followed by electron capture at Cr^{2+}. We have observed a broad maximum at 3μ in the photoexcited Cr^+ EPR signal which we attribute to optical ionization of Ga donors. The thermal depth of Ga donors has been determined from thermoluminescent measurements as 0.4 eV,[9] and our measurements can be interpreted as evidence for the optical depth being approximately the same value.

IV. THEORETICAL ASPECTS

The energy of the chromium acceptor in zinc sulfide has been estimated by approximate theoretical methods using tight-binding methods.[10] The basic assumption of the calculation is that the conduction band can be approximated in terms of states of the cation. In this way, effects of the crystal field are minimized since the ionization of an electron from the substitutional chromium involves charge transport between equivalent sites. Independently of the ionic-covalent character the ground state of $^6S\,3d^5$ substitutional Cr in ZnS is found to lie within approximately an electron volt of the

conduction band edge. Our experimental results are consistent with the results of the simple theory.

From general theoretical considerations one predicts pairing of Ga donors with Cr acceptors in compensated crystals in which the Fermi level lies near or preferably above the chromium level. In this case these impurities are oppositely charged and attract each other Coulombically. The resulting donor-acceptor pairs would be expected to have unusual properties because the ground states of the Ga and Cr are separated in energy by only 0.3 eV. Among these unusual properties is a predicted far infrared absorption corresponding to the optical transfer of an electron from the Cr to the Ga. Nearer infrared absorption is expected if an excited state of either Ga or Cr is involved, as noted earlier in the discussion of $1.6-\mu$ absorption. Work is in progress to observe the effect of these transitions on the Cr^+ EPR signal and any detectable spin resonance of the photoexcited Cr-Ga pairs.

ACKNOWLEDGMENTS

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Electronic Structure and Superconductivity of Indium-Cadmium Alloys*

M. F. MERRIAM

Department of Physics and Institute for the Study of Matter, University of California, San Diego, La Jolla, California

(Received 30 September 1965)

The superconducting transition temperatures (in zero magnetic field) of In-Cd alloys in the range 0–60 at.% cadmium have been measured. T_c decreases from 3.406 to 3.245°K in the tetragonal solid solution and from 3.55 to 3.00°K in the cubic phase, with increasing Cd content. A kink in the T_c-versus-composition curve at 2 at.% Cd is attributed to Fermi-surface–Brillouin-zone interaction. This interpretation is supported by lattice-parameter determinations which show an anomaly at 2% Cd, and also by the magnetic susceptibility measurements of Verkin and Svechkarev. The existence of the superconductivity anomaly at $Z = 2.98$ supports a recent hypothesis of Svechkarev concerning the electronic structure of indium. Measurement of reduced resistance ratio $\rho \equiv R_{4.2}°/(R_{273}° - R_{4.2}°)$ show ρ to be linear in Cd concentration x up to the solubility limit at 5 at.% Cd, with a slope of 0.042/(at.% Cd). The data for the tetragonal phase are not linear on a plot of $\Delta T_c/x$ versus $\ln x$, and thus do not fit the present theory of T_c variation in primary solid solutions. At the tetragonal-cubic phase transition, T_c jumps by 10% without change of electron/atom ratio, cell volume, or ionic mass. The superconductivity data are all consistent with the published phase diagram of Heumann and Predel.

INTRODUCTION

IT is not yet possible to theoretically predict the superconducting transition temperature (T_c) of any material from first principles, or even from the values of other electronic properties. Empirical rules[1] have

been successful in many cases, but these have no firm foundation in physics, although attempts[2] have been made to connect them with the microscopic theory.[3] To attack the general problem we have undertaken to measure the composition dependence of T_c in nontransition metal alloy systems, since the electronic structure of these metals is presumably less complicated

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[2] D. Pines, Phys. Rev. 109, 280 (1958).
[3] J. Bardeen, L. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

than in the case of transition metals. Also, of course, the study of continuous phases (alloys), allows a more controllable variation of composition-dependent properties than does the study of discrete phases (compounds and separate elements). Experimental work along this line has been done in dilute solutions, first by the Rutgers group[4–6] and then at IBM.[7] Following the experimental work, a detailed calculation, based on the microscopic theory, was carried through by Markowitz and Kadanoff,[8] and was able to rationalize the results. Recent extensions of the Markowitz-Kadanoff treatment have been made by Ginsberg[9,10] and by Gayley.[11] Our data, however, do not fit the Markowitz-Kadanoff theory. The recent work[12] of Gamari-Seale and Coles, on Pb-rich binary alloys, also illustrates the incompleteness of the Markowitz-Kadanoff theory.

As part of an experimental program directed toward understanding how T_c depends on chemical and metallurgical composition in more concentrated alloys we have been measuring transition temperatures in some nontransition metal alloy systems based on indium. Data on the indium-mercury[13] and indium-tin[14] alloy systems have been published. Papers covering In-Bi, In-Tl, and In-Pb are in preparation. Indium is attractive among the superconducting nontransition metals since it shows extensive solubility with neighboring elements, and a high degree of comparability in its phase diagrams with these elements.

This paper deals with superconducting transition temperatures of In-Cd alloys in the range 0–60 at.% Cd. The specific questions which this study was designed to answer were: (1) Does T_c change discontinuously at the tetragonal-cubic phase boundary, and if so how; (2) what is the general composition dependence in the In solid solution; and (3) are there any Brillouin-zone effects similar to the ones found previously in other indium alloys.[15] As a matter of lesser interest we had hoped to obtain the transition temperature of the recently discovered compound $InCd_3$, but this was not accomplished.

