERIMENTAL PROCEDURE

The alloys used for these measurements were prepared from 99.999% pure indium[8] and triple-distilled mercury. The materials were weighed, placed in a Pyrex tube, sealed off in vacuum, melted, mixed vigorously, and quenched in an oil bath. Quenching was of particu-

---

* This work was supported in part by the Department of Defense.

[1] For a general discussion of the properties of pure elemental and alloy superconductors see D. Shoenberg, *Superconductivity* (Cambridge University Press, New York, 1952).

[2] W. J. deHaas and J. Voogd, Commun. Phys. Lab. Univ. Leiden No. 208b (1930).

[3] P. R. Doidge, Proc. Roy. Soc. (London) **A248**, 553 (1955).

[4] B. G. Laserew and A. A. Galkin, J. Phys. (USSR) **8**, 371 (1944).

[5] D. Shoenberg, Nature **142**, 874 (1938).

[6] B. G. Laserew and I. E. Nakhutin, J. Phys. (USSR) **6**, 116 (1942).

[7] J. W. Stout and L. Guttman, Phys. Rev. **79**, 396 (1950).

[8] Johnson Matthey & Company, Catalog No. 380.

lar importance in achieving the goal of homogeneity. The process of making single crystal specimens by slowly cooling through the liquid plus solid region usually leads to long-range segregation of the constituents. The distances involved are such that it is impossible for normal solid diffusion to decrease significantly the variations in compositions through subsequent annealing. The quenching process, on the other hand, results in a fine grained polycrystalline specimen with segregation limited to variations within the individual crystallites. After quenching, the 19-mm diameter alloy block was extruded through a 1.2-mm die which was polished with 0.1-micron abrasive powder. This working of the specimen further reduced the distances over which diffusion would have to take place by mechanically mixing the solution while in the solid state. The resulting specimen was a rod approximately 5 meters long. It was found, by chemical analysis of sections cut periodically from the rod, that there was a monotonic change in composition along the rod which amounted to less than 2% of the Hg content. Thus the variation in composition along a 75-mm sample was expected to be less than 0.04% of the impurity added.

The specimens were annealed at 90% of the Kelvin solidus temperature (in an evacuated tube) for varying periods of up to 2000 hours. It was found, by x-ray analysis of the annealed specimens, that there was a great variety of crystallite sizes, and that the lattice constants agreed with those reported by Tyzack and Raynor.[9]

Transitions from the superconducting to the normal state, at constant temperature, were measured by plotting continuously the variation of specimen resistance as a function of longitudinally applied magnetic field on an $X-Y$ recorder. The term resistance transition will be used for convenience in referring to transitions measured by means of this technique. In addition, for some specimens, the variation of susceptibility through the transition was measured using a technique similar to that employed by Doidge,[3] and transitions measured in this way will be called flux transitions.

Groups of four specimens, including a pure indium specimen as a standard, were mounted in V grooves in anodized aluminum blocks. A carbon resistor imbedded in the block was used as the control element in a temperature regulating scheme similar to that described by Sommers.[10] This system, in conjunction with a bellows type manostat, was designed to keep the specimen temperature constant to 10^{-4} °K during the course of a single measurement. The longitudinal magnetic field was supplied by a coil wound according to a method described by Garrett[11] and the field obtained was calculated to be uniform to one part in one thousand over the volume occupied by the samples. The over-all accuracy of the field measurement was approximately $\frac{1}{2}$% of the applied field, the limit being set by the accuracy with which the field coil current was measured, and the accuracy with which the relation between field coil current and magnetic field was established.

