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Superconductivity of Dilute Primary Solid Solutions of In-Mg and In-Pb*

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Synopsis

By measuring magnetic moments and electrical resistances of pure indium and indium alloys containing 0.28 to 13.7 atomic per cent of magnesium and 0.06 to 0.73 atomic per cent of lead at liquid helium temperatures, the variation of the superconducting critical temperature, T_c , with the concentration of solute metals was studied. T_c decreases initially with the increasing concentration of solute in so far as a small amount of solute metals is concerned. When the amount becomes large, the alloying effect of magnesium differs from that of lead, i.e., in the former case T_c continues to decrease steadily, while in the latter it shows a gradual increase after passing through a minimum. These results qualitatively agree with the theoretical consideration of Anderson and of Nakamura. The threshold magnetic field at 0°K and the coefficient of electronic specific heat in the normal state were estimated from the data obtained.

I. Introduction

Recently, the superconducting critical temperature, T_c , of a pure metal has become higher with incessant progress in the techniques of metal purification. For instance, about 20 years ago T_c of tin, a typical superconductor, was reported to be 3.6°K. However, from the experiments with a highly purified sample at present, it is believed to exceed 3.73°K. The explanation of this fact may be found in that the trace of impurities in the so-called pure superconductor gives rise to the decrease in T_c . It is very interesting, therefore, to study how the characteristics of superconducting primary solid solutions depend on the amount of solute metals added and on the difference in valency between the solvent and the solute metals.

The solute metals can be divided into two groups, non-magnetic and magnetic. Superconductivity of the primary solid solutions containing two kinds of non-magnetic solute metals was dealt with in the present work. The alloying causes the difference in the number of conduction electrons and the impurity scattering of conduction electrons; the former gives rise to a variation in the state density at the

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Fermi surface, because the band structure of an alloy containing a small amount of solute does not seem to be appreciably different from that of the solvent metal, and the latter changes the magnitude of V effectively by adding the third interaction, the electron-impurity interaction to $-V$ in the BCS theory⁽¹⁾. It may be conceivable also that the average value of the phonon energy, $\langle \hbar\omega \rangle$, varies with alloying.

Mann *et al.*⁽²⁾ reported the experimental results on the impurity effect in superconductors, i.e., the superconducting threshold magnetic field decreased when 0.5 per cent Bi, 0.5 per cent Pb or 0.7 per cent Tl was added to tin. A systematic work on tin was made by Lynton and his co-workers⁽³⁾. In the course of the present study, works on indium and aluminium alloys by Chanin *et al.*⁽⁴⁾ and on In-Hg system by Reeber⁽⁵⁾ were reported.

In the present work, indium metal of 99.999 per cent nominal purity was used as the solvent metal, and magnesium and lead as the minor solutes.

II. Specimens

For In-Pb alloys lead was added to pure indium up to 0.73 atomic per cent. The phase diagram of In-Mg system has not been reported in full detail, especially in the indium-rich region. According to Raynor⁽⁶⁾, however, a considerable range of solid solution exists extending from In to Mg side. Hence, magnesium was added to pure indium to 13.7 atomic per cent.

Mother alloys were prepared with 13.7 atomic per cent of Mg for In-Mg alloys and those with 0.73 atomic per cent of Pb for In-Pb alloys, being kept molten *in vacuo* for 24 hours to make the solute atom distributions uniform. Then, the specimens containing various amounts of solute were prepared by weighing a suitable amount of the mother alloys. Specimens containing various amounts of solute were melt in argon atmosphere, sucked up into glass tube, and cooled in the furnace. Each specimen was annealed *in vacuo* at 120°C for 7 days.

All specimens, 3 mm in diameter and 70 mm in length, were polycrystalline, and the magnetic moment and the electrical resistance were measured in one run.

The concentration of each specimen is given in Table 1.

