Effect of Transition-Metal Impurities on the Critical Temperature of Superconducting Al, Zn, In, and Sn†

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The depression in critical temperature T_c of several dilute solid solutions of transition elements in Al, Zn, In, and Sn was measured as a function of residual resistivity and concentration. In Zn-Mn and Zn-Cr, localized moments are present and T_c decreases linearly with concentration with a slope $-dT_c/dc$ of 315 and 170°K/at.%, respectively. By comparing these numbers with theory, a value of about 1.4 eV was found for the s-d exchange integral. In all other alloys, the critical temperature is still depressed but much less than in Zn-Mn and Zn-Cr, and the depression becomes less rapid with increasing concentration of impurities. However, no saturation is found up to the maximum concentrations reached. The effect here found is different from that taking place in dilute alloys containing nontransition metals in that the depression of T_c is larger, giving rise to suppression of superconductivity at sufficiently high impurity concentration. An analysis of the data for Al-Mn, Al-Cr, Al-Fe, Zn-Fe, Zn-Co, and Zn-Ni shows that in these systems the observed decrease of T_c is satisfactorily accounted for by the smoothing out of the gap anisotropy and by the formation of localized virtual states, whose effect on the superconducting properties has been studied theoretically by Zuckermann. In-Mn and Sn-Mn do not fit the foregoing picture; however, the results obtained rule out the presence of magnetic moments in these two systems in bulk form. The apparent contrast with the results obtained in thin films is discussed. Some results on ternary alloys are also reported. It is shown that no effect on the critical temperature of In-Mn dilute solutions is produced by the addition of Pb.

1. INTRODUCTION

IT is well known that magnetic impurities cause a strong depression in the superconducting transition temperature T_c, which is linear with concentration. This fact was first observed by Hilsch and co-workers at Göttingen[1] in studying thin films of Sn, In, Pb, and Bi, containing impurities of the iron group, prepared by deposition on substrates at liquid-helium temperatures. Matthias and co-workers[2] dissolved rare-earth metals in bulk lanthanum and also found that the critical temperature decreases linearly with concentration, with a maximum slope for Gd, the rare-earth metal with the highest spin. Other measurements confirmed this view more recently.[3,4] This effect is now well understood theoretically[5-9] and is associated with gapless superconductivity. However, more experimental data on bulk systems are thought to be useful for a better understanding of the phenomenon.

On the other hand, when nontransition metals are added to pure superconductors, a much smaller effect on T_c is observed.[10-12] The major decrease of T_c is limited to the dilute concentration range of the impurities, and is related to the smoothing out of the anisotropy of the effective electron-electron interaction leading to superconductivity. This fact was suggested by Anderson,[13] and the theory was worked out by various authors.[14-16]

A third case, that of transition metal impurities not carrying magnetic moments, was very little studied up to now. Since in this case a broad "virtual localized d-state" is formed around each impurity,[17] it is interesting to explore if there is an effect on the critical temperature of the pure metal matrix. We thought that a detailed study of the effect of iron group impurities on the critical temperature of nontransition superconducting metals could be useful toward an understanding of these problems.

Preliminary measurements on Al-Mn, Al-Cr, Al-Fe, and Zn-Mn systems were already reported.[18,19] In

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this paper we present a more complete account of the previous work and new measurements on various Zn base alloys, on In-Mn, Sn-Mn, and In-Pb-Mn.

The main experimental difficulty in the study of these dilute alloys is the very limited solid solubility of transition metals in nontransition metal matrices. A careful study of the solubility limit of the alloys and of the homogeneity of the solid solutions thus prepared was therefore undertaken. The results are published elsewhere,[20] together with a detailed discussion of the residual resistivity and its concentration dependence. We should like to point out that resistivity and superconductivity measurements carried out on the same specimens complement each other in a useful way, and that often definite conclusions can be reached only because careful data on both properties are available.

2. EXPERIMENTAL

Samples and sample preparation have been described in Ref. 20. The specimens used in the present work were cut from the same rods used for resistivity measurements. They were cylindrical in shape, 1.5 to 2 mm o.d., and 5 cm long. We believe that in all alloys complete solid solution was reached during preparation and maintained until the measurements were completed. For further discussion and possible exceptions see Ref. 20. In addition we prepared a series of In-Pb-Mn solid solutions. These specimens contained 50 ppm (atomic) of Mn and variable amount of Pb, up to about 2 at.%. They were prepared by melting together, under vacuum, In-Mn and In-Pb alloys previously casted under vacuum.