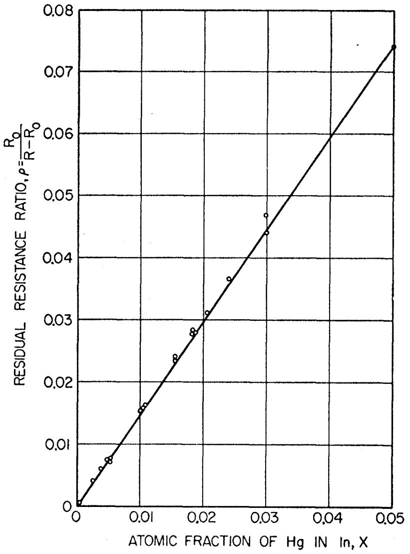

FIG. 1. The residual resistance ratio of In-Hg alloys.

The critical field at 0°K was determined from an analytic expression obtained by a least squares fit of the data points using an IBM 704 computer. The form chosen for the expansion was $H_c=C_1+\sum_{i=2}^{n} C_iT^i$ where H_c is the critical field, T is the temperature, and the C_i's are determined by the fitting procedure. The expansion was ended at $i=3$ since expansions of higher order gave no better fit according to Gauss' criterion.[12]

EXPERIMENTAL RESULTS

1. General Behavior

Measurements of the resistance of the specimen at 300°K (R) and at 4.2°K (R_0) enabled the ratio $\rho=R_0/R-R_0$ to be calculated for the alloys. According to Mathiesen,[13] the total resistivity is equal to the sum of the temperature dependent lattice scattering and the temperature independent impurity scattering. Within the precision of the measurement, no change in resistance could be detected at temperatures below 4.2°K, except for the pure In specimen. Consequently, R_0 is a measure of the impurity scattering alone and hence is proportional to the Hg concentration up to the limit of solid solubility, assuming, of course, that the alloying element is added homogeneously. Measurements of the resistance at nitrogen temperatures allowed for an estimate of the Debye temperature, which within the limits of accuracy, did not change with alloying.

---

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

[10] H. S. Sommers, Jr., Rev. Sci. Instr. **25**, 793 (1954).

[11] M. W. Garrett, J. Appl. Phys. **22**, 1091 (1951).

[12] A. G. Worthing and J. Geffner, *Treatment of Experimental Data* (John Wiley & Sons, New York, 1943), pp. 260.

[13] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1953), 2nd ed., p. 310.

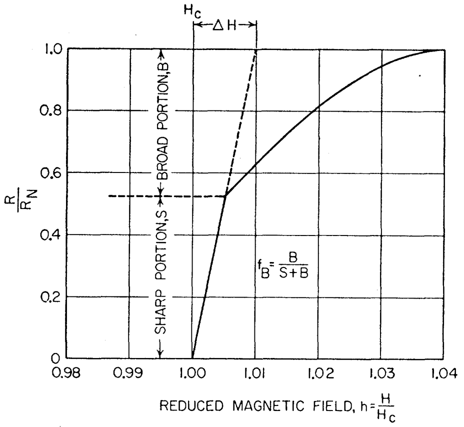

FIG. 2. A typical resistance transition of an alloy.

Examination of Fig. 1, which contains a plot of the change in resistivity ratio with increasing Hg content, shows that ρ was linear with Hg concentration up to 5 atomic percent Hg. For groups of adjacent specimens cut from the same rod and given different annealing treatments, the variation in ρ was less than 2%, independent of annealing. This variation can be accounted for by a change in composition of 0.04% of the impurity along the length of a 75-mm sample.

The resistance transitions in general took the form of an abrupt introduction of resistance over a field interval of less than 0.008 H_c, followed by a further increase to the resistance R_n of the normal state in a field interval that was often a large fraction of H_c.[14] One such typical transition is shown in Fig. 2 and others in Fig. 3.