The results obtained are discussed in the light of (1) the metallurgical features of the phase diagram, and (2) the recent applications of the microscopic theory of superconductivity to alloys. A Brillouin-zone effect was

discovered in the In-rich tetragonal solid solution at 2 at.% Cd.

EXPERIMENTAL

Samples

The samples were compounded from In and Cd shot, both of nominally 99.999+% purity, obtained from Asarco and Cominco, respectively. After weighing, the metals were loaded into Pyrex sample tubes approximately 6 mm i.d.×8 mm o.d., which were then sealed off under helium gas at a pressure of 100–200 mm Hg. After sealing off, the tubes were 7–10 cm long and contained 2–4 g of metal. The tubes were then placed in a rocking furnace at a temperature above the melting point of Cd (except that some of the indium-rich compositions were melted at 200°C) and the liquid metals mixed by sloshing them back and forth in the tube for 45 min or more. The samples were then removed, quenched into water, and set aside to anneal for periods of several weeks to several months. This was done in order to avoid the "quench effect."[14,16] Samples containing 0–5 at.% Cd were annealed at 130°C, the others at 120°C. After annealing, the samples were allowed to stand at room temperature (25°C) for periods of from several weeks to a year, except in the case of the samples shown in Fig. 2, which were quenched from 120°C into liquid nitrogen just before measuring, in an attempt to retain the cubic phase. These samples were held at 77°K for periods up to an hour, but were not allowed to warm up before measurement.

Several samples were remeasured, in some cases more than once, and in no case was the transition temperature found to depend on how long the sample had been stored at room temperature.

The compositions given in Figs. 1 and 2 and in Table I are nominal compositions, obtained from the weights of the constituent elements. Chemical analysis was not attempted. The nominal compositions are, however, believed to be correct, since the samples were prepared in sealed tubes, annealed, and measured for superconductivity (inductively), without breaking the tubes. The alloys did not wet the Pyrex, and consequently no appreciable amount of material was removed from the sample by sticking to the upper walls of the tubes. The homogeneity of the alloys was also not checked by any direct method, but the fact that the superconducting transitions were sharp (i.e., well defined in temperature) was taken as evidence that the annealed samples, at least, were homogeneous.

MEASUREMENTS

The superconducting transition temperatures were measured by placing the sample tubes in coils which could be immersed in liquid helium.[14] The coils were connected into an ac bridge operated at 1 kc/sec. The

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[15] M. F. Merriam, Rev. Mod. Phys. **36**, 152 (1964).

[16] M. F. Merriam and M. A. Jensen, Cryogenics **2**, 301 (1962).
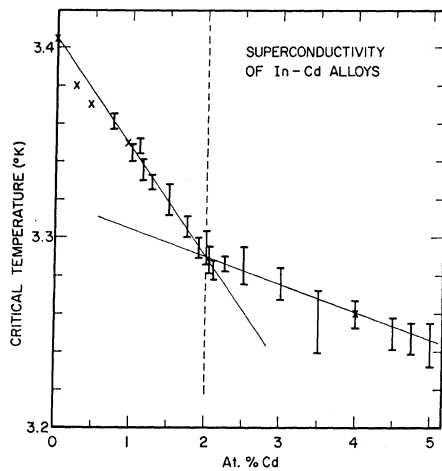
FIG. 1. Superconducting transition temperature as a function of composition for In-Cd alloys. The spreads shown are total transition widths and do not indicate experimental errors. The crosses are the data of Seraphim et al. (Ref. 7). All compositions shown here are single-phase, primary indium solid solution, the kink at 2% Cd arises from an electronic structure effect. This figure was previously published in Phys. Letters.

bridge became unbalanced when the samples went superconducting, and the imbalance signal was amplified, detected, and displayed on an x-y plotter. Temperatures were determined from the He^4 vapor pressure, using the 1958 scale.[17] This method of detecting superconductivity responds to infinite electrical conductivity in the samples, and not to the Meissner flux exclusion. The magnitude of the ac magnetic field at the samples
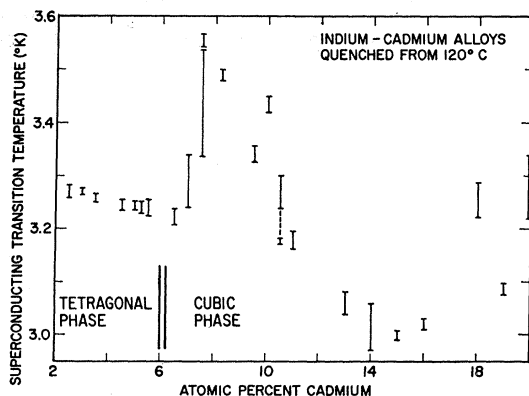

FIG. 2. Superconductivity in indium-cadmium alloys. For results at other compositions, or for more accurate values of the temperatures shown in this figure, see Table I. The spreads shown do not represent measurement errors, but rather the widths of the measured transitions, as discussed in the text. In some samples (7.5 and 10.5 at.% Cd) two discrete transitions were observed. The vertical lines drawn between the tetragonal and cubic phases are at the maximum Cd solubility (in the tetragonal phase) indicated by the work of Heumann and Predel (Ref. 18); this occurs at about 20°C. The T_c data alone would suggest a solubility about 0.5 at.% greater than this.