The superconducting transition temperatures of Al- and Zn-alloys were measured in a He^3 cryostat designed and built in our laboratory. The cryostat is of similar design to that described by Peshkov and Zinoveva,[21] but exchange gas was not used. Temperatures as low as 0.32°K can be reached and maintained constant within a millidegree. A simplified drawing of the cryostat is shown in Fig. 1. For measuring transition temperatures, up to seven specimens could be accommodated in the experimental space and measured during the same run. In and Sn alloys were measured in a conventional cryostat.

The superconducting critical temperature of each alloy was determined by plotting the critical magnetic field H_c versus temperature at small fields and linearly extrapolating to $H_c = 0$. At each temperature, the critical field was determined by increasing the external field, applied parallel to the cylindrical specimens. The field was increased linearly at a speed of about 0.2 G/sec by using a high-stability power supply. At the superconducting transition, a signal was detected at
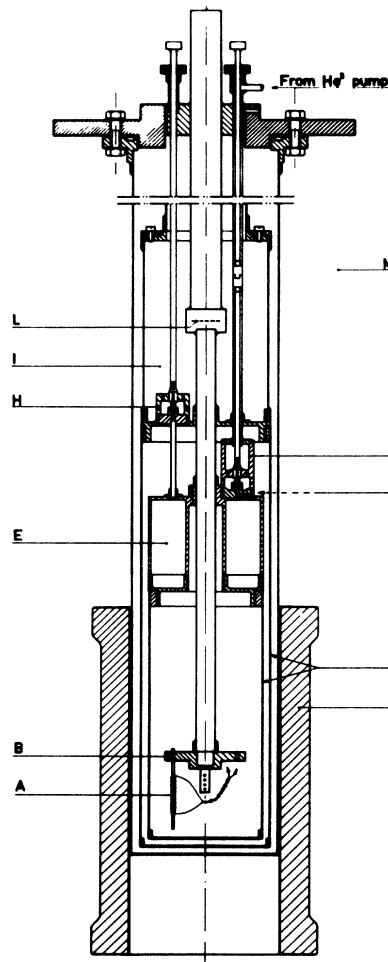
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Fig. 1. The helium-3 cryostat. A–A mounted specimen. B–Helium-3 evaporator. C–Garret solenoid. D–Radiation shields. E–Pumped liquid helium. F–Helium pumping line (in the back—not shown). G–Helium-3 condenser and needle valve. H–Needle valve to fill can E with liquid helium. I–Liquid helium at atmospheric pressure. L–Radiation shield along the He^3 pumping line. M–Liquid nitrogen.

the ends of a coil would around the specimen, by means of a Kipp recording microvoltmeter. The coil was made of about 3000 turns of enameled copper wire of 0.06 mm diameter. The external field was provided by a Garrett-type solenoid, kept at liquid-nitrogen temperature, which was capable of giving fields up to 500 G, with a uniformity of about 0.1% in the experimental space. Care was taken to avoid any superconducting or magnetic materials in the measuring cell of the cryostat. This method of detecting transition temperatures has proved to be very convenient and sensitive in determining both the critical field and the transition width. Transitions in a field as low as 0.3 G are easily detected. The detection sensitivity can be changed by varying the rate of change of the magnetic field. The magnitude of the (constant) signal observed outside the transition region enabled us to check whether the specimen was superconducting or not.

The effect of the local (earth) magnetic field was taken into account in the measurement of transition temperature of pure specimens. The width of the magnetic transition was found to be about 0.3 G for the pure metals and the most dilute alloys. In a few samples

quenched from the melt the transition width was as large as 0.6 G. From these data a width of the transition temperature could be obtained, the width being about 3 mdeg and 6 mdeg, respectively, for the most dilute alloys and for the less homogeneous samples. Samples with larger transition widths were discarded.