The broad fraction, f_B, of the transition is defined here as the fraction of resistance not introduced abruptly (see Fig. 2). f_B was sensitive to many variables some of which can be described at least in qualitative terms. The effect of measuring current on f_B (see Fig. 3) was particularly important and in all cases f_B decreased with increasing measuring current. Thus in those cases where an initial abrupt increase of resistance could not be observed it was possible to produce one by sufficiently increasing the specimen measuring current. The almost completely broad transition shown in Fig. 3 (0.005-ampere curve) is a typical example of this behavior. As shown in the figure, increasing the measuring current to 0.5 ampere produces the initial abrupt increase in resistance. A careful examination of the toe of the 0.005-ampere transition will also reveal the presence of this abrupt increase. Expanding the scale by a factor of 20, as in the inset of Fig. 3, shows that even at 0.005 ampere the abrupt increase in resistance is present. Sufficient amplification was available to observe the abrupt increase in resistance for all specimens.

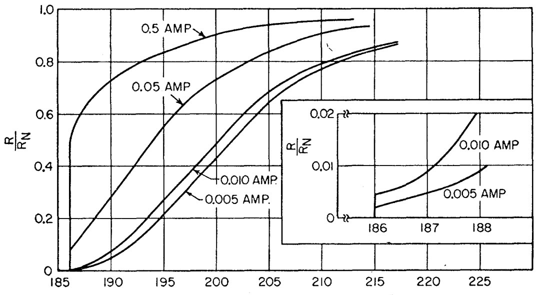

FIG. 3. The effect of measuring current on the resistance transition. $x=0.066$; annealed at 296°K for 100 hours.

f_B also depended upon the reduced temperature, $t=T/T_c$ at which the transition was measured. Although variable for different specimens, f_B consistently decreased rapidly as the measuring temperature approached the critical temperature, as shown in Fig. 4.

Annealing the specimen was always effective in decreasing f_B. For specimens with compositions of less than 2 atomic percent Hg content, f_B could, by annealing, eventually be reduced to zero. Above 2 atomic percent Hg, f_B increased with increasing impurity content and could not always be reduced to zero. In fact, prolonged annealing (about 3000 hours) increased f_B in some of the higher concentration alloys, and the possibility exists that in a lengthy anneal the mercury tends to segregate out at the grain boundaries. This was dramatically illustrated by a high concentration (10 atomic percent), large polycrystal sample that, following a lengthy anneal at room temperature, fell apart. The grain boundaries of this sample were liquid, indicating a Hg content at the boundaries of greater than 30 atomic percent.

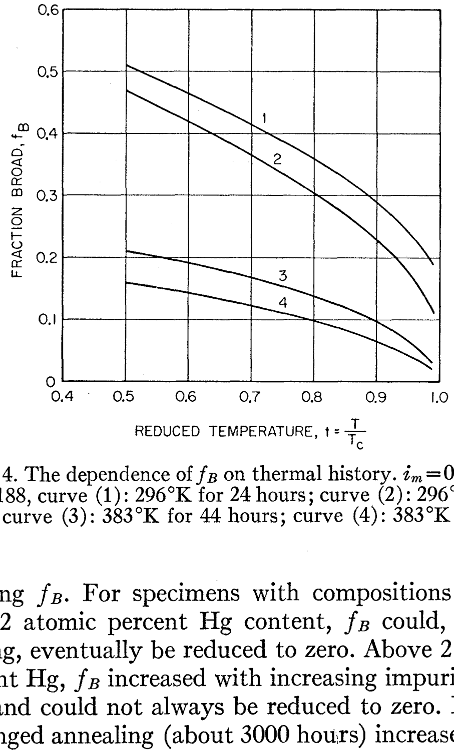

FIG. 4. The dependence of f_B on thermal history. $i_m=0.10$ amp, $x=0.0188$, curve (1): 296°K for 24 hours; curve (2): 296°K for 66 hours; curve (3): 383°K for 44 hours; curve (4): 383°K for 1440 hours.

