

Superconductivity in the Alloy System Cadmium-Mercury and the Effect of Ordering upon Superconductivity*

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The superconducting transition temperatures of Cd-Hg alloys covering the complete composition range have been determined. The solubility of Cd in Hg has been accurately determined; it is 1.5 ± 0.25 at. % at 193°K. The terminal solid solubility of Hg in Cd is found to be 26 ± 2 at. % at 418°K. Boundaries of the ω phase occur at 88 ± 1 at. % Hg at 193°K and at 35 ± 2 at. % Hg at 383°K. Ordering occurs in the intermediate ω phase at compositions based on Cd_2Hg and CdHg_2 . The effect of ordering upon the superconducting transition temperature is observed for the first time. The transition temperature for the ordered phase is lower than the one for the disordered. This is presumably caused either by a reduced electron-phonon interaction, which is reflected also in a lower measured normal-state resistivity of the ordered phase, or by changes in the electronic density of states at the Fermi surface, which would be expected as a consequence of the subdivision of the Brillouin zones by the superlattice formation.

INTRODUCTION

DETAILED studies of the variation of the superconducting transition temperature T_c with composition in binary metal alloys have been made in recent years using transition metals^{1,2} and nontransition metals.^{3,4} The bulk of the experimental work has been concentrated upon systems containing at least one transition metal, primarily because of the extensive ranges of solubility that can be found among these systems. In nontransition metal alloys, large ranges of solubility and large numbers of isostructural compounds are much less common. The rule of Matthias,⁵ connecting T_c with the average number n of valence electrons per atom has been successful in predicting transition temperatures for a large number of transition metal alloy systems. For nontransition metals this rule has not been very successful. It is partly in the hope of finding some alternative rule, relating T_c to accessible chemical parameters, that this and earlier studies in the nontransition elements have been undertaken. Such studies also yield useful information on the equilibrium diagram and the electronic structure of the alloys involved.

It has previously been reported that the intermediate ω phase of the Cd-Hg alloy system exhibited arrests in the heating and cooling curves, indicating a discontinuity in specific heat or possibly a small latent heat.⁶ As reported in our earlier publication,⁷ discontinuities

in electrical resistance versus temperature and extra x-ray reflections in the phase formed below the transformation temperature were found. We regard it as established that ordered phases form, corresponding to formulas Cd_2Hg and CdHg_2 , respectively. These superlattices are of the *Strukturbericht* type *C11b*. The effect of ordering upon the superconducting transition temperature has not been studied previously experimentally or theoretically to our knowledge, except for the rather uncertain case of Tl-Bi reported by Coles.⁸ In this case the measured shift in T_c was unmistakable, but the existence of the order-disorder transformation was not well established. As ordering presumably will affect both the lattice vibrational spectrum and the electronic density of states, it was regarded as a worthwhile subject for experimental study.

Studies of T_c versus composition in the nontransition metal alloy systems Hg-In,³ In-Sn,⁴ In-Pb,⁹ and Cd-In¹⁰ have been made. Discontinuities in the slope of T_c versus composition within crystallographically homogeneous solid solutions have been explained as electronic "Brillouin zone effects," i.e., Fermi surface-Brillouin zone interactions. The Cd-Hg system has a substantial range of intermediate solid solutions, but is at least nominally isoelectronic. If the number of valence electrons per atom does not change with composition, then the Fermi sphere does not change size relative to the Brillouin zone in the rigid-band approximation. Brillouin zone effects can still occur, since the shape of the zone can change if the lattice constants vary, as they do in this case.

The superconducting transition temperatures of a few Cd-Hg compositions have been measured,¹¹ but no comprehensive study has previously been done.

Aside from the possibility of observing new Brillouin zone effects it was hoped that the superconductivity

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

⁴ M. F. Merriam and M. von Herzen, *Phys. Rev.* **131**, 637 (1963).

⁵ B. T. Matthias, *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. 2.

⁶ R. F. Mehl and C. S. Barrett, *Trans. AIME* **89**, 575 (1930).

⁷ T. Claeson, H. L. Luo, T. R. Anantharaman, and M. F. Merriam, *Acta Met.* (to be published).

⁸ B. R. Coles, *IBM J. Research Develop.* **6**, 68 (1962).

⁹ M. F. Merriam, *Phys. Rev. Letters* **11**, 321 (1963).

¹⁰ M. F. Merriam, *Phys. Letters* **17**, 16 (1965).