The temperature was measured by means of a carbon resistor thermometer, clamped to the copper support of the specimens. The thermometer was calibrated against He^3 vapor pressure, the calibration being checked at every run against the transition temperature of a pure superconducting specimen chosen as a standard.

3. RESULTS

The transition temperatures of the pure metals were the following.[22]

Al, pure Raffinal ISML   99.995 $T_c = 1.180 \pm 0.002°K$
Zn, pure Montevecchio   99.995 $T_c = 0.850 \pm 0.0005°K$
In, pure ASARCO   99.999+ $T_c = 3.405 \pm 0.001°K$
Sn, extrapure VULCAN 99.9995 $T_c = 3.710 \pm 0.003°K$.

The transition temperatures of the dilute alloys were measured relative to the pure metals. Since we are mostly interested in the depression of T_c produced
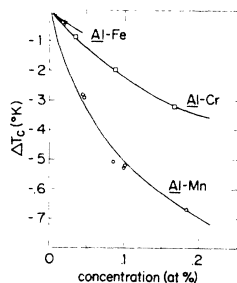
FIG. 2. ΔT_c versus concentration for all aluminum systems.

by impurities, we express our results as differences $\Delta T_c = T_c - T_{c0}$ from the critical temperature of the pure metal T_{c0}. For each alloy, the residual resistivity ratio ρ due to impurities was measured before and after the measurement of the critical temperature. ρ is defined as

$$[R_{4.2}/(R_{273} - R_{4.2})]_{alloy} - [R_{4.2}/(R_{273} - R_{4.2})]_{pure\ metal}.$$

Since a proportionality law was established in all samples between ρ and the concentration c,[20] in plotting our data we will use indifferently c or ρ values. Comments on this will be made later.

The results for Al alloys are given in Fig. 2, as a plot of ΔT_c versus concentration in atomic percent. The transition temperature of the 0.18 at.% Al-Mn alloy was just within the reach of our He^3 cryostat.

[22] Aluminum was obtained from Istituto Sperimentale Metalli Leggeri (ISML), Novara, Italy; zinc from Società Monteponi e Montevecchio, Marghera, Italy; indium from American Smelting and Refining Company, South Plainfield, New Jersey; and tin from Vulcan Material Company, Gary, Indiana.
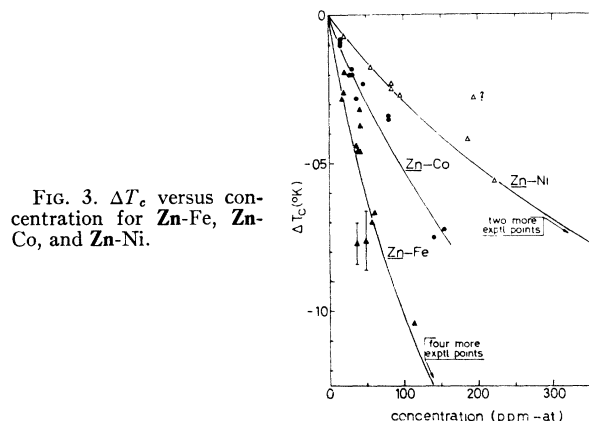
FIG. 3. ΔT_c versus concentration for Zn-Fe, Zn-Co, and Zn-Ni.

More concentrated Al-Mn alloys showed no superconductivity above 0.35°K. Al-Fe was not measured at concentrations larger than 0.018 at.%, since the iron cannot be kept in solution above this limit. The results obtained for the systems Zn-Fe, Zn-Co, and Zn-Ni are shown in Fig. 3. Again the transition temperature decreases with respect to the pure metal matrix: the lowest transition temperatures reached were fixed by the solubility of the transition metals (see Ref. 20). If higher concentrations of the transition metal are reached, superconductivity will soon disappear. In Fig. 4 the transition temperatures of Zn-Mn and Zn-Cr alloys are displayed. By linear interpolation of the data one can estimate that superconductivity is destroyed at a concentration of 25 ppm of Mn and about 45 ppm of Cr. In Fig. 5 the decrease of T_c for various Zn base systems is plotted versus the residual resistivity ratio ρ, for the purpose of comparison. In this plot data obtained by us for the system Zn-Al are reported. The difference between transition metal impurities and nontransition metal impurities is clearly seen. In Fig. 6 the results for the system In-Mn are shown, plotted again versus ρ, together with results recently obtained by Martin[23] at higher concentrations. In the
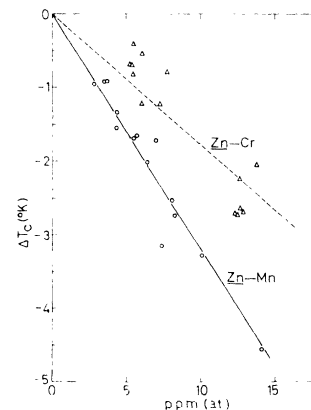
FIG. 4. ΔT_c versus concentration for Zn-Mn and Zn-Cr.