In contrast to the sensitive variation of the broad fraction with measuring current and annealing treatment, the sharp portion of the transition occurred at a well-defined value of the magnetic field independent of

---

[14] Transitions of a similar form were also observed in Ta specimens by D. P. Seraphim and R. A. Connell, Phys. Rev. **116**, 606 (1959).

the specimen current and annealing treatment. That is, changing the annealing treatment or measuring current did not shift the sharp portion of the transition along the field axis, as is illustrated in Figs. 3 and 5. The nonsensitive behavior of the sharp portion of the transition suggested that perhaps the greater fraction of the material was involved in the sharp portion of the transition. To investigate this possibility, simultaneous resistance and flux transitions were measured, and a series of these are shown in Fig. 6. Examination of the curves will reveal that where a sharp step in the resistance transition can be observed, the smallest magnetic field for which R is unequal to zero is the same field at which approximately 50% of the magnetic flux is excluded from the superconductor. This defines the critical magnetic field, H_c, which separates the superconducting from the normal state. Curve VII of Fig. 6, because of the scale used, does not appear to have a sharp step. If the resistance scale were expanded as in the inset of Fig. 3, the step would appear at the point marked H_c, or alternatively, the step could be observed by increasing i_m. According to the Silsbee hypothesis,[15] increasing i_m from 0.005 ampere to 0.5 ampere at a critical field of 185 oersted will shift the critical field in this particular sample by only 0.01%, which is well below the limit of sensitivity of the field measuring apparatus. Figure 3 shows no discernable shift in H_c for the sharp portion of the transition. Consequently, it is possible to identify the broad portion of the resistance transition with small, nonuniform regions of the specimen, and the sharp portion with the bulk of the alloy. This experiment also emphasizes the difficulties involved in the often used criterion for the critical field of the specimen, that is, the field at which 50% of the normal resistance is returned. Using this criterion, one would say that the critical field of the specimen in Fig. 3 had shifted by more than 10%, even though the critical field of the great majority of the specimen has not changed. For this reason, alloy behavior as exemplified by the In-Hg system was investigated by means of the sharp portion of resistance transitions.

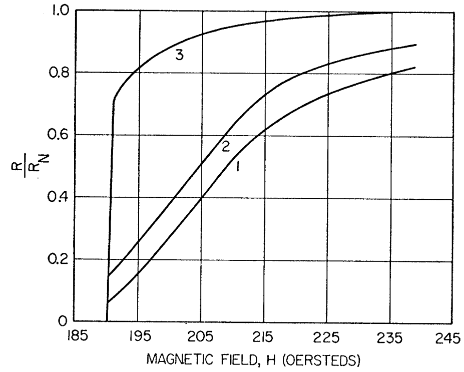

FIG. 5. Resistance transitions for specimens with different thermal history. $x=0.0498$, $t=0.62$; $i_m=0.10$ amp, curve (1): 296°K for 725 hours; curve (2): 368°K for 100 hours; curve (3): 383°K for 100 hours.

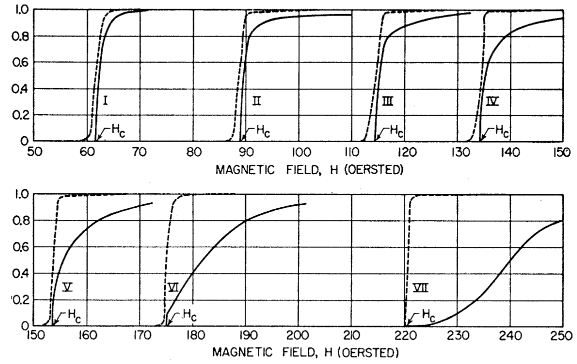

FIG. 6. Comparison of flux and resistance transitions. $i_m=0.05$ amp, $x=0.068$, solid curves: R/R_n; broken curves: the fraction of material in the normal state.

The change in resistance at the sharp step was not discontinuous, however. Over the resistance interval 0 to $1-f_B$ this change appeared to be linear with field, as a consequence of which a ΔH could be defined as the H interval over which R would change from 0 to R_n if f_B were equal to zero (Fig. 2). The width of the transition can be expressed in terms of $\Delta H/H_c$, a quantity which is roughly independent of measuring current and reduced temperature for a well-annealed specimen. The transition width defined in this way showed a regular dependence on composition (Fig. 7), with a minimum at 1.75 atomic percent Hg. For specimens of this shape the width of the transition due to demagnetizing effects was calculated to be $\Delta H/H=0.0010$. The sharpest transition in the presence of field occurred with $\Delta H/H=0.0015$, while in the absence of a field the temperature interval required was less than 0.4×10^{-3} °K (Fig 8).