¹¹ W. J. de Haas and J. de Boer, *Proc. Acad. Sci. Amsterdam* **35**, 128 (1932).

measurements would settle some questions arising out of the present imperfect state of knowledge of the phase diagram, including particularly the determination of the solubility limit in the Hg phase. The question of a possible transformation in the ω phase and of a possible compound Cd_3Hg also seemed suitable for investigation. It was indeed possible to make considerable progress with these phase-diagram questions; some of the results have already been reported.⁷

EXPERIMENTAL TECHNIQUE

The mercury and cadmium used were both nominally at least 99.999% pure. The mercury was "Vacumetal" from Metalsalts Corporation, and the cadmium was obtained from Cominco. The samples were weighed into quartz tubes, sealed off under a reduced pressure of helium, and heated to above their melting point. As the liquid easily stuck to the tube wall, the tubes were gently rolled, rather than tipped, to obtain mixing. When the melting point was below 100°C, the samples were mixed in an ultrasonic bath. With care it was possible to completely avoid the problem of liquid sticking to the tube walls. After being thoroughly mixed, the (liquid) samples were quenched in liquid nitrogen or ice water, without breaking the tubes. They were then homogenized by annealing at one of the following temperatures: 145°C (oven), 110°C (oven), 23°C (room), 4°C (refrigerator), -14°C (freezer), or -80°C (dry ice-acetone). In order to reach equilibrium in the superconducting properties, annealing times from a week to several months were needed, depending upon composition and annealing temperature, particularly upon the proximity of annealing temperature to solidus. Samples were annealed in the same tubes in which they were made. Some use was made of acetone baths cooled by throwing in chunks of CO₂ to temperatures intermediate between 0 and -80°C, particularly in cases where it was desired to anneal just below the ordering temperature to develop the superlattice in samples already homogenized.

The superconducting transitions above 1.3°K were observed with the aid of an impedance bridge that compared the inductance of a coil containing the sample with the inductance of an empty coil. Both coils were immersed in liquid helium. When the alloy sample became superconducting, an unbalance signal resulted which was fed to an x - y recorder. The bridge operated at 160 cps and produced an ac magnetic field at the sample of less than 1 G. The temperature of the He⁴ for a given vapor pressure was taken from the 1958 He⁴ scale.¹² The absolute error in temperature determination was estimated to be $\pm 0.01^\circ K$ while the relative uncertainty did not exceed $0.005^\circ K$.

Below 1.3°K the superconducting transitions were measured in a similar manner, by monitoring the self-

inductance of a coil containing the sample. The latter was submerged in liquid He³. The magnetic field at the sample was approximately 0.1 G peak to peak at a frequency of 95 cps. The temperature was determined by measuring the vapor pressure of liquid He³ with a McLeod manometer and using the 1962 He³ vapor pressure scale.¹³

Resistivities were measured with a conventional 4-wire method, using a Leeds and Northrup K-3 potentiometer. The sample was submerged in liquid helium, liquid nitrogen, ice water, or acetone cooled by dry ice, as appropriate. When necessary, the temperature was measured with a copper-constantan thermocouple.

RESULTS AND DISCUSSION

The suggested phase diagram is shown in Fig. 1. The superconducting transition temperature as a function of composition for annealed samples is listed in Table I and shown in Fig. 2. This is not identical with the phase diagram we reported previously,⁷ but it is nearly the same. The transitions are usually rather sharp. Some samples showed two transitions, these are connected in the figure by a vertical dashed line. Results for samples annealed at several temperatures are included. The annealing temperature of the sample varied with the composition and is given in Table I along with the annealing times.

The depression of T_c with increasing solute concentration for the solid solution of Cd in Hg is shown, on an expanded scale, in Fig. 3. The depression of T_c with increasing solute concentration in dilute solid solutions is known as the "mean free path effect," and has been studied extensively.¹⁴⁻¹⁹ It is virtually the only situation where the composition dependence of T_c in an alloy is understood in a fundamental way.

In Fig. 4 we plot the variation of T_c with composition in a region of the ω phase. Transition temperatures for samples annealed above and below the ordering temperature (the temperature at which order-disorder transformation occurs) are plotted. The discontinuity in the slope of the curve at 68 at.% Hg is well outside experimental error.

The increase in T_c and the transition width by rapidly solidifying an inhomogeneous sample was observed. This probably arises³ from inhomogeneous strains in the sample. The effect anneals out, after an annealing time dependent upon the annealing temperature and its prox-

¹² R. H. Sherman, S. G. Sydorik, and T. R. Roberts, Los Alamos Report No. LAMS 2701, 1962 (unpublished).