III. Experimental apparatus and measurements

The apparatus for the measurement, shown in Fig. 1, is mainly the same as used previously⁽⁷⁾. The specimen was set at the bottom of a thin-walled glass tube. A search coil was fixed around the center of the specimen and a compensating coil

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- (1) Bardeen, Cooper and Schrieffer, *Phys. Rev.*, **108** (1957), 1175.
 - (2) Mann, G. Smith and Wilhelm, *Phys. Rev.*, **54** (1938), 758.
 - (3) Lynton, Seran and Zucker, *J. Phys. Chem. Solids*, **3** (1957), 165.
 - (4) Chanin, Lynton and Seran, *Phys. Rev.*, **114** (1959), 719.
 - (5) Morton and D. Reeber, *Phys. Rev.*, **117** (1960), 1476.
 - (6) G.V. Raynor, *Trans. Far. Soc.*, **44** (1948), 15.
 - (7) Y. Shibuya, *J. Phys. Soc. Japan*, **13** (1958), 684.

Table 1.

a) Percentage of Mg in the In-Mg system

Specimens	pure	No.5	No.4	No.3	No.2	No.1
Nominal weight per cent	0	0.06	0.13	0.21	1.4	3.3
Nominal atomic per cent	0	0.28	0.61	0.99	6.3	13.7
Analytical weight per cent	0.000	0.017	0.030	0.041	0.086	2.02

b) Percentage of Pb in the In-Pb system

Specimens	pure	No.5	No.4	No.3	No.2	No.1
Nominal weight per cent	0	0.05	0.11	0.28	0.86	1.3
Nominal atomic per cent	0	0.06	0.16	0.27	0.48	0.73
Analytical weight per cent	0.000	0.048	0.12	0.11	0.57	0.68

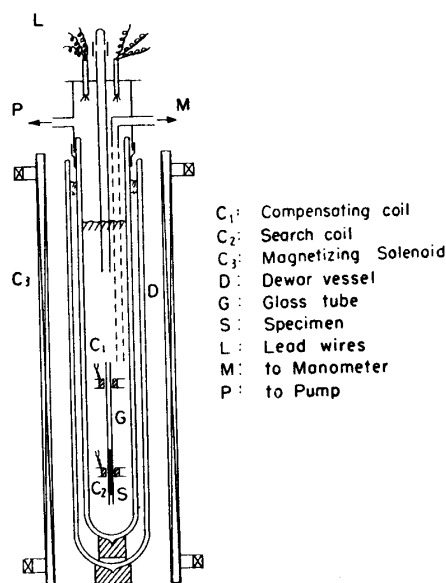


Fig. 1. Schematic diagram of the experimental apparatus, but two pairs of large Helmholtz coils of square-type are not shown.

connected in opposition to the search coil was fixed, sufficiently far from the specimen, at the upper position of the glass tube. The glass tube and the coils were made with great care in order to reduce the space between the surface of the specimen and the inside of coils as small as possible. The search coil and the compensating coil were connected with a ballistic galvanometer. The Dewar vessel system was placed in the P.V.F. wire-wound solenoid system which, having

a coil constant 66.45 oersted/ampere, gives a uniform longitudinal magnetic field. The whole system was placed in the central position of two pairs of large Helmholtz coil of square type to neutralize the earth magnetic field.

1. Magnetic moment

When a cylindrical superconductor having a large dimension ratio, the diameter being large enough in comparison with the penetration depth λ ($\lambda \approx 10^{-5} \sim 10^{-6}$ cm), is placed in a uniform, longitudinal, external magnetic field, the internal magnetic field in the superconductor, $H_i = B - 4\pi I$, is equal to the external field H , since in this case the demagnetizing field can be neglected. As the superconducting state shows practically a perfect diamagnetism ($B=0$), the magnetic moment per unit volume is given by the following formula⁽⁸⁾:

$$I = -\frac{1}{4\pi} H \quad (1)$$

The demagnetizing field in the specimen used was estimated to be very small, since the demagnetizing coefficient $n \approx 6 \times 10^{-3}$. The dimension of all the specimens was much larger than λ so that it could be neglected.

When the external magnetic field is reversed, the mirror of galvanometer is deflected by an induction current only in the compensating coil, since that in the search coil is kept zero when the specimen is superconducting. The deflection of the ballistic galvanometer is proportional to the magnetic moment of the specimen.