[23] D. L. Martin, Phys. Rev. 138, A464 (1965).

TABLE I. Observed initial decrease of transition temperature and residual resistivity ratio of dilute alloys.

Alloy	$\dfrac{dT_c}{d\rho}$(initial)	$\dfrac{\rho}{c}$(c in atoms %)	$\dfrac{dT_c}{dc}$(initial)
Al-Cr	2.4[a]	3.37	8.1
Al-Mn	4.2[a]	3.22	14
Al-Fe	3.5[a]	2.3	8.0
Zn-Cr	≈80[b]	2.2	≈170[b]
Zn-Mn	105[c]	3.0[c]	315[c]
Zn-Fe	5	2.8	13
Zn-Co	5.2	1.25	6.4
Zn-Ni	6.5	0.45	2.9
Zn-Al	>3.0	0.10	>0.3
In-Mn	>250[d]	0.095	>24[d]
Sn-Mn	≈0	1.85	≈0

[a] Derived from data of Aoki and Ohtsuka (Ref. 24).
[b] From linear interpolation.
[c] These values differ somewhat from those given in a previous communication (Ref. 19).
[d] See Fig. 5.

inset, the detailed behavior in the extreme dilute region of the plot as explored by us is shown.

Table I summarizes the results for binary alloys, by showing the initial decrease of the critical temperature as a function of ρ and c, and the residual resistivity ratio per unit concentration ρ/c of all dilute alloys. In this table the values for the initial decrease of T_c in Al-Cr, Al-Mn, and Al-Fe, are not ours. They were derived from experimental data recently obtained by Aoki and Ohtsuka.[24] These authors carried out very careful measurements of T_c in Al base dilute alloys containing the impurities Ti, V, Cr, Mn, Fe, and Ni, in a concentration range a factor of ten lower than ours. The results of Aoki and Ohtsuka are in substantial agreement with ours and they provide a way of obtaining much more accurate values for the observed initial $dT_c/d\rho$ (and consequently for dT_c/dc, as derived from $dT_c/d\rho$ using our ρ/c values). We point out that the observed initial decrease of T_c, as given in Table I, is not necessarily the true initial decrease, since, except
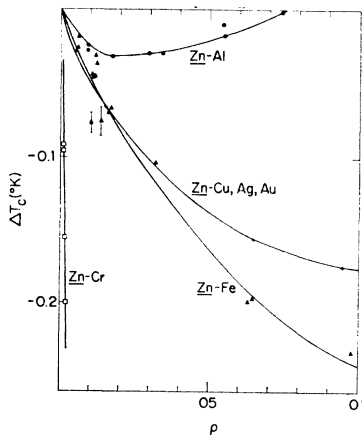

FIG. 5. ΔT_c versus residual resistivity ratio for Zn-Mn and Zn-Fe as compared with Zn-Al (measured by us) and Zn-Cu, Ag, Au (Ref. 35).
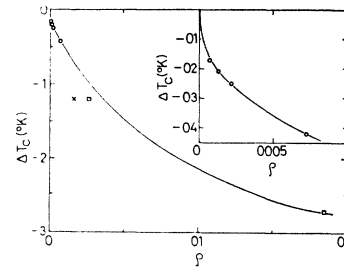
[24] R. Aoki and T. Ohtsuka (private communication).

FIG. 6. ΔT_c versus residual resistivity ratio for In-Mn: □ Data by Martin (Ref. 22); × Datum by Merriam (Ref. 39); ○ Present data. In the inset, the low concentration region is shown in more detail.

for Zn-Mn, there is no experimental evidence that the initial part of the curve ΔT_c versus c is linear.