¹³ D. P. Seraphim, C. Chiou, and D. J. Quinn, *Acta Met.* **9**, 861 (1961).

¹⁴ G. Chanin, E. A. Lynton, and B. Serin, *Phys. Rev.* **114**, 719 (1959).

¹⁵ E. A. Lynton, B. Serin, and M. Zucker, *J. Phys. Chem. Solids* **3**, 165 (1957).

¹⁶ P. W. Anderson, *J. Phys. Chem. Solids* **11**, 26 (1959).

¹⁷ D. Markowitz and L. P. Kadanoff, *Phys. Rev.* **131**, 563 (1963).

¹⁸ D. M. Ginsberg, *Phys. Rev.* **138**, A1409 (1965).

¹⁹ H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, *Natl. Bur. Std. (U. S.) Monograph* **10** (1960), Part 2, p. 12.

TABLE I. Transition temperatures of annealed Cd-Hg alloys.

Composition (at.%Hg)	Annealing temperature (°C)	Annealing time (weeks)	Superconducting transition (upper and lower limit in °K)
5.0	145	4	0.65 -0.50
9.9	145	5	0.77 -0.74
15.1	145	5	0.98 -0.94
20.1	145	11	1.24 -1.10
23.2	145	5	1.36 -1.26
24.9	145	9	1.40 -1.33
29.4	145	7	(1.48 -1.35) ^a
			(1.27 -1.26)
35.0	110	10	1.42 -1.32
35.0	23	8	(1.51 -1.44) ^a
			(1.38 -1.32)
39.0	110	4	1.45 -1.42
40.0	110	9	1.50 -1.46
45.0	110	5	1.65 -1.58
50.0	110	7	1.74 -1.71
50.1	110	7	1.74 -1.71
55.1	23	5	1.88 -1.84
60.3	23	10	1.98 -1.92
65.0	23	5	2.07 -2.03
66.7	45	3	2.15 -2.09
67.4	23	7	2.16 -2.11
68.0	23	7	2.20 -2.16
68.3	23	7	2.20 -2.15
68.6	23	7	2.19 -2.15
68.9	23	7	2.20 -2.16
69.6	23	7	2.28 -2.24
69.9	23	10	2.27 -2.21
72.0	23	7	2.41 -2.34
73.9	23	7	2.52 -2.49
74.9	4	9	2.60 -2.57
77.0	4	9	2.71 -2.68
78.0	4	1	2.77 -2.74
80.8	-14	10	2.94 -2.90
86.0	-80	9	3.22 -3.18
87.5	-80	9	3.26 -3.24
88.75	-80	10	(4.11 -4.0) ^a
			(3.41 -3.37)
89.90	-80	7	(4.11 -4.0) ^a
			(3.42 -3.37)
92.00	-80	7	(4.11 -4.07) ^a
			(3.41 -3.38)
94.00	-80	7	(4.11 -4.08) ^a
			(3.49 -3.36)
96.01	-80	7	4.109-4.090
97.01	-80	7	4.109-4.088
98.00	-80	8	4.106-4.082
98.51	-80	10	4.108-4.088
98.75	-80	10	4.112-4.094
99.01	-80	10	4.145-4.126
99.75	-80	10	4.151-4.136
100	-80	1	4.151-4.142

^a Two transitions were found in this sample.

imity to the solidus temperature. In this system the difference in transition temperature between the unannealed and annealed samples was less than 0.1°K. The specimens investigated were annealed a sufficiently long time for the superconducting transition to reach a limiting value of temperature and width. The data in Table I, and in Figs. 2-4, are characteristic of samples annealed to equilibrium, according to the limiting value criterion.

Terminal Solid Solutions

Figure 3 shows that the solid solubility of Cd in Hg is 1.5 ± 0.25 at.% at -80°C . The transition temperature decreases with increasing Cd concentration, the

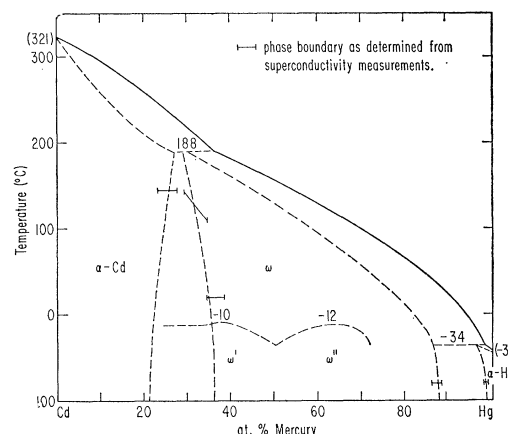


FIG. 1. Phase diagram of the Cd-Hg system. This is based on the work reported in Ref. 7, supplemented by superconductivity measurements as indicated.

decrease amounting to 0.05°K in the saturated solid solution. The data fit rather well with the two-parameter equation of Seraphim *et al.*¹⁴ ($T_c = k_1x + k_2x \ln x$), where T_c is the change in transition temperature by variation of x , the mole fraction of solute, and k_1 , k_2 are parameters. In the Hg solid solution with Cd solute $k_1 \approx 8.8$ and $k_2 \approx 1.2$. However, any two-parameter function would probably fit, since the data are very smooth and have a restricted range.