[17] F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, Natl. Bur. Std. (U. S.) Monograph 10, 12 (1960); J. Res. Natl. Bur. Std. 64A, 1 (1960).

was estimated to be not over half an oersted. This is not a critical point in any case, since the measurements requiring the most careful determination of transition temperature, those on alloys containing 0–5 at.% Cd, were made relative to a pure In standard. The transition temperature of the pure In standard was taken to be 3.406°K, and the observed manometer readings were corrected so that the measured In transition occurred at this temperature. This procedure ensured that the results were not being influenced by residual magnetic fields, manometer zero shifts, or other systematic

TABLE I. Superconducting transitions, normal-state resistance, and lattice parameters of In-Cd alloys.[a]

Composition[b] (at.% Cd)	Temperature limits of superconducting transition (°K)	Reduced resistivity ratio ρ^c
0	3.406[d]	
0.24	3.385[e]	0.0097[f]
0.45[f]	3.366[e]	
0.75	3.365–3.357	0.0321
0.91[f]	3.352[e]	
1.00	3.349–3.340	0.0433
1.10	3.352–3.344	
1.15	3.341–3.330	
1.27	3.333–3.325	
1.50	3.328–3.312	0.0656
1.75	3.311–3.300	0.0747
1.90	3.300–3.289	
2.00	3.303–3.286	0.0839
2.05	3.295–3.281	
2.10	3.288–3.278	
2.25	3.290–3.282	0.0936
2.50	3.295–3.275	
3.00	3.284–3.267	
3.50	3.272–3.239	
4.0	3.26[f]	
4.00	3.267–3.252	0.1689
4.50	3.258–3.241	
4.75	3.255–3.239	
5.00	3.255–3.232	0.2087
6.0	3.247–3.228	
7.5	3.267–3.238	
8.25	3.247–3.238	
14	3.272–3.255	
15	3.284–3.241	
22	3.275–3.232	
40	3.266–3.232	

[a] Equilibrated at room temperature. The data on quenched samples (Fig. 2) are not included in this table.
[b] From weights of constituents.
[c] $\rho \equiv R_{4.2}/(R_{273}-R_{4.2})$.
[d] Not a datum point. This temperature was used to calibrate the manometer.
[e] Taken from Ref. 5.
[f] Taken from Ref. 7.

errors. In fact, for the data of Table I, the corrections were quite small, never exceeding 6 mdeg.

The lattice-parameter measurements were done at room temperature on filings taken from the samples used previously for the superconductivity tests. The filings were passed through a 37-μ screen, then annealed for seven days at 140°C in sealed tubes containing helium. The filings, mixed with SiC powder, were sprinkled on a glass slide and placed on the stage of a GE XRD-5 diffractometer. The diffractometer was operated in a step scanning mode, counting for 400 sec

and stepping in intervals of 0.01 deg through the profile of the 113, 311, and 222 reflections. The SiC was intended as an internal standard, but gave rather inconsistent results, for reasons which remain unclear. Consequently the data of Fig. 4 are not relative to SiC but are "absolute" values. No effort was made to obtain high absolute accuracy in the measurements, however, and the accuracy is in fact rather poor. Even the relative accuracy is not outstanding, but it is sufficient to demonstrate (1) that there is no crystallographic phase transition at 2% Cd and (2) that there is a probable Brillouin-zone–Fermi-surface interaction at 2% Cd, resulting in the observed wiggles in a and c.

On the hope of improving the accuracy of the lattice-parameter determination we also tried using a film technique. We hoped to resolve the form of the wiggles in the a and c versus composition curves, and thus make it possible to draw conclusions about the detailed nature of the interaction causing the wiggles. The camera was an 11.46-cm Norelco, film shrinkage was allowed for, and the usual extrapolation to $\theta = 90°$ was made. However the computer fits to the data showed the dependence of apparent lattice parameter on θ to be quite steep, leading to a loss of confidence in the systematic error suppression. Also there was considerable scatter, at least some of which could be attributed to unsharp lines on the films. Consequently use of the film did not result in any improvement over the diffractometer.

The resistance ratio measurements were done in a conventional manner, using a four terminal method and a Leeds and Northrup K-3 potentiometer.

RESULTS

The results of the transition temperature measurements are shown in Table I, and in Figs. 1 and 2. It is useful to consider these results in relation to the equilibrium diagram of the In-Cd system, recently determined by Heumann and Predel.[18] This phase diagram is reproduced as Fig. 3.

First we consider the alloys containing 0–5 at.% Cd, which fall in the indium primary solid solution (tetragonal phase). The results of measurements on quite a large number of alloys show a kink in the plot of T_c versus x (composition) at 2% Cd (Fig. 1). The kink is, however, sufficiently small so that an unsympathetic observer could replace the intersecting straight lines of Fig. 1 with a smooth curve going through all, or nearly all, the points. The spreads shown in Fig. 1, incidentally, and in Fig. 2 as well, do not represent error limits in the usual way, but show the actual limits (in temperature)
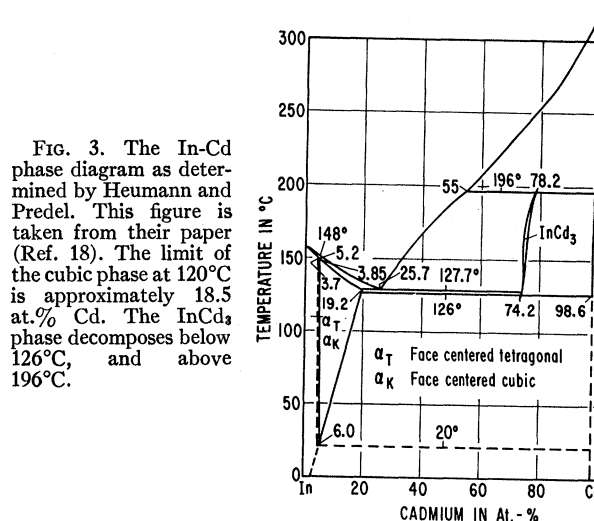