MATERIAL PROPERTIES

Pure Indium

The measured value of T_c for indium, 3.407±0.002°K (1958 temperature scale[16]) is compared with the values

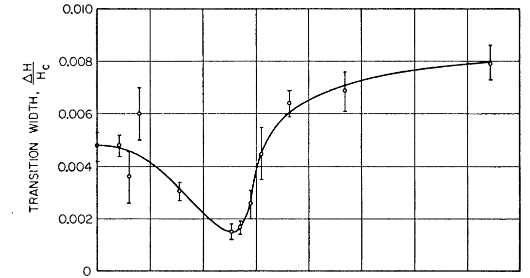

FIG. 7. The width of the resistance transitions for dilute In-Hg alloys.

---

[15] F. B. Silsbee, J. Wash. Acad. Sci. **6**, 597 (1916).

[16] H. van Dijk, M. Duriex, J. Clement, and J. Logan, *Proceedings of the Kammerlingh-Onnes Conference on Low-Temperature Physics, Leiden, 1958* [Suppl. Physica **24**, 5129 (1958)].

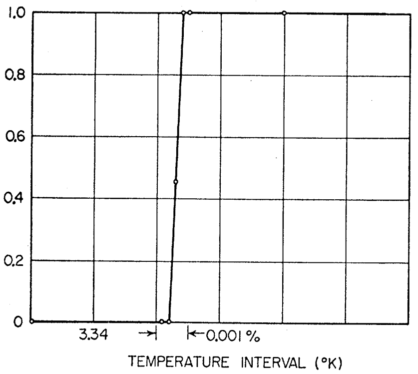

FIG. 8. The transition to superconductivity of indium with 1.85 atomic percent mercury at $H=0$. $i_m=0.010$ amp.

reported in the literature after 1952[17–20] and listed in Table I. Clement and Quinnell's are the only results that differ by more than the stated experimental error. The discrepancy probably arises here because of the relatively impure indium used by them (1000 ppm impurity content; an impurity content which, by interpretation of the present results and those of Lynton, Serin, and Zucker,[21] could depress T_c by 0.02°K). The high value of H_0 reported here may have resulted from the long extrapolation used to obtain it, since the temperature measurements extended no lower than $t=0.4$. This high value of H_0 gives rise to the high value of γ.

Indium-Mercury Alloys

The addition of Hg to In initially depresses T_c (Fig. 9). Although the depression is not linear, the initial slope as a function of reciprocal mean free path is $-1.9\pm0.6\times10^{-6}$ deg-cm which agrees with other results on In alloys.[22] Increasing the amount of mercury further depresses T_c until a minimum is reached at 1.75 atomic percent Hg, T_c having dropped 0.064°K. T_c then rises as the Hg concentration is increased beyond 1.75 atomic percent and with 5 atomic percent Hg it is 0.020°K above T_c for pure In.

TABLE I. Comparison of recently reported constants for pure indium.

T_c °K (1958)	Impurity content parts per million	H_0 oersted	$(dHc/dT)\|_{Tc}$ oe/deg	$\gamma\times10^4$ cal/mole/deg^2	Ref.
3.387 ±0.005	1000	278.4		4.33 (cal)	17
3.409 ±0.002	less than 5	275.0	−142.2	4.0 (mag)	18
3.404 ±0.003	300	284.5	−155.8		19
3.408 ±0.005	300		−137.6		20
3.407 ±0.002	less than 5	293.0 ±2%	−155.5 ±3%	4.6 (mag)	this work

If the analytic form of the critical field curve is expressed as $h=1-\alpha t^2+(\alpha-1)t^3$, then the curve fitting procedure which determined H_0 also determines α. For all the specimens tested, α varied in a random manner by less than 4%. The slope of the critical field at T_c remained constant at $-155.5\pm3\%$ oe/deg. Thus within the limits of experimental accuracy, the reduced critical field curves were invariant.