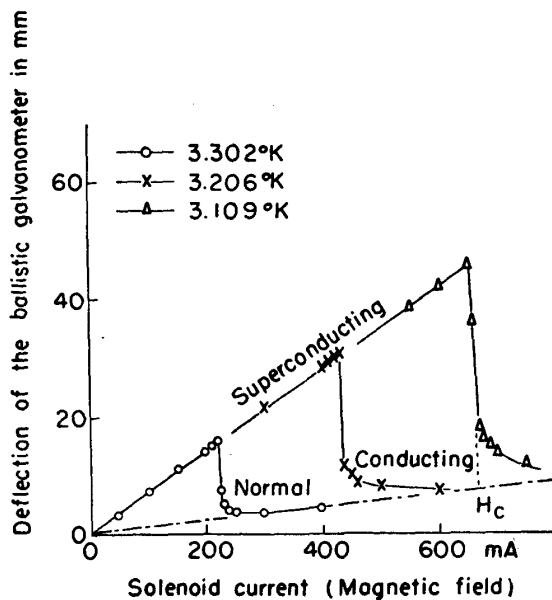


Fig. 2a.

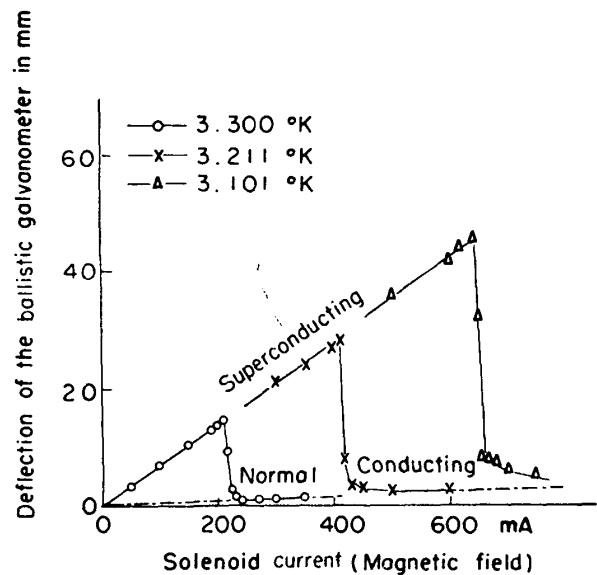


Fig. 2b.

Fig. 2a. Magnetization curves for pure In at the specified temperatures.

Fig. 2b. Magnetization curves for one of In-Pb specimens (0.16 atomic per cent Pb) at the specified temperatures.

(8) D. Shoenberg, *Superconductivity*, 2nd ed. Cambridge (1952), 22.

Magnetization curves of pure indium and an In-Pb specimen containing 0.16 at. per cent Pb are shown in Figs. 2a and 2b, respectively. Owing to an imperfect compensation, the normal state line does not coincide with the abscissa in these figures.

2. Electrical resistance

Using the electrical resistance at 4.2°K, $R_{4.2}$ (resistance due to the impurity scattering) and that at 273°K, R_{273} , the residual resistance ratio ρ is given by

$$\rho = \frac{R_{4.2}}{R_{273} - R_{4.2}} \quad (2)$$

According to the Matthiessen's rule, the denominator is the resistance due to the lattice scattering at 273°K, which is determined by characteristics of the pure metal and assumed to be independent of the impurity concentration of the specimen. The effect of impurities is included in the numerator $R_{4.2}$. The value of ρ is equal to the ratio of the ideal specific conductivity at 273°K, σ_{id273} , to the specific conductivity at 4.2°K, $\sigma_{4.2}$. For any material the ratio of the electronic mean free path, l , to the conductivity, σ , is a constant independent of temperature, so a linear relationship can be found between the resistance ratio and the reciprocal of the mean free path at low temperatures. The value of l/σ can be obtained from the measurement of AC surface conductivity in the limit of anomalous skin effect⁽⁹⁾. For the indium specimen, the values adopted by Chanin et al.⁽⁴⁾ were used.

$$l/\sigma = 0.89 \times 10^{-11} \text{ ohm. cm}^2 \text{ and } \sigma_{id273} = 13 \times 10^4 \text{ ohm}^{-1} \text{ cm}^{-1}.$$

$$1/l = (0.87 \times 10^6) \rho \text{ cm}^{-1}. \quad (3)$$

The resistance was measured by the direct current method using the potentiometer having the accuracy of 10^{-8} V. The current through the specimen was kept around 0.8 A. Results obtained in reversed current directions were averaged in order to eliminate the thermoelectric effect.