The solubility of Hg in Cd seems to be about 25 at.% at 145°C . The transition temperature increases linearly with increasing Hg content, over the range of measurement. An initial depression of T_c with increasing amount of solute in a dilute solution is probable since the T_c versus x line extrapolates to a transition temperature below that of pure Cd.

Two-Phase Regions

A two-phase region occurs between about 88 and 98.5% Hg for samples annealed at -80°C . For the alloys with a Hg content higher than 94 at.%, only the higher temperature transition is observable. Evidently, the Hg-rich phase is able to form a closed shell around the ω -phase inclusions and shield out the lower temperature transition completely. Another two-phase region is present in alloys from about 26 to about 35 at.% Hg. Two transitions were observed for samples containing 29.5 and 35 at.% Hg annealed at 145°C and room temperature, respectively, while only one transition could be detected in samples with 25 at.% Hg annealed at 145°C and 35 and 39 at.% Hg annealed at 110°C . These observations help to fix the location of the ω -phase boundary on the Cd side, and have been incorporated into Fig. 1.

Omega Phase, Ordering

The ω phase has a tetragonal body-centered structure with 2 atoms per unit cell.²⁰ The lattice constant a in-

²⁰ R. F. Mehl, J. Am. Chem. Soc. 50, 381 (1928).

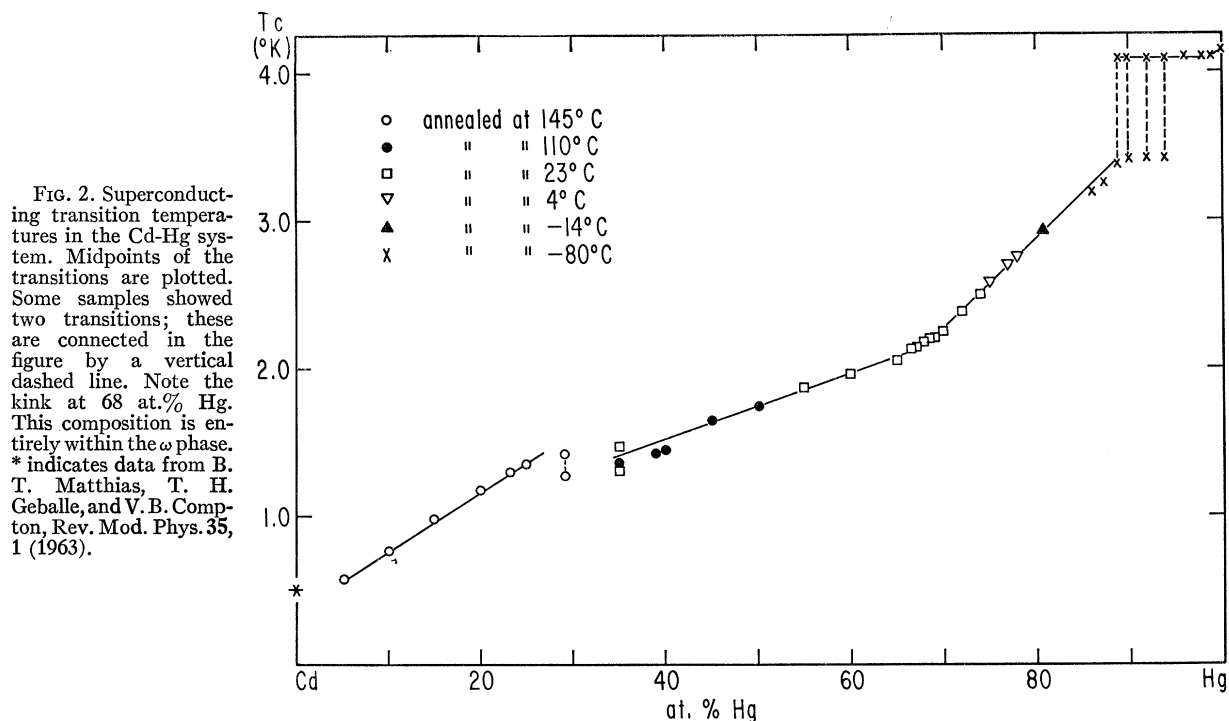


FIG. 2. Superconducting transition temperatures in the Cd-Hg system. Midpoints of the transitions are plotted. Some samples showed two transitions; these are connected in the figure by a vertical dashed line. Note the kink at 68 at. % Hg. This composition is entirely within the ω phase. * indicates data from B. T. Matthias, T. H. Geballe, and V. B. Compton, Rev. Mod. Phys. 35, 1 (1963).