The variation in H_0 with Hg concentration was similar to the variation in T_c, and showed a minimum at the same Hg concentration.

The coefficient of the linear term of the electronic specific heat in the normal state, γ, was calculated using the relation[23]

$$\gamma=\frac{0.17H_0^2V_m}{T_c^2 4.186\times10^6}\ \text{calories/mole-deg}^2.$$

The scatter was appreciable, as can be seen from Fig. 10,

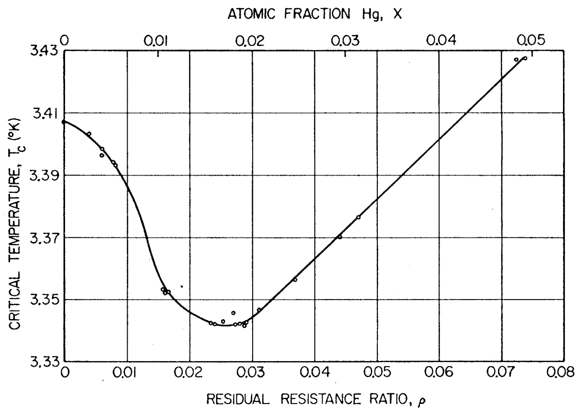

FIG. 9. The variation of critical temperature with mercury content in indium.

but all the experimental points fell within 2% of the line drawn in the figure. Thus γ appears to be increasing at the rate of approximately 3×10^4 cal/mole-deg^2 per unit change in ρ.

Discussion

A conclusion that can be drawn from this work is that the two portions of the resistance transition can be considered separately. The sharp portion of the transition can be identified with the bulk transition of the specimen, and is the property of a homogeneously distributed alloy of the given composition. The simultaneous susceptibility and resistance measurements confirm this by showing that the nearly discontinuous appearance of resistance corresponds to the penetration of magnetic field throughout the volume of the alloy. Even in the In+6.6 atomic percent Hg alloy the penetration of field was 98% complete in a field interval of 1 oersted at

---

[17] J. R. Clement and E. H. Quinnell, Phys. Rev. **92**, 258 (1953).
[18] E. Maxwell and O. S. Lutes, Phys. Rev. **95**, 333 (1954).
[19] N. L. Muench, Phys. Rev. **99**, 1814 (1955).
[20] H. Meissner and R. Zdanis, Phys. Rev. **109**, 681 (1958).
[21] E. A. Lynton, B. Serin, and M. Zucker, J. Phys. Chem. Solids **3**, 165 (1957).
[22] G. Chanin, E. A. Lynton, and B. Serin, Cambridge Conference on Superconductivity, Cambridge, 1959 (unpublished).
[23] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

$H_c = 248$ oersted and resistance (although only a small fraction of the normal resistance) appeared abruptly at this field.

Since the magnitude of f_B is dependent upon annealing, it is doubtful that f_B is an intrinsic property of the alloy system. f_B is probably due to irregularities, possibly in composition, which exist throughout the specimen. Data on specimens with different numbers of grain boundaries and defects remaining after plastic deformation show that these two effects are of minor importance in producing the broad transition. This behavior indicates that a homogeneous distribution of the solute is of major importance in achieving sharp transitions.

Doidge[3] has measured similar transitions in a different system, tin-indium, and has interpreted his results as evidence for the existence of a critical mean free path below which alloy behavior becomes evident. Since the electronic mean free path for a given indium content in tin is an order of magnitude smaller than that for the same mercury content in indium, it is difficult to compare the two systems directly. However, for In-Hg samples with small differences in mean free path, f_B showed no dependences on mean free path. Annealing treatment, on the other hand affected f_B strongly without changing the resistivity ratio or the mean free path.