In the system Sn-Mn, no change of the critical temperature was found within the experimental error, up to a Mn concentration of about 100 ppm. Measurements of T_c were carried out also in specimens of Zn-Ti; the experimental data are somewhat scattered but, as a whole, they seem to indicate no change of T_c with concentration. Since the ratio ρ/c found for these Zn-Ti specimens was anomalously low, we think Ti was not dissolved in Zn; and we will not discuss this alloy system further.

The ΔT_c values for In-Pb-Mn ternary alloys are given in Table II. These values were calculated by first subtracting the small difference in T_c produced in In by addition of Pb alone.

TABLE II. The decrease in T_c for In-Pb solid solutions, produced by the addition of 50 ppm Mn.

At.% Pb	ΔT_c(°K)
0	−0.021
0.49	−0.018
0.94	−0.015
1.93	−0.016

4. DISCUSSION

A. Zn-Mn and Zn-Cr

We will first discuss the systems in which localized magnetic moments are present, namely Zn-Mn and Zn-Cr. That localized moments exist in these two systems is proved beyond any doubt by other experiments[25–27] and is confirmed by the present measurements. The drop of critical temperature with concentration is distinctly different from the other systems investigated, i.e., it is very steep and linear (see Fig. 5). The linear change of T_c with concentration is very

[25] E. W. Collings, F. T. Hedgcock, and Y. Muto, Phys. Rev. 134, A1521 (1964).
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[27] F. T. Hedgcock and W. B. Muir, Phys. Rev. 129, 2045 (1963).

clear in Zn-Mn, but not so definite in Zn-Cr, because of the larger scatter of the experimental points. We believe that this scatter is to be ascribed to the difficulty of keeping the chromium atoms in solution. Some precipitation or other reaction of Cr atoms seems to occur even in extremely dilute solutions. Linear interpolation of the data furnish $-dT_c/dc=315\pm10$ for Zn-Mn and $-dT_c/dc=170\pm25$ for Zn-Cr.

The effect of impurities carrying localized moments on the critical temperature has been discussed theoretically by various authors.[5-9] The phenomenon bears its origin in the exchange interaction between localized d electrons and conducting s electrons. This exchange interaction destroys the coherence of Cooper pairs through a lifetime effect. The theory predicts a linear decrease of T_c with concentration, the slope being proportional to $S(S+1)$ where S is the spin on the impurity and to J^2, J being the s-d exchange integral. Numerically one can write[8]

$$dT_c/dc = -37.4\ 10^{-3}J^2S(S+1)/kE_F, \qquad (1)$$

c being expressed in atoms percent. This formula allows a straightforward calculation of J. The spin value S in Zn-Mn was determined by Hedgcock and co-workers[25] by means of susceptibility measurement and was found to be $\frac{3}{2}$. Using our value for dT_c/dc of -315 and a Fermi energy $E_F=1.6\ 10^{-11}$ erg, one finds[28]

$$J = 2.2\ 10^{-12}\ \mathrm{erg}(1.4\ \mathrm{eV}).$$

Comparable values of J were obtained by Hedgcock et al.,[25] from measurements of magnetoresistance and resistance anomalies at low temperature. We note that the s-d exchange energy in the metal is about 5 times larger than that derived for the free manganese ion ($3.5\ 10^{-13}$ erg). This fact is in agreement with the presence of Friedel's virtual levels,[17] through which an enhancement of the s-d exchange interaction[29] occurs due to the s-d admixture effect.[30] Assuming that the same interaction J is present in Zn-Mn and Zn-Cr, the superconductivity data for Zn-Cr can be explained by taking $S=1$ for this system.