creases from 3.913 Å at 40 at. % Hg to 3.978 Å at 72 at. % Hg, while the parameter c decreases from 2.892 Å at 40 at. % Hg to 2.863 Å at 72 at. % Hg.⁷

During the investigation it was discovered that ordering occurs, based on the compositions Cd_2Hg and CdHg_2 . The ω' and ω'' superlattices are formed by a threefold extension of the body-centered tetragonal unit cell of the ω phase in the c direction. The new unit cell is also body-centered tetragonal and contains six atoms, two of one kind constituting the corners and the body-centered position of the cell and the other four occupying the positions between. The atom positions are illustrated in Ref. 7.

From Fig. 2 it is seen that T_c increases quite strongly with increasing Hg content. Most remarkable is the

change in slope at about 68 at. % Hg. We discuss this feature later in this section. The effect of ordering on T_c was investigated, resulting in the observations shown in Fig. 4. A small decrease in T_c is observed for samples annealed below the ordering temperature (for ordering temperatures see Fig. 1) compared with the values of the same samples quenched from above the ordering temperature.

The interpretation of the observations in connection with the effect of ordering on T_c is, however, not completely straightforward. For one thing, it is impossible to be sure that the samples quenched from above the ordering temperature are completely disordered. In fact, they almost certainly are ordered to some extent, since resistance measurements⁷ have shown that the resist-

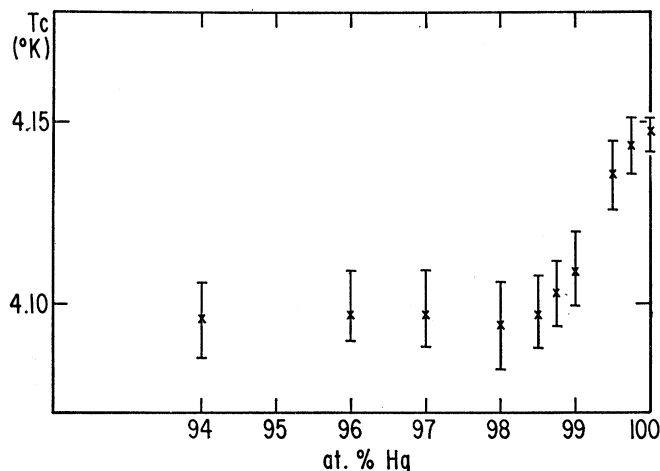


FIG. 3. T_c for Cd-Hg in the 94-100 at. % mercury region. The widths and the midpoints of the transition temperatures are plotted. The solid solubility of Cd in Hg is determined to be 1.5 ± 0.25 at. % at -80°C .