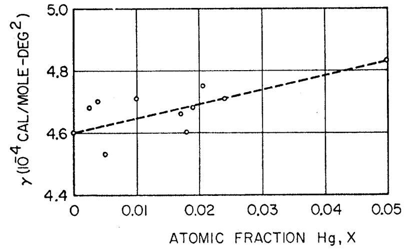

FIG. 10. The variation of the coefficient of the normal electronic specific heat in the normal state with mercury concentration in indium.

The argument for a mean free path dependence of alloy behavior is based on the concept of an interphase surface energy between normal and superconducting regions.[24] This surface energy presumably becomes less positive as the alloy content increases until finally it is energetically favorable for the specimen to form a large number of interphase surfaces under conditions of field and temperature for which full superconductivity is unstable. Such concepts can be used successfully to explain the stability of small superconducting regions (filaments). The question that is raised here is if negative interphase surface energy can justifiably be associated with the bulk of the alloy. An alternate possibility is that the negative interphase surface energy is associated with regions of inhomogeneity in the alloy. In this respect it is interesting to note that in tin-indium the separation between resistance and flux transitions occurred at approximately the same atomic composition as the appearance of a broad fraction that could not be annealed out occurred in indium-mercury.

The evidence presented here does not indicate that there is no surface energy dependence on alloying, but rather that one must be extremely careful in interpreting the available data to avoid confusing effects due to inhomogeneity.

The change in width of the sharp portion of the resistance transition with Hg content is logically explained if we realize that there is a slight (0.04%) change in composition along the length of a single sample. We can consider our specimen as a number of superconductors, with slightly different superconducting properties, in series. Using this approach, the width of the transition should depend on the total change in composition along the sample and the rate of change of the superconducting properties with composition. The transition width curve (Fig. 7) shows a general increase proportional to composition which arises from the increased difficulty of maintaining homogeneity for higher concentration alloys. Superimposed on this is a decrease in width which varies with the slope of the T_c vs Hg content curve. It should be noted that the minimum transition width occurs at that composition for which dT_c/dx equals zero. The transition in zero field for a specimen of this composition was measured, and it occurred in less than 0.4×10^{-3} °K, which compares favorably with the sharpest transition on record.[25] This is particularly interesting in view of the fact that this was a polycrystalline specimen.

The determination of the coefficient of the electronic specific heat from critical field data appears at first glance to be a straightforward affair. A simple thermodynamic treatment together with some very reasonable assumptions[1,26] yields

$$\gamma = -\frac{V_0}{8\pi T}\lim_{T\to 0}\frac{d}{dT}H_c^2 = a\frac{H_0^2}{T_c^2},$$

where a is proportional to the coefficient of the quadratic term in the expansion of $H_c(T)$. As measurements are extended to lower temperatures, the coefficient of the quadratic term that gives the best power series fit to the data changes. Consequently this method of determining γ is unsatisfactory unless measurements are carried out to extremely low temperatures. If the form of the superconducting electronic specific heat, C_{es}, is known as a function of temperature, then this together with critical field data can be used to determine γ accurately.[17] Unfortunately, this function is not known accurately for In.

A value of γ can be determined in the absence of detailed knowledge of C_{es} and in the absence of extremely

---

[24] T. E. Faber and A. B. Pippard, *Progress in Low-Temperature Physics* (Interscience Publishers, New York, 1955), Vol. 1, p. 159.

[25] W. J. deHaas and J. Voogd, Commun. Phys. Lab. Univ. Leiden No. 214c (1931).

[26] D. E. Mapother (unpublished).