IV. Experimental results

Magnetic moments of the specimens were measured at several temperatures. The threshold magnetic field H_c was determined by the extrapolation of the linear part near H_c of the magnetic moment *versus* magnetic field curve to the normal line. The typical relationship between the solenoid current and the deflection of galvanometer for pure indium at 3.109°K is shown in Table 2 and graphically in Fig. 2a. It can be seen that the critical magnetic field of pure indium at 3.109°K is $H_c = 665$ mA expressed with the solenoid current. In Fig. 2b magnetization curves of an In-Pb specimen containing 0.16 at. per cent Pb are shown. The relation between H_c and the temperature for pure indium is given in Table 3 and graphically in Fig. 3. H_c decreases with the increase in temperature and the curve is nearly parabolic.

(9) R.G. Chambers, Proc. Roy. Soc. (London) **A 215** (19652), 481.

Table 2. The relation between the magnetic field (current in solenoid) and the magnetic moment (deflection of galvanometer) in the case of pure In at 3.109°K.

Magnetic field		Magnetic moment
(Current in solenoid)	H	(Deflection of galvanometer)
200 mA	13.3 oe	14.1 mm
400	26.6	28.2
550	36.6	38.5
600	39.9	42.3
650	43.2	45.5
660	43.9	36.2
670	44.5	18.0
680	45.2	16.0
690	45.9	15.0
700	46.5	14.0
750	49.8	12.0
800	53.2	11.5
900	59.8	11.5

Table 3. The relation between the critical magnetic field and the temperature in the case of pure In.

Temperature	Critical magnetic field
3.348 °K	7.6 oe
3.302	14.8
3.254	21.7
3.206	28.9
3.151	36.9
3.109	44.2
3.005	57.6
2.853	78.4
2.704	97.7
2.550	117
2.405	135
2.245	153
2.098	172
1.882	193
1.727	208

While H_c is a linear function of T to a good approximation in the temperature range $0.9 T_c < T < T_c$, the transition temperature T_c is obtained by the extrapolation to the abscissa. Assuming that H_c follows a parabolic function of T to the lowest temperature, the critical magnetic field at 0°K, H_0 , is estimated by the extrapolation to the ordinate (See Fig. 4). The values of T_c and H_0 for each specimen are also listed in Table 4. The gradient at the point of $T=T_c$ on H_c - T curve for pure indium is as follows:

$$(dH_c/dT)_{T=T_c} = 147.0 \text{ oe/deg.}$$

In Table 4 the values of $1/l$ for each specimen are also shown. In Table 5 the specific resistivities of some specimens are given. The resistivity increases with increasing concentration of impurity. In the case of pure indium the ratio of the resistance at 4.2°K to that at room temperature is nearly equal to 7/10,000.

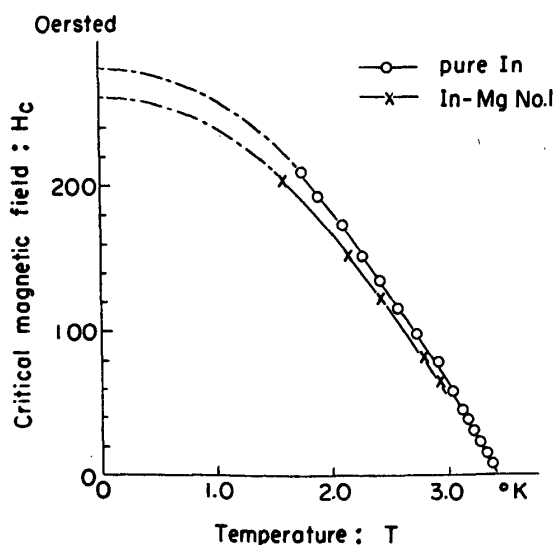


Fig. 3.

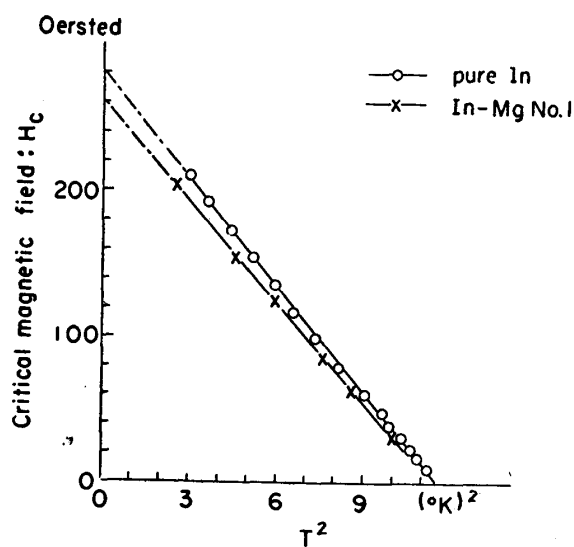


Fig. 4.