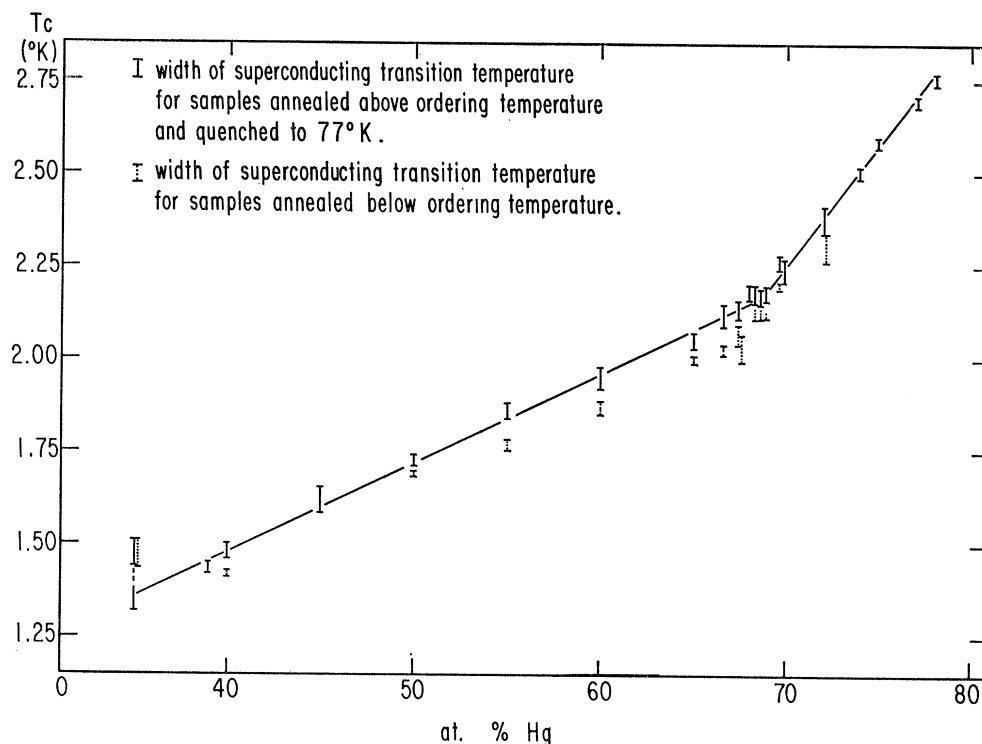


FIG. 4. T_c for samples in the intermediate ω phase annealed above and below the ordering temperature. The ordering lowers T_c . Samples of composition 65.0, 67.4, and 69.9 at.% Hg once showed no transition above 1.3°K, as discussed in the text.

ance in thin samples quenched directly into liquid nitrogen falls below the value expected from the extrapolation of the resistance-versus-temperature curve above the ordering temperature. The resistance value does not change during 12 h at nitrogen temperature. For samples taken through the ordering temperatures very slowly, however, the resistance at nitrogen temperature falls well below the value obtained for quenched samples. This indicates that even with rapid cooling ordering takes place. The decreased resistance arises from the presence of ordered antiphase or out-of-step domains, which can have a measurable effect even when the domains are very small. In Cu_3Au , Jones and Sykes²¹ found that ordered domains 38 Å in dimension (as measured by x-ray line broadening) reduced the resistivity approximately 5% below the extrapolation of the high-temperature, disordered, curve. The size of the ordered domains depends primarily on the cooling rate through the transformation temperature. The domains grow larger with slower cooling and annealing just below the transformation temperature. Growth of domains of this sort has been studied in electrical resistivity investigations²¹ and in the variation of Young's modulus with annealing temperature and time.²²

No difference in T_c between bulk samples and thin sheets quenched to liquid-nitrogen temperature could be detected (since the thin-sheet samples cool much more rapidly, they should contain antiphase domains of a smaller size). This indicates either that T_c is not affected very much by a change of domain size, as long

as the domains are very small, or that the domain size does not depend strongly on the cooling rate so long as this exceeds a certain value.

In order to check the possibility that our samples contained a substantial amount of temperature-dependent short-range order at room temperature (25°C) we quenched two samples (32.6 and 33.3 at.% Hg) from 50°C into liquid nitrogen, and looked for a change in T_c from the value obtained on quenching from room temperature. No change was found.

Another problem in interpretation of the effects of ordering on T_c arises from the fact that samples which have been carefully annealed in order to promote maximum order cannot be expected to consist of a single domain. In general many domains are nucleated and grow until they contact each other, at which point almost all the atoms see an ordered environment, but the different domains are not in phase with each other from the over-all point of view. Conversion of the multidomain structure into a single-domain structure proceeds very slowly, in practice often at an inconsequential rate.²³ The fact that the sample is multidomain broadens the superlattice reflections measurably if the domain size is less than 1000 Å, whereas the regular reflections are, of course, unaffected. The broadening of the superlattice reflections, over and above the background breadth observed in the other lines, thus makes possible a reliable measurement of the size of the antiphase domains. In our case broadening was clearly present, yielding domain size estimates in the range 300–1000 Å.

²¹ F. W. Jones and C. Sykes, Proc. Roy. Soc. (London) **A166**, 376 (1938).

²² N. W. Lord, J. Chem. Phys. **21**, 692 (1953).

²³ A. Taylor, *X-Ray Metallography* (John Wiley & Sons, Inc., New York, 1961), p. 674.

Since the boundaries between domains are regions of disorder (they are so thin as to be essentially two-dimensional), it is clear that even in a "well-ordered" sample the disordered phase exists in a continuous multiply connected cellular structure, somewhat like a soap froth. It is well established²⁴ that in a geometrically analogous situation, where a tiny amount of superconducting phase has precipitated in the grain boundaries of a nonsuperconducting matrix, the entire sample appears superconducting in an ac susceptibility measurement, which is the measurement we are making here. Consequently, if the T_c of the ordered phase of Hg-Cd were lower than that of the disordered phase we might well observe only the transition of the disordered phase.