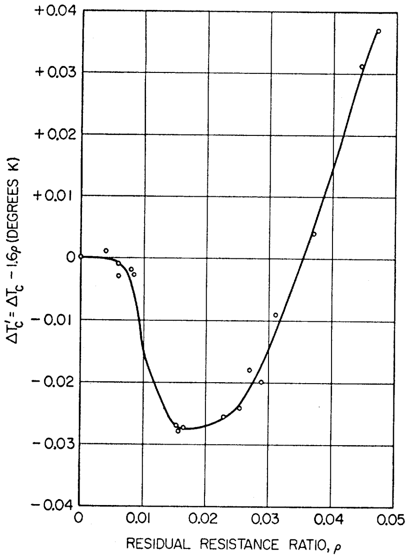

FIG. 11. The nonlinear portion of the change in critical temperature as a function of composition.

low-temperature measurements by using the BCS expression for γ. This will not give the correct answer since it is based on the assumption that the low of corresponding states is valid, but the number obtained can be easily revised when the BCS theory is improved. The various alloys, however, all have the same reduced critical field within the range of temperature over which the measurements extend. The variation of γ with composition will thus be independent of the specific formula that is used to calculate γ. Unfortunately, the measurement of critical field did not extend to low enough temperatures to allow for an accurate determination of H_0, and consequently there is considerable scatter in the plot of γ vs composition. Thus no attempt will be made to draw any conclusions from this data.

The variation in T_c with composition, while not unlike that of other dilute In alloys,[22] nevertheless cannot be described in the terms used by Lynton, Serin, and Zucker.[16] If one writes as they do, that the total change in critical temperature, $\Delta T_c = A\rho\Delta T_c'$, where ρ is the resistivity ratio and A is constant then $\Delta T_c'$ does not increase monotonically as Lynton et al., suggest. This is illustrated in Fig. 11 where $\Delta T_c'$ is as large as -0.027°K, which is an order of magnitude larger than the experimental error of the determination.

ACKNOWLEDGMENTS

The author wishes to thank D. P. Seraphim and W. B. Ittner, III, for many stimulating suggestions and discussions, and M. Charap of the computing center and S. Phillips of the analytic chemistry departments of the IBM Research Laboratory for their help in various phases of this project.

PHYSICAL REVIEW VOLUME 117, NUMBER 6 MARCH 15, 1960

Photovoltaic Effects in CdS Crystals*

HARTMUT KALLMANN, BERNARD KRAMER,† JULIUS SHAIN, AND GRACE MARMOR SPRUCH
Department of Physics, New York University, Washington Square, New York, New York

(Received October 6, 1959)

Photovoltages were obtained in CdS crystals using inhomogeneous excitation; that is, the excitation at one electrode was much larger than at the other electrode. Voltages in the range of 200 millivolts were obtained, with the region of high excitation always becoming positive. Two types of electrode arrangements were used. Some crystals were contacted directly with electrodes, others were insulated from the electrodes by thin Mylar sheets. In the first arrangement the photovoltages were permanent, in the second transient. The photovoltage showed only a weak dependence on intensity, and only wavelengths near or shorter than that corresponding to the absorption edge were effective. With metal electrodes the photovoltages were small. However, with jelly electrodes contacting the crystals photovoltages were almost as large as for the insulated crystals.

A. INTRODUCTION

PHOTOVOLTAGES in semiconductors normally arise at the metal-semiconductor interface or at a transition region such as an n-p junction between two differently activated sections of the semiconductor. The photovoltages to be discussed here, however, are due primarily to the inhomogeneous excitation of the samples, which produces a concentration gradient of free charges in the material. Photovoltages due to concentration gradients (Dember effect) have also been given some attention in the literature.[1]

The measurements which comprise the subject matter of the present paper were designed to dis-

---

* This investigation was supported by Geophysics Research Directorate, Air Force Cambridge Research Center.

† Also with Physics Department, Hunter College, Bronx, New York.

[1] L. Bergmann and F. Ronge, Physik. Z. **41**, 349 (1940); L. Bergmann, *ibid.* **33**, 209 (1932); H. Dember, *ibid.* **32**, 554 (1931); **32**, 856 (1931).