 Fig. 3. H_c - T relations for pure In and In-Mg No. 1.

 Fig. 4. H_c - T^2 relations for pure In and In-Mg No. 1.

 Table 4. Impurity concentration, residual resistance ratio ρ , $1/l$, T_c , H_0 and γ .

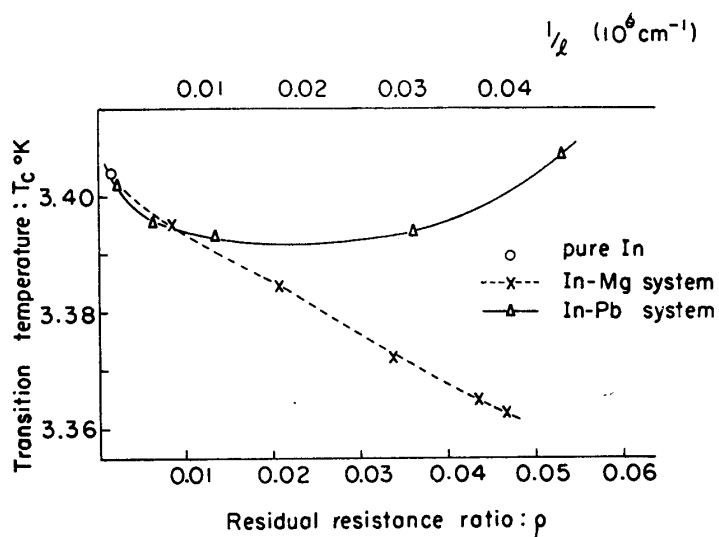
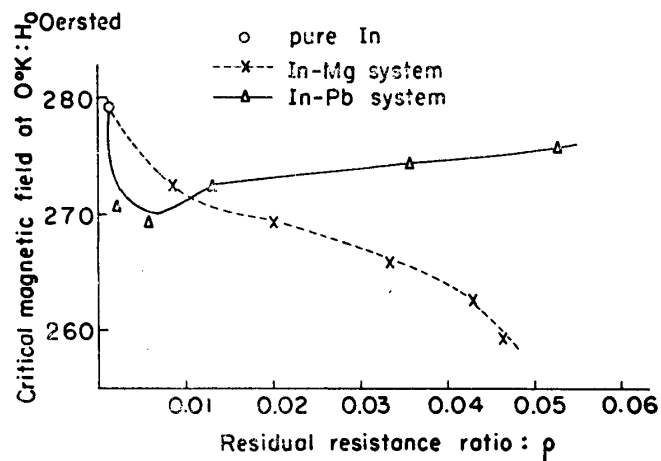
	Impurity concentr. wt. %	Residual resistance ratio ρ	$1/l \times 10^{-6}$ cm^{-1}	Transition temperature T_c °K	H_0 oe	$\gamma \times 10^4$ calories/ mol. deg ²
Pure In	0	0.0013	0.0011	3.404	279.1	4.29
In-Mg system						
No. 5	0.06	0.0081	0.0071	3.395	272.4	4.11
No. 4	0.13	0.0200	0.0174	3.385	269.1	4.03
No. 3	0.21	0.0334	0.0291	3.372	265.8	3.96
No. 2	1.4	0.0432	0.0376	3.365	262.5	3.88
No. 1	3.3	0.0463	0.0403	3.363	259.2	3.79
In-Pb system						
No. 5	0.05	0.0018	0.0016	3.402	270.8	4.04
No. 4	0.11	0.0056	0.0049	3.396	269.1	4.00
No. 3	0.28	0.0128	0.0111	3.393	272.4	4.11
No. 2	0.86	0.0354	0.0308	3.394	274.1	4.16
No. 1	1.3	0.0526	0.0458	3.407	275.6	4.17

T_c for In-Mg and In-Pb system is plotted against ρ in Fig. 5. Since ρ is proportional to $1/l$, the abscissa is scaled also by $1/l$. In the region of small ρ , T_c decreases with increasing ρ in both systems. In the region of relatively large ρ these systems show different behaviours from each other; in the In-Mg system it still continues to decrease, while in the In-Pb system it shows a gradual increase after passing through a minimum. H_0 versus ρ is plotted in Fig. 6. It can be seen that these curves take a behaviour similar to that of T_c - ρ curves.