FIG. 3. The In-Cd phase diagram as determined by Heumann and Predel. This figure is taken from their paper (Ref. 18). The limit of the cubic phase at 120°C is approximately 18.5 at.% Cd. The InCd₃ phase decomposes below 126°C, and above 196°C.

of the superconducting transition—i.e., its breadth—measured for each sample. The kink shown in Fig. 1 does not correlate with any known feature in the phase diagram, but does resemble kinks found previously in In-Sn and In-Pb alloys,[15,19] which, in the light of the lattice-parameter measurements, and later magnetic measurements,[20] almost certainly arise from Brillouin-zone overlap effects. Consequently, lattice-parameter measurements on the In-Cd alloys were undertaken in order to verify the existence of the supposed overlap, with the results shown in Fig. 4. These results show (1) that a "wiggle" in lattice parameter does occur at the composition (2% Cd) of the superconductivity kink, and (2) that the composition range 0–5 at.% Cd is indeed a homogeneous solid solution in the usual metallurgical sense.

In Fig. 2 we plot the data for T_c of alloys quenched from 120°C in the composition range 0–20 at.% Cd. The cubic phase is stable at 120°C for cadmium contents above about 4.5 at.%, according to the rather
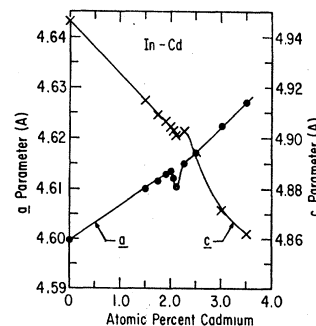

FIG. 4. Lattice parameters of the (tetragonal) primary indium solid solution with cadmium. The feature at 2% Cd arises from a Fermi-surface–Brillouin-zone interaction, which is also reflected in other properties, as explained in the text.

[18] T. Heumann and B. Predel, Z. Metallk. 53, 240 (1962). For earlier, less complete, work reported in English see T. Heumann and B. Predel, *The Physical Chemistry of Metallic Solutions and Intermetallic Compounds* (Chemical Publishing Company, New York, 1960), Vol. II, p. 144; and M. Hansen and K. Anderko, *Constitution of Binary Alloys* (McGraw-Hill Book Company, New York, 1958).

[19] M. F. Merriam, Phys. Rev. Letters 11, 321 (1963).
[20] S. Gygax, J. L. Olsen, and R. H. Kropschot, in *Proceedings of the Ninth International Conference on Low Temperature Physics, Columbus, Ohio, 1964*, edited by J. G. Daunt, D. V. Edwards, F. J. Milford, and M. Yaqub (Plenum Press, Inc., New York, 1965), p. 587.
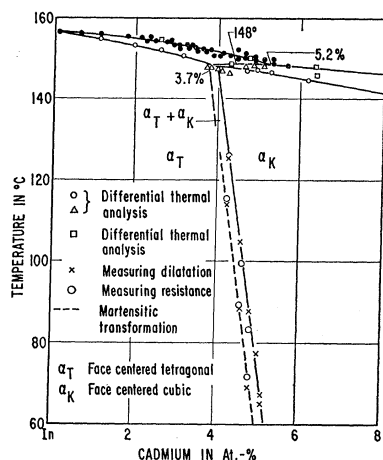
FIG. 5. Portion of In-Cd phase diagram, showing the tetragonal-cubic transformation, which has been located very carefully in this system. Note the very narrow two-phase region. (This figure is taken from Ref. 18.)

careful work of Heumann and Predel.[18] The relevant portion of their phase diagram is shown in Fig. 5. The quenching procedure used (plunging the Pyrex sample tubes into liquid nitrogen) was evidently not drastic enough to retain the cubic phase completely, since samples up to 6.5 at.% Cd show transitions which are erratic, sometimes broad, sometimes double, and generally not characteristic of a homogeneous, single-phase, well-annealed solid solution. Nevertheless, it would appear that the data of Fig. 2 in the range 8–16 at.% Cd are characteristic of the cubic phase in a rough sense. The transition temperatures of the 13, 14, 15, and 16% samples, for example, are too low to be explained in any other way. Examination of the complete phase diagram, Fig. 3, shows that the tetragonal phase contains a maximum of 6% Cd at the most favorable temperature. Since Fig. 2 shows no transition temperatures characteristic of the cubic phase for samples containing less Cd than this, we conclude that the quenching treatment we used was incapable of preventing the cubic-tetragonal transformation. It was however able to retain the cubic phase (although somewhat imperfectly) against precipitation of the Cd-rich solid solution, at least up to 16% Cd. At the higher concentrations of course the temperature at which precipitation begins increases, as does the amount of precipitate in equilibrium with the cubic phase at any given temperature. It thus becomes easier to understand the disappearance of the low T_c's of Fig. 2 at 16% Cd, rather than at the solubility limit, which occurs at about 18.5% Cd at 120°C. The scatter in the data of Fig. 2 for 7–20 at.% Cd is a consequence of variations in quenching rate (sample sizes were different, sample handling was not identical) and of nucleation conditions for the different samples.

The principal experimental result implied by the Fig. 2 data, then, is that the cubic phase is more favorable for superconductivity than the tetragonal phase since T_c jumps by a few tenths of a degree on passing from tetragonal to cubic. It is also clear that T_c is a

somewhat steeper function of composition in the cubic phase than it is in the tetragonal.

The measured transition temperatures of alloys containing 20 through 40 at.% cadmium are not shown graphically, but are included in Table I. The transition temperature is flat beyond the solubility limit, as expected.