In a recent paper,[31] Griffin has shown that, when localized moments are present, the transition temperature of the superconductor is affected by the presence of the Kondo-Suhl-Abrikosov resonance.[32-34] Griffin's calculation shows that the right-hand side of Eq. (1) should be multiplied by a complicated correction factor dependent again on J, E_F, and on the ratio of the characteristic temperature of the resonance over the

critical temperature of the pure superconductor. The correction factor is quite large when J is large, so that a more careful evaluation of J than that found by means of Eq. (1) seems to be necessary. However, Griffin's formula shows that in Zn, for J larger than 0.5 eV, dT_c/dc depends very slightly on the product $J^2S(S+1)$ and therefore a meaningful calculation of J is impossible. Since this small dependence of dT_c/dc on $J^2S(S+1)$ is questionable and the theory of the Suhl-Abrikosov resonance is not yet completely settled, we think that a more complete discussion of our results on Zn-Mn and Zn-Cr should be postponed to a later time.

B. Al-Mn, Al-Cr, Al-Fe, Zn-Fe, Zn-Co, and Zn-Ni

We now proceed to discuss the remaining zinc base systems, namely Zn-Fe, Zn-Ni, and Zn-Co, and the alumininum base systems. Here the transition temperature decreases less rapidly than in Zn-Cr and Zn-Mn, but more rapidly than in Zn and Al doped with nontransition metal impurities; a downward curvature is present in the plot of ΔT_c versus c. We believe that the behavior of T_c in these systems can be understood on the basis of (i) the reduction in gap anisotropy brought about by mean-free-path effects, (ii) the existence of a virtual d-level lying in the proximity of the Fermi level. The relevant theoretical discussions regarding these two effects were given, respectively, by Markowitz and Kadanoff[16] (hereafter called MK) and by Zuckermann.[35]

We must first examine more carefully the experimental dependence of ΔT_c on concentration or residual resistivity ratio. We may notice that the experimentally observed initial values of $-dT_c/dc$ are large and remarkably different from each other; however, this difference is greatly reduced when the values of $-dT_c/d\rho$ are considered separately for Al and Zn base systems, indicating that there is a correlation between $-dT_c/dc$ and ρ/c. The observed initial values of $-dT_c/d\rho$ are, on the average, higher than those found in the case of nontransition metal impurities[11,36] but their order of magnitude is comparable (see Fig. 5 for Zn-base systems). These considerations suggest that, although some peculiar depression effect on T_c is operating, the mean-free-path effect leading to the smoothing out of gap anisotropy is still an important factor here in decreasing the critical temperature. The present case is therefore much different from that of Zn-Cr and Zn-Mn, where, owing to the extremely high value of the initial $-dT_c/d\rho$, the mean-free-path effect could actually be neglected.

For a more through discussion of the experimental data, we try to plot $\Delta T_c/\rho$ versus $\ln\rho$, as suggested initially by Seraphim et al.[12] on a purely empirical

[28] This value is somewhat larger than that calculated by Hedgcock (Ref. 25) from our preliminary measurements of dT_c/dc.

[29] A. Blandin and J. Friedel, J. Phys. Radium **20**, 160 (1959).

[30] P. W. Anderson, Phys. Rev. **124**, 41 (1961).

[31] A. Griffin, Phys. Rev. Letters **15**, 703 (1965).

[32] J. Kondo, Progr. Theoret. Phys. (Kyoto) **32**, 37 (1964).

[33] H. Suhl, Phys. Rev. **138**, A515 (1965).

[34] A. A. Abrikosov, Zh. Eksperim. i Teor. Fiz. **48**, 990 (1965) [English transl.: Soviet Phys.—JETP **21**, 660 (1965)].

[35] M. J. Zuckermann, Phys. Rev. **140**, A899 (1965).

[36] D. Farrel, J. G. Parks, and B. R. Coles, Phys. Rev. Letters **13**, 328 (1964).
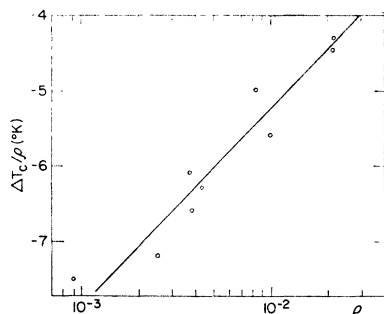
FIG. 7. $\Delta T_c/\rho$ versus residual resistivity ratio ρ in a logarithmic scale for Zn-Ni. The plot is linear within experimental errors.