The coefficients of electronic specific heat in the normal state were evaluated from the data by using the following expression⁽¹⁾;

Table 5. Specific resistivity at T °K in 10^{-6} ohm.cm.

	Concentr. wt. %				
T °K		3.59	4.24		290
Pure In	0.00	0.00483	0.00887		7.341
T °K		3.50	4.24	77.4	290
In-Mg system					
No.5	0.06	0.0499	0.0654	1.842	8.793
No.4	0.13	0.1422	0.1582	1.932	8.903
No.3	0.21	0.2823	0.2758	2.167	9.289
No.2	1.4	0.3325	0.3557	2.238	10.16
No.1	3.3	0.7837	0.9480	8.184	23.29
T °K		3.52	4.24		287
In-Pb system					
No.5	0.05	0.0147	0.0147		8.908
No.4	0.11	0.0470	0.0467		9.016
No.3	0.28	0.0598	0.1075		9.054
No.2	0.86	0.3013	0.3320		9.056
No.1	1.3	0.4857	0.4385		9.404

Fig. 5. T_c - ρ relations for In-Mg and In-Pb systemsFig. 6. H_c - ρ relations for In-Mg and In-Pb systems

$$\gamma = \frac{0.170 H_0^2 V_m}{4.186 \times 10^7 T_c^2} \text{ calories/mole-deg}^2. \quad (4)$$

The results are given in Table 4, from which it will be seen that the values for alloyed specimens are smaller than the value for pure indium. The behaviours of γ against ρ in the cases of In-Mg and In-Pb system are similar to those of T_c respectively.

V. Discussions

The theory of superconductivity of a pure metal has been proposed by Bardeen et al.⁽¹⁾ In the BCS theory, it is essential for the occurrence of superconductivity that the electron-phonon interaction dominates over the Coulomb interaction between electrons, so that the total interaction, $-V$, becomes negative;

$$\begin{aligned} -V &\equiv (\text{electron-phonon interaction}) + (\text{Coulomb interaction}) \\ &\equiv \left[-\frac{2|M_k|^2}{\hbar \omega_k} + \frac{4\pi e^2}{k^2} \right]_{Av} < 0, \end{aligned} \quad (5)$$

where M_k is the matrix element for the electron-phonon interaction and $4\pi e^2/k^2$ the repulsive Coulomb interaction. The average value of these interactions, $-V$, is related to T_c expressed by the following equation:

$$k T_c = 1.14 \langle \hbar \omega \rangle \exp \left\{ -\frac{1}{N(0)V} \right\} \quad (6)$$

where $\langle \hbar \omega \rangle$ is the average value of the phonon energy and $N(0)$ the density of Bloch states of one spin per unit energy at the Fermi surface. T_c decreases with the decrease of V , if $-V$ is negative.

Pippard⁽¹⁰⁾ has suggested that the magnitude of V is related to the reciprocal of the electronic mean free path. Nakamura⁽¹¹⁾ and Suhl et al.⁽¹²⁾ have shown independently with respect to the alloys containing a small amount of non-magnetic impurities that the magnitude of V decreases effectively through alloying due to the impurity-scattering of electrons, thence T_c of the alloy becomes lower than that of the solvent metal, and the decrease of the transition temperature, ΔT_c , is proportional to the reciprocal of mean free path irrespective of the properties of the impurities added. For a large concentration of impurity, that is, for dirty superconductors, Anderson⁽¹³⁾ has indicated that the value of V is almost constant, and that the effect of $N(0)$ on T_c becomes dominant.

In Fig. 5, T_c initially decreases with the addition of magnesium and lead respectively in systems of In-Mg and In-Pb but these systems take different trends with a further addition of solute metals; i.e., in the former T_c still continues to

(10) A.B. Pippard, J. Phys. Chem. Solids, **3** (1957), 175.