Also not shown graphically are the T_c results of some measurements on samples containing 74 and 75 at.% Cd. These samples were annealed for some weeks at 182°C and then quenched into liquid nitrogen and measured without warming above 77°K. The temperatures measured were 3.03–2.90 for the 74% sample and 3.00–2.86 for the 75% sample. After 4 months at room temperature the 75% sample was then remeasured, yielding 3.24–3.10, a result more nearly consistent with Figs. 2 and 3. It thus seems probable that the $InCd_3$ compound discovered by Heumann and Predel (Fig. 3) has a lower T_c than the two-phase composition at that stoichiometry, but no value can be given, since we do not know how much decomposition (of $InCd_3$) occurred during our quenching treatment and subsequent handling. We did not consider this point sufficiently important to justify more complicated experiments.

The results of the resistance ratio measurements are shown in Fig. 6. The value of $\rho \equiv R_{4.2°}/(R_{273°} - R_{4.2°})$ is found to be a linear function of composition over the entire range 0–5% Cd, the slope of the line being 0.042/at.% Cd. This agrees well with the value 0.040 obtained earlier by Chanin, Lynton, and Serin[5] in the very dilute concentration range.

DISCUSSION

Tetragonal Solid Solution

The work of Markowitz and Kadanoff[8] was the first serious attempt to discuss the composition dependence of T_c over a wide composition range in the primary solid solutions of the simple (nontransition) metals in terms of the microscopic theory. The change in transition temperature caused by a magnetically neutral solute $\Delta T_c = T_c - T_c^{(0)}$ (the superscript refers to the pure element) is the sum of two terms, the so-called "anisotropy effect" and the "valence effect." The "anisotropy effect" is dominant in the very dilute range. As solute is added to the pure element, T_c drops rapidly. When the normal-state electronic mean free path is reduced to a value somewhat smaller than the superconducting coherence length of the pure element, the "valence" effect becomes dominant. The valence effect depends on the valence difference between solvent and solute, as well as on mean-free-path reduction, whereas the anisotropy effect depends only on mean-free-path reduction and is independent of the nature of the impurity causing the reduction. The anisotropy effect is observed even in pure elements, when the mean free path is reduced by surface scattering,[21] or dis-
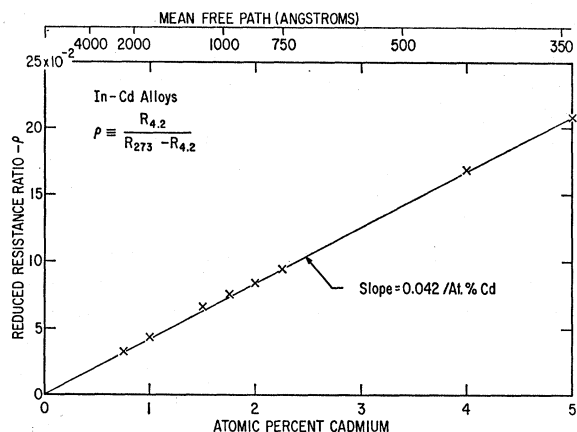
FIG. 6. Reduced resistance ratio ρ and mean free path as a function of cadmium concentration in tetragonal In-Cd alloys. The linearity indicates that, for resistance purposes at least, the solute atoms act independently of each other.

locations.[22] The anisotropy effect always results in a decrease in T_c, whereas the valence effect can have either sign. It is important to realize[8,9] that the anisotropy effect contributes a term linear in ρ to ΔT_c. Thus the valence effect is not simply the change in T_c for small mean free paths. The anisotropy effect is not only well documented experimentally but well understood theoretically (see Markowitz and Kadanoff's paper for a summary of this) and we will not be concerned with it further.

The valence effect, on the other hand, comes perilously close to being simply a name which is applied, to cover our ignorance, to all T_c variation other than the anisotropy effect. The basis for a firm calculation of the Markowitz-Kadanoff type becomes more and more precarious as the solute becomes more and more concentrated, for a number of reasons. At concentrations where the ρ-versus-x relation is nonlinear [as occurs for example in In-Tl,[23] though not in In-Cd (Fig. 6)], the impurities are not acting additively as seen by the normal electrons, so there is no reason to suppose that they can be treated linearly in a calculation of ΔT_c. A related difficulty is that the formula by which mean free path is obtained from ρ is valid in the approximation that the effective average velocity $\bar{V}_F$ at the Fermi surface is not changed by alloying. Clearly, this approximation gets steadily worse as solute concentration increases, though the quantitative degree by which it is in error in any particular case is difficult to determine. On a free-electron model, the addition of 5% Bi, or 10% Pb, to In would result in an increase of only 1.1% in $\bar{V}_F$, since $\bar{V}_F$ depends only on the cube root of n, but the free-electron model is probably not appropriate. The value of $\bar{V}_F$ depends markedly on the position of the Fermi surface relative to the zone boundaries ($\bar{V}_F$

[21] E. A. Lynton and D. McLachlan, Phys. Rev. 126, 40 (1962).
[22] W. C. H. Joiner, Phys. Rev. 137, A112 (1965).
[23] J. W. Stout and L. Guttman, Phys. Rev. 88, 713 (1952).

goes to zero at a zone boundary), and since the Fermi surface of a polyvalent metal such as indium is close to many zone faces, the addition of electrons is almost certain to result in changes in the degree of contact or overlapping of many faces of the appropriate Brillouin zones. This could make a considerable change in $\bar{V}_F$, even though the Fermi surface as a whole continues to approximate a sphere. That such overlaps can have a marked effect on the composition dependence of T_c has already been demonstrated[15,19] in the In-Sn and In-Pb cases, and that they need not have a measurable effect on T_c is probable also from the In-Pb studies of Gygax, Kropschot, and Olsen[20] which showed structure at 3.5% Pb without any effect on T_c. The entire microscopic theory of superconductivity, of which the Markowitz-Kadanoff work is an application, does not of course include Fermi surface-zone boundary interaction effects.