What was actually observed in all but a few samples is shown in Fig. 4. Annealing a sample below the ordering temperature lowered the superconducting T_c a small but distinctly measurable amount, as compared with that of the same sample equilibrated above the ordering temperature and quenched into liquid nitrogen. The simplest conclusion possible from this information alone is that what is being measured is the T_c difference between the ordered and disordered phases, the ordered phase being slightly lower. However, we are not at all sure that this is correct, since the transition observed could very well arise from the small amount of disordered phase present in the antiphase domain boundaries, as discussed above. True, the temperature is slightly lower than it is when the sample is all disordered phase, but this could be because the disordered layer is thin and in contact with a large amount of nonsuperconducting ordered phase, thus having its transition temperature lowered through a proximity effect.²⁵ The T_c of the ordered phase is then known only to be lower than for the disordered. A hint that it may actually be much lower, below 1.3°K, is given by the results of experiments on three samples (65.0, 67.4, and 69.9 at.% Hg) annealed below the ordering temperature in which no superconducting transition could be observed down to 1.3°K. If the samples were warmed to above the ordering temperature, then cooled and reannealed below it, then measured again for superconductivity the previous result could not be reproduced and the usual slightly depressed transition was observed. Quite possibly the true T_c of the ordered phase is below 1.3°K, and the three anomalous samples did not contain enough domain boundaries in the right configuration to support superconductivity in the disordered phase. The only way to settle this question would be to use a method of detecting superconductivity which is sensitive to bulk properties, such as specific heat.²⁵ It is not sure that the measured T_c for samples quenched from room temperature to liquid-nitrogen temperature is the T_c of the disordered phase, as ordering in small-size domains

still occurs. This could depress the transition temperature but to a smaller extent than in samples with larger domain sizes. This possibility is discussed later.

The sample of composition 35 at.% Hg showed two transitions, one characteristic of the Cd phase and one characteristic of the ω phase, when annealed above the ordering temperature. When subsequently annealed below the ordering temperature, the transition temperature of the Cd phase remains unchanged compared to the disordered sample, while that of the ω phase drops below 1.3°K (the limit of observation). However, as can be seen from Fig. 4, this does not imply a very large drop.

In either case the ordering evidently lowers the superconducting transition temperature. This is in line with the general trend that lower normal-state resistivity is associated with weaker superconductivity (lower T_c) since both depend on the electron-phonon interaction.

The ordering ought to affect all of the three parameters in the BCS formula for the transition temperature²⁶:

$$T_c \approx 1.14\theta \exp[-1/N(0)V],$$

where θ is the Debye characteristic temperature, $N(0)$ is the density of electronic states at the Fermi energy, and V is a parameter which measures the strength of the electron-phonon coupling responsible for the superconductivity. The lattice vibrations are expected to be affected by the ordering process. It is known that in many cases the elastic moduli (e.g., shear constants and Young's modulus) increase slightly with ordering. A small increase in the Debye temperature for ordered alloys of composition AuCu₃ compared to disordered samples of the same composition has been observed.²⁷ The increase is rather small due to the averaging over lattice frequencies in computation of the Debye temperature. A detailed picture of the effect of ordering upon the lattice spectrum would be of value, since the lower frequencies, which are quite important in determining θ , do not have much effect on T_c .

The density of electron states per unit energy at the Fermi level can be expected to change on ordering. In the same way as the Brillouin zone is split in half in a diatomic one-dimensional chain, the ordering that converts three tetragonal unit cells stacked in the c direction into a single large cell has the effect of subdividing the Brillouin zone. This will affect the density of states at the Fermi surface because the relative positions of the Fermi surface and the Brillouin zone boundaries will be changed. To get a decrease of the superconducting transition temperature a smaller density of states at the Fermi level is needed and it is not difficult to imagine an E -versus- k characteristic in which the splitting of the bands (subdivision of the zone) will produce this effect.

The parameter V in the BCS formula is dependent

²⁴ G. Arrhenius, R. Fitzgerald, D. C. Hamilton, B. A. Holm, B. T. Matthias, E. Corenzwit, T. H. Geballe, and G. W. Hull, Jr., *J. Appl. Phys.* **35**, 3487 (1964).