basis, and theoretically justified by MK.[16] A plot of this type for the system Zn-Ni is shown in Fig. 7. The other systems behave in a similar fashion. We find that, within the experimental errors (in fact the scatter of experimental points is in most cases rather large), the plot is linear. Aoki and Ohtsuka[24] find that the plot is remarkably linear in the low-concentration range for all Al-systems studied by them; their experimental errors are smaller than ours. The linearity of the plot of $\Delta T_c/\rho$ versus $\ln\rho$ suggests that, as in MK's analysis of superconductors with nontransition metal impurities, the change in the critical temperature ΔT_c may be split into two terms,

$$\Delta T_c = (\Delta T_c)_{\text{anis}} + (\Delta T_c)_{\text{lin}}. \qquad (2)$$

The first term is negative and due to the smoothing out of gap anisotropy; the second term contains all other effects linear in ρ. The exact expression for $(\Delta T_c)_{\text{anis}}$ is given by MK's formula (45). An approximate expression was written by MK as

$$(\Delta T_c)_{\text{anis}} = \langle a^2\rangle T_{c0}(0.078X \ln X - 0.36X), \qquad (3)$$

where $\langle a^2\rangle$ is the gap anisotropy parameter, T_{c0} is the critical temperature of the host metal, and

$$X = b\lambda_i\rho. \qquad (4)$$

Here b is a characteristic dimensionless constant of the host metal, equal to 500 for Al and to 360 for Zn; and λ_i is an unknown constant for each host and impurity. λ_i is theoretically interpreted by MK as the ratio τ_{tr}/τ_a of the relaxation time τ_{tr} for transport processes over the mean collision time τ_a for smoothing out the gap anisotropy. Expression (3) is valid in the range $1 < X < 100$, which usually coincides with the range of ρ values accessible to experiment. By using (4), Eq. (3) may be written in the form

$$(\Delta T_c)_{\text{anis}} = A\rho + C\rho \ln\rho, \qquad (5)$$

where

$$C = 0.078 T_{c0} b\lambda_i\langle a^2\rangle, \qquad (6)$$

$$A = C[-4.6 + \ln(\lambda_i b)]. \qquad (7)$$

If we write

$$(\Delta T_c)_{\text{lin}} = B\rho, \qquad (8)$$

Eq. (2) becomes

$$\Delta T_c/\rho = A + B + C \ln\rho. \qquad (9)$$

From the experimental linear plot of $\Delta T_c/\rho$ versus $\ln\rho$, we obtained C and $A + B$. We then derived $\lambda_i\langle a^2\rangle$ from Eq. (6). In order to obtain B, we must know A and therefore the quantity λ_i for each impurity. This quantity was evaluated by assuming $\langle a^2\rangle$ to be a constant for a given base metal and λ_i to be 1 for an average nontransition metal impurity [that is, for Al-X and for Zn-X (see below)].[37]

The values of $\lambda_i\langle a^2\rangle$ and B derived from the experimental data are given in Table III. Also shown in Table III are the values of $\lambda_i\langle a^2\rangle$ and B for hypothetical Al- and Zn-based alloys (called Al-X and Zn-X) containing nontransition metal impurities which produce no change in the electron concentration of the host metal. The value of $\lambda_i\langle a^2\rangle$ for Al-X is that obtained by MK[16] from an analysis of the experimental data of Chanin, Lynton, and Serin.[11] The value of B for Al-X was derived by Markowitz.[16] The values of $\lambda_i\langle a^2\rangle$ and B for Zn-X were interpolated from our results for Zn-Al and the results of Farrel, Park, and Coles[36] for Zn-Cu, Zn-Ag, and Zn-Au.

The quantity $\lambda_i\langle a^2\rangle$ derived for transition metal impurities has the same order of magnitude as that derived for nontransition metal impurities. This fact shows that we are dealing with the same anisotropy parameter. It is however disappointing that the values

TABLE III. Gap anisotropy parameter, linear effect of ρ on ΔT_c, and effect of virtual states as deduced from the experimental data by using a Markowitz-Kadanoff type of plot.