There does seem to be a Brillouin-zone overlap effect in the In-Cd alloys, at 2% Cd, which we discuss below, but without considering this we can make an over-all check of the Markowitz-Kadanoff theory by making a so-called 'Seraphim Plot.'

According to Seraphim, Chiou, and Quinn,[7] the change in T_c caused by alloying can be fit empirically in a number of primary solid solutions based on Sn, Al, and In with an expression of the form

$$\Delta T_c = k_1 x + k_2 x \ln x, \tag{1}$$

where x is mole fraction solute and k_1 and k_2 are constants. This is equivalent to the more general form

$$\Delta T_c = k_1' \rho + k_2' \rho \ln \rho \tag{2}$$

in the case of In-Cd, since ρ is proportional to x over the entire solubility range (Fig. 6). The existence of this apparently successful empirical rule was part of the background for the Markowitz-Kadanoff theory, and their theory does in fact yield an expression of the form (2), with a microscopic interpretation of the constants. Thus a plot of $\Delta T_c/x$ versus $\ln x$ should yield a straight line. Our data are displayed on a plot of this sort in Fig. 7. The straight line obtained by Seraphim et al. for this alloy system is also shown. Although none of the points lie too far from this line, they clearly do not fit any single straight line. There is a break in the curve at the x value corresponding to 2% Cd, as might be expected, but there is also a break at approximately 0.7% Cd. No physical reason for this latter break is apparent. Thus the Markowitz-Kadanoff theory does not seem to describe our experimental results in this alloy system. We therefore make no attempt to compare our data with recent extensions of the Markowitz-Kadanoff theory.[9–11]

Considering now the In-Cd data of Fig. 1, a Brillouin-zone effect appears to be present at 2% Cd. The kink in T_c versus x could conceivably arise from causes other than Fermi-surface–Brillouin-zone interaction, but two
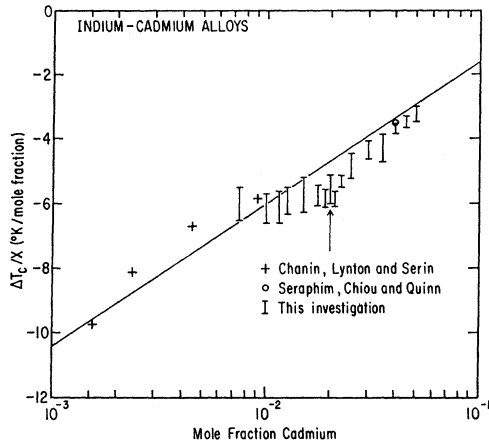
FIG. 7. Test of the relation $\Delta T_c = k_1 x + k_2 x \ln x$ for indium-cadmium alloys in the tetragonal phase. It is apparent that this simple relation fails to describe the data. The kink at 2% Cd (arrow) arises from Fermi-surface–Brillouin-zone interaction.

plausible alternative possibilities which come to mind can be ruled out. The first of these is that the kink is not really a sharp kink at all, but rather a smooth curvature, representing a transition from the region where ΔT_c is dominated by the anisotropy effect to the region where the valence effect is dominant. However the cadmium concentration at which the impurity scattering mean free path is equal to the coherence length in the pure metal is only 0.4 at.% (using[24] $\xi_0 = 4.4 \times 10^{-5}$ cm and $l^{-1} = 1.40 \times 10^6 \rho (\text{cm}^{-1})$ and $\Delta \rho / \Delta x = 0.040/\text{at.}\%$ Cd). The mean free path at 2% Cd, according to the above, is shorter than ξ_0 by a factor of 5. Thus the kink is certainly not associated with the transition from mean free path dominated to valence dominated behavior because it occurs at the wrong composition. The same reason allows us to rule out another possibility—that the kink is in some way connected with the transition from first-kind to second-kind superconductivity. The work of Chiou, Connell, and Seraphim[25] fixes this transition at 3.5 ± 0.5 at.% Cd. No effect is visible in our data at that concentration, which is reassuring, since our data are supposed to refer to zero magnetic field. Actually there is some doubt that this composition does in fact mark the transition to second-kind superconductivity, since the author, in collaboration with F. Otter and G. Yntema of the United Aircraft Research Laboratories, has recently found a 4.5 at.% Cd sample to be first kind, even at 2°K. However, it is at least true that there is no first-kind–second-kind transition at 2% Cd.

Supposing that the kink in Fig. 1 at 2% Cd does arise from a Brillouin-zone effect we may ask (1) what other properties show, or might be expected to show, an anomaly at this composition; and (2) which zone face is being overlapped and just how is the Fermi surface

changing shape. In answer to the first question, in the analogous case of In-Pb, where a similar kink is found at 8% Pb, anomalies have been observed in lattice parameter,[15] thermoelectric power,[26] Hall effect,[27] and electronic specific heat.[20] Attempts to find an anomaly in electrical resistance were unsuccessful[28] and no careful study has been made of magnetic susceptibility. In the In-Cd case the measurements of lattice parameter versus composition (Fig. 4), show an anomaly at 2% Cd. The precision and accuracy of the lattice-parameter measurements could be improved. Specific-heat measurements are planned. The electrical resistance ratio measurements (Fig. 6) show no anomaly. We know of no Hall effect or thermopower measurement in this alloy system. The recent magnetic susceptibility data of Verkin and Svechkarev[29] on single crystals closely spaced in composition show a pronounced diamagnetic maximum in χ_{II} at almost exactly 2% Cd. To see how such a maximum can arise from a Fermi-surface–Brillouin-zone interaction as the Fermi "sphere" shrinks (adding cadmium to indium effectively removes electrons) we consider the theory of diamagnetism in metals for a particular simplified case, which is only an approximation to the case we are dealing with here.