(11) K. Nakamura, Prog. Theor. Phys., **21** (1959), 435.

(12) H. Suhl and B.T. Matthias, Phys. Rev., **114** (1959), 435.

(13) P.W. Anderson, J. Phys. Chem. Solids, **11** (1959), 997.

decrease, while in the latter it makes a gradual increase after passing through a minimum. It can be considered that ΔT_c , being a difference between T_c of pure indium and that of the alloy, consists of two parts:

$$\Delta T_c = \Delta T_{c1}(\rho) + \Delta T_{c2}(\rho, Z, M), \quad (7)$$

where Z is the difference between the valencies of solvent and solute atoms and M the mass of a solute atom. In the case of In-Mg system ΔT_{c2} , similar to ΔT_{c1} , is negative, while in the case of In-Pb system ΔT_{c2} is positive in contrast to the negative value of ΔT_{c1} , and in the region of small ρ , ΔT_{c1} is dominant over ΔT_{c2} which is dominant in the region of larger ρ . As is described above, the alloying causes the number of conduction electrons in unit volume to change, i.e., it causes ΔT_{c2} to be negative in the former system and positive in the latter.

As the valency of magnesium is equal to that of cadmium or mercury, the data of the In-Mg system are compared with those of the In-Cd and the In-Hg system graphically in Fig. 7.

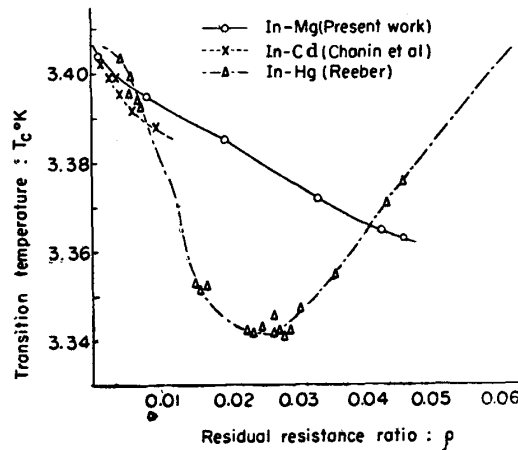


Fig. 7. Comparison between In-Mg (present work), In-Cd (Chanin et al.) and In-Hg system (Reeber).

Since T_c decreases with the decrease of $N(0)$ from Eq. (6), in these cases T_c must continue to decrease on the assumption of no variation in the band structure. But in the case of the In-Hg system it makes the increase after passing through a minimum. Seeing that T_c of mercury is 4.15°K , that of cadmium 0.56°K and magnesium has not been discovered to be a superconductor, it can be expected that in the In-Hg system T_c increases after passing through a minimum and that on the other hand in the cases of the In-Mg and the In-Cd system T_c continues to decrease. In the In-Pb system it can be considered also that since T_c of lead is 6.22°K , being higher than that of indium, ΔT_{c2} takes positive values reasonably. Seeing this problem from the above point of view, it may be interesting to use the solute metal, T_c of which is lower than that of the solvent, and the valency of which is larger than that of the solvent.

Values of T_c , H_0 , $(dH_c/dT)_{T=T_c}$ and γ for pure indium are listed, together with those from other works, in Table 6. Finally, it can be deduced from the ρ -dependence of T_c in Fig. 5 that the transition temperature of the purest indium is 3.407°K .

Table 6. Constants for pure indium

T_c °K	H_0 oe	$\left(\frac{dH_c}{dT}\right)_{T_c}$ oe/deg	$\gamma \times 10^4$ calories/ mol. deg ²	Reference number
3.404 ± 0.002	279.1	-147.0	4.29 (mag)	Present work
3.4075 ± 0.0005	285.7		4.55 "	(18)
3.407 ± 0.002	293.0	-155.5	4.6 "	(13)
3.408 ± 0.005		-137.6		(17)
3.404 ± 0.003	284.5	-155.8		(16)
3.409 ± 0.002	275.0	-142.2	4.0 "	(15)
3.387 ± 0.005	278.4		4.33 (cal.)	(14)

N.B. (mag.) means the value derived from magnetic measurement, and (cal.) means that from calorimetric.

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 (18) R.W. Shaw, Mapother and Hopkins, Phys. Rev., **120** (1960), 88.