²⁵ C. A. Shiffman, J. F. Cochran, and M. Garber, *Rev. Mod. Phys.* **36**, 127 (1964).

²⁶ J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).

²⁷ D. B. Bowen, *Acta Met.* **2**, 573 (1954).

upon the matrix element for phonon-electron interaction and the screened Coulomb repulsion. Hence a weaker phonon-electron interaction (which will give a longer mean free path and a lower resistivity) will decrease V and give a lower T_c . Presumably a combination of the decrease in V and the change in density of states is mainly responsible for the drop in T_c reported here.

Considering now the kink in T_c versus composition at 68 at.% Hg, Merriam²⁸ has reported changes of slope in T_c versus composition for nontransition metal alloy systems. These changes were explained as arising from Fermi surface-Brillouin zone interaction. The kink in the ω phase may also arise from a similar situation. The radius of the free-electron Fermi sphere, for two electrons per atom, exceeds the distance from the center to the (011) plane of the first Brillouin zone by about 2%, considering the measured⁷ lattice parameters of the ω phase. This is close enough so that it is possible that the Fermi surface is contained by this plane, through deformation of the sphere, since the zone boundary implies an energy gap. The shape of the Brillouin zone changes as the c/a ratio varies with composition. However, the change is rather small and the distance to the (011) plane is changed very little, and the observed kink could arise from the Fermi surface breaking through the zone boundary, which would give a small change in the density of electron states and hence in the superconducting transition temperature. As the (110) planes of the first Brillouin zone already are crossed by the Fermi surface, a phase change of the Hume-Rothery type is not expected. However we may speculate that the proximity of the Fermi surface to the (011) plane may be connected with the order-disorder transformation since the electron contribution to the free energy is dependent upon the relative positions of the Fermi surface and the Brillouin zone.

To check this electronic structure explanation, 1 at.% of Ag and Pb, respectively, were added to samples with compositions in a range around the one where the kink in T_c versus composition is observed. Presumably this would only change the radius of the Fermi sphere as the number of free valence electrons was decreased and increased, respectively. However the results were inconclusive. Judging from the distribution of the superconductivity data, the Ag atoms might not be dissolved while the Pb atoms might be dissolved. The kink in transition temperature versus composition was not shifted appreciably for samples with Ag added, while the shift for samples with Pb added was slightly less than 2 at.%. This was less than the expected shift, and considering the solubility uncertainty is not conclusive.

Another possible, and perhaps more probable, explanation is that the kink is connected in some way with the order-disorder transformation, since it is rather suggestive that it occurs near 67 at.% Hg, which is the 1:2 atom ratio composition, and thus the point at which

ordering tendencies are strongest. Since, as discussed above, the disordered phase cannot be retained completely by quenching, and some ordered phase will form, it is conceivable that T_c is depressed below the (unrealizable) "true disordered" phase, most strongly so at the kink composition. This explanation has a severe disadvantage in the fact that the kink is rather sharp and not rounded.

However, in the vicinity of the 2:1 atom ratio composition at 33 at.% Hg the curve of T_c versus composition seems to be bending over. The presumed tendency to ordering at this composition might help to explain why the measured T_c 's at this end of the ω phase seem to fall mostly below the straight line drawn through the bulk of the ω -phase data at Hg concentrations below 68% (see Fig. 2). It seems rather reasonable that residual effects of the small amounts of order present in the disordered phase should be greatest at the 1:2 and 2:1 atom ratio compositions.

Intermediate Compound Cd₃Hg

On the basis of x-ray investigation it has been claimed²⁹ that the phase Cd₃Hg forms somewhere between 147 and 170°C. Other authors^{30,30} have not found such a compound. The superconducting transition temperature gives no indication that the proposed phase exists. Samples annealed at 175 and 145°C, respectively, showed no difference in transition temperature. Resistance measurements showed no anomalies between -80 and 175°C. We conclude that there is no such compound.

Summary of Superconductivity Results

Looking at the Cd-Hg system as a whole, one notices the general trend is for increase of T_c with increasing Hg content. In any given phase the increase is linear, except for a kink in the ω phase at about 68 at.% Hg, which may arise from an ordering at the 1:2 atom ratio composition or maybe from a Brillouin zone effect. Ordering in the ω phase apparently reduces T_c . The reduction is discussed in terms of a smaller electron-phonon interaction indicated by the lower resistivity in the ordered state, and also by considering a possible change in density of states.

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²⁹ N. W. Taylor, J. Am. Chem. Soc. **54**, 2713 (1932).

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²⁸ M. F. Merriam, Rev. Mod. Phys. **36**, 152 (1964).