The magnetic susceptibility arising from the conduction electrons (or holes) is the sum of two terms, the Pauli paramagnetism and the Landau diamagnetism. By "Landau diamagnetism" we mean the diamagnetism of the conduction electrons, though this is given by Landau's formula only when the electrons are free. When the Fermi surface is in close proximity to a zone boundary the Landau formula must be extended, and this has been done by Peierls. The net result as given for example by Wilson[30] is

$$\chi_D = (4m^2\mu^2/3m^*\hbar^2)(3\pi^2 n)^{1/3}, \qquad (3)$$

where χ_D is the diamagnetic susceptibility of the conduction electrons (or holes) having effective mass m^*, μ is the Bohr magneton, m is the free-electron mass, and n is the number of electrons (or holes) per unit volume which are available for conduction (i.e., outside filled zones). This formula represents the lowest approximation in kT/E_F, where E_F is the Fermi energy, and in addition rests on the assumption that the band is of "standard form," i.e., that

$$E = \hbar^2 k^2/2m^*,$$

with positive m^*. If the band curvature is negative ($d^2E/dk^2 < 0$) then the carriers are to be regarded as holes having positive m^*.

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The total susceptibility per unit volume is

$$\chi = \chi_p + \chi_D,$$

where χ_p is the Pauli paramagnetism and χ_D is the diamagnetism discussed above. Substitution of the usual formula for the spin paramagnetism gives

$$\chi = (4m^*\mu^2/h^2)(3\pi^2 n)^{1/3}(1 - m^2/3m^{*2}). \qquad (4)$$

If we measure single-crystal susceptibilities the value of the effective mass which must be put into this formula can depend on crystalline orientation. For example if we measure $\chi_{||}$ and $\chi_{\perp}$ for a tetragonal crystal (magnetic field parallel and perpendicular to c axis) we would not be surprised to find them unequal because the deviations from free-electron behavior are different in the a and c directions. The zone boundaries occur at different distances from the origin, and deviations from free-electron behavior arise from the proximity of the Fermi surface to a zone boundary. If the Fermi surface should just overlap a zone boundary leading to small pockets of electrons in a higher zone, or just fail to fill a zone, leading to small pockets of holes in the lower zone, or both, then crystal symmetry requirements lead to large band curvatures where the Fermi surface meets the zone boundary and very large values of $1/m^*$ occur. The large diamagnetic susceptibilities observed in bismuth and gamma brass arise from this cause.

It is implicit in the derivation of Eqs. (3) and (4) that m^* is to be taken as positive, and the large diamagnetism arises only from the large curvatures near the zone boundaries. Thus a "Landau paramagnetism" such as would arise from Eq. (3) with a negative m^* does not occur, although of course Eq. (4) may yield paramagnetism, if $m^*/m > \frac{1}{3}$.

It is possible to get a rough idea of the magnitude of susceptibility increase possible when the Fermi surface is in close proximity to a zone boundary by noting a special case considered, for example, by Mott and Jones.[31] Consider a plane of energy discontinuity (Brillouin-zone face) perpendicular to the k_x direction, and suppose that the Fermi surface has just slightly overlapped this plane, so that a small pocket of electrons exists in the higher zone. Then, writing

$$E = (\hbar^2/2m)(\alpha_1 k_x{}^2 + \alpha_2 k_y{}^2 + \alpha_3 k_z{}^2) \qquad (5)$$

for the energy of these electrons in the absence of a field (so that m/α_1, m/α_2, m/α_3, are the effective masses of the electrons in the k_x, k_y, and k_z directions, respectively), it turns out that α_2, $\alpha_3 \approx 1$, but that $\alpha_1 \approx 1 + 4E_0/\Delta E$, where E_0 is the energy a free electron would have at the point where the k_x axis intersects the plane of energy discontinuity and ΔE is the energy gap at that point. The value of α_1 is obtained by perturbation theory and is only valid if $\Delta E \ll E_0$, which is, however, usually the case. The conduction-electron diamagnetic suscepti-

bility, assuming the field is applied in the Z direction, is

$$\chi_D = (4m\mu^2/3h^2)(3\pi^2 n)^{1/3}[(\alpha_1\alpha_2)^2/\alpha_3]^{1/3}, \qquad (6)$$

which reduces to Eq. (3) if $\alpha_1 = \alpha_2 = \alpha_3 = \alpha$. Since typically $\Delta E \approx 1$ eV and $E_0 \approx 6-10$ eV, α_1 can be 30 to 40 times as large as α_2 and α_3, assuming the latter do not differ greatly from unity. This gives an enhancement of χ_D by a factor of 3 to 4. It is important to note that the enhancement becomes a reduction if the magnetic field is perpendicular to the plane of energy discontinuity rather than parallel to it.

The theory embodied in Eqs. (3) through (6) is not valid in the event that the zones in question are separated only by very small energy gaps (0.1 eV or less). In this case the virtual transitions of electrons between zones give use to an additional diamagnetism. This effect has been considered by Adams,[32] and it is in terms of his theory that Verkin and Svechkarev have discussed their data, since they feel that the states responsible for the magnetism are those in the corners, not on the faces of the zone, and that the energy gaps become small in the corners. The sign and the general magnitude of the range of variation of $\chi_{||}$ are consistent with theory, although no direct numerical correspondence can be made at this time, owing to a lack of detailed information about the electronic states.

The question of just which zone face or faces are being overlapped has been considered in a previous communication[33] in relation to the recent work of Svechkarev.[34] Svechkarev has independently interpreted the Z dependence of c/a in In-Cd alloys as evidence for a qualitative change in the relationship of the Fermi surface to the boundaries of the first through fourth zones at $Z = 2.98$ (corresponding to 2% Cd). This change consists of the filling of the last of the first zone holes and the initiation of overlap into the higher zones in the corners corresponding to the a axis directions. (The first four zones meet in a common corner.)

Even without assuming the Svechkarev hypothesis, it seems likely that the relevant overlap is closely connected with the tetragonality of indium. That the tetragonal-cubic transformation in In-Cd is controlled by electronic structure (i.e., by energetics of the conduction-electron distribution) and that no substantial changes occur in the ion cores is strongly suggested by the fact that the cubic and tetragonal phases have almost exactly the same cell volume.[18]

Tetragonal-Cubic Transformation

The qualitative behavior of T_c at the tetragonal-cubic transformation has one feature in common with the other In alloy systems (In-Hg, In-Sn, In-Pb, In-Tl) studied to date, in which similar transformations occur.

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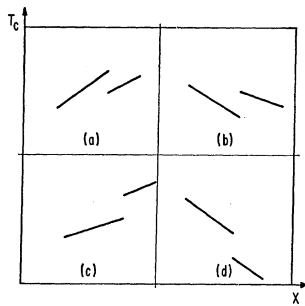
FIG. 8. This figure illustrates schematically four geometrically possible situations at a T_c discontinuity. The ordinate is super-conducting transition temperature (T_c), and the abscissa is composition (x), in each of the four figures. Only the sign, not the magnitude, of the slope of T_c versus x is important for this illustration. Jumps in T_c versus x for indium alloys occur when the tetragonal indium solid solution transforms; this happens with increasing solute concentration in all the indium solid solutions except In-Bi; viz., In-Hg, In-Cd, In-Tl, In-Pb, In-Sn. In all five cases, the observed jumps are of the form (a) or (b); the cases (c) and (d) are not observed.

The jump in T_c at the transformation is always of the form of Fig. 8(a) or (b) and never of the form of Fig. 8(c) or (d); i.e., always such as to oppose the trend in T_c versus x. Quantitatively we note that the jump in T_c in In-Cd is about 10%.

We may talk about the T_c discontinuity in terms of the well-known formula

$$T_c \approx 1.1\Theta_D \exp[-1/N_0 V], \qquad (7)$$

where Θ_D is the Debye characteristic temperature, N_0 is the density of states at the Fermi surface, and V is the parameter expressing the strength of the electron-electron coupling which makes superconductivity. We may ask whether the T_c discontinuity arises primarily from Θ_D, N_0, or V, or indeed whether the discontinuity can be meaningfully understood in terms of this formula. The high-temperature electrical-resistance measurements of earlier workers[18] show a jump of less than 1% at the cubic-tetragonal phase transition, from which we conclude that any jump in Θ_D would be expected to be correspondingly small. Thus the T_c jump, which is some ten times larger, cannot be attributed to a jump in Θ_D [objections to the effect that the phonon spectrum cannot really be approximated by a single constant (Θ_D) insofar as its effects on T_c or on the resistance are concerned are not to be considered, as we are using our data as a simple-minded test of the utility of Eq. (7)]. With regard to N_0, a discontinuity at the phase transition is expected, and the sign expected is such as to be consistent with the sign of the discontinuity observed in T_c. The magnitude of discontinuity required in N_0 cannot be ruled out as unreasonable in the absence of specific-heat data. However it is a little surprising that so few other features in T_c attributable to changes in N_0 appear. For example, usual alloy theory calls for the density of states to begin to drop sharply shortly *before*

a phase transition, and no evidence of this is seen in Fig. 2, although admittedly the cubic-phase data are not very precise. The T_c-versus-x curve in both Figs. 1 and 2 is a straight line with the exception of the kink at 2% Cd. The T_c-versus-x curves for all concentrated non-transition metal alloy phases so far investigated are either simple straight lines or two straight-line segments. Although direct measurements are not too extensive, N_0-versus-x curves are usually thought of as having considerable structure. No reasonable comment on the magnitude and sign of a possible discontinuous change in V at the phase boundary can be made without a detailed calculation.

It is worth noting that we have here a 10% change in T_c without change of electron/atom ratio, cell volume,[18] or ionic mass. This should lay to rest the idea that the superconducting transition temperature, a measure of an electronic phenomenon, is in any fundamental way *determined* by purely chemical parameters such as the three factors cited. This is not to deny the usefulness of the correlations and regularities connecting T_c with chemical parameters obtainable directly from the periodic table; these correlations and regularities have led to the discovery of a large number of new super-conducting materials, particularly materials involving transition metals.

The composition dependence of T_c is obviously much stronger in the cubic phase than in the tetragonal phase. The reason for this is not clear. The same phenomenon is observed in the In-Tl system.[35]

SUMMARY AND CONCLUSIONS

A kink in dT_c/dx occurs at 2 at.% cadmium. Anomalies in magnetic susceptibility and lattice parameter, but not electrical resistance, also occur at this composition. The kink and the anomalies arise from Fermi-surface–Brillouin-zone interaction, probably in the zone corners associated with the a axis.

The composition dependence of T_c in the tetragonal solid solution does not fit the existing microscopic theory. In addition to the kink at 2% Cd, a feature not consistent with theory occurs at about 0.7 at.% Cd.

A discontinuous 10% increase in T_c occurs at the tetragonal-cubic phase transition, the cubic phase having the higher T_c. This probably arises from a discontinuity in density of states.

ACKNOWLEDGMENTS

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