Alloy	$\lambda_i\langle a^2\rangle \times 10^2$	$B(°K)$	$B-(\alpha+\beta\Delta zc/\rho)^e$ (°K)
Al-Ti[a]	0.87±0.05	−0.1 ±0.1	−0.3
Al-V[a]	0.87±0.05	−0.3 ±0.1	−0.5
Al-Cr[b]	0.85±0.05	−0.7 ±0.1	−0.9
Al-Mn[b]	1.2 ±0.05	−1.9 ±0.1	−2.1
Al-Fe[b]	2.1 ±0.25	+0.1 ±0.3	−0.1
Al-Ni[a]	2.2 ±0.5	−0.8 ±0.4	−0.5
Al-X[c]	1.1	+0.33±0.2	⋯
Zn-Fe	3.4 ±0.4	−1.3 ±0.6	−2.0
Zn-Co	3.6 ±1.8	−0.7 ±2	−1.3
Zn-Ni	4.7 ±0.7	−1.3 ±0.7	−1.7
Zn-Al	5.6 ±0.2	+1.8 ±0.2	⋯
Zn-X[c]	5.5[d]	+0.7 ±0.2	⋯

[a] Experimental data by Aoki and Ohtsuka (Ref. 24).
[b] Experimental data both by us and by Aoki and Ohtsuka.
[c] See text for explanation.
[d] This value was evaluated from our data on Zn-Al and the data by Farrel, Park, and Coles (Ref. 36). The value for $\langle a^2\rangle$ thus found is larger than that given by the last authors, namely 4.7×10^2.

[37] The assumption that λ_i is 1 for an average non-transition-metal impurity is a rough one (see MK for a discussion). However, it has a minor effect on the calculated values of B. One could think that a better evaluation of B may be done by determining the initial slope of the experimental curve of ΔT_c versus ρ. However this is not the case, because the linear region for smoothing out the gap anisotropy begins at ρ values smaller than 2×10^{-4} for Al and smaller than 7×10^{-4} for Zn, a factor of 10 below the lowest experimental values of ρ.

of $\lambda_i\langle a^2\rangle$ for different impurities are considerably different from each other, the differences being larger in the case of transition metal impurities. Since these differences cannot be ascribed merely to experimental errors, we are led to the conclusion that λ_i changes considerably from impurity to impurity. The reason for this change is presently not understood.

The values of B for Al and Zn containing transition metal impurities are all negative or about zero. We think that this fact is caused by the presence of a virtual state at the Fermi level. The origin of B (which is a change in T_c per unit ρ) in superconductors containing nontransition metal impurities was discussed by MK, by Markowitz, and by Ginsberg.[16] These authors write

$$B=\alpha+\beta\Delta zc/\rho. \qquad (10)$$

Here α is the isotropic mean-free-path effect on T_c, which is the same as our B for Al-X or Zn-X in Table II. The second term is the true valence effect, Δz being the difference between the impurity ion charge and the host ion charge. α and β depend on the host metal only. From the measurements of T_c in Al and Zn doped with nontransition metals,[11,36] β is found to be $(0.13\pm0.01)°\mathrm{K/at.\%}$ for Al and $(0.11\pm0.01)°\mathrm{K/at.\%}$ for Zn.

The B values derived for transition metal impurities cannot be explained by (10). If we assume that α and β are the same constants for transition and nontransition metal impurities—and we cannot see any reason for the contrary—the B values calculated by (10) are much smaller than the experimental values even if we take a value for Δz as large as -3. We therefore reach the conclusion that another effect linear in ρ is present, which always decreases the superconducting critical temperature. We ascribe this effect to the presence of virtual states in metals doped with transition metal impurities.

The change in T_c brought about by the virtual state effect—expressed as $\Delta T_c/\rho$—may be obtained by subtracting from the experimental B values the quantity $\alpha+\beta\Delta zc/\rho$. The results are shown in the last column of Table III. They were obtained by assuming α and β to have the same value as measured for nontransition metals and by taking Δz equal to -2 for Al and to -1 for Zn. The Δz values are not necessarily integer. However, there is sufficient evidence[17,38] that transition metal impurities contribute about one s-electron to the conduction band of the host metal.

The effect of a nonmagnetized virtual d level on the superconducting properties was recently studied by Zuckermann.[35] Zuckermann's theory is based on Anderson's model of localized states[30] and is worked out for an isotropic superconductor. A decrease in T_c is found as a function of impurity concentration. The effect is due to the s-d admixture and is caused by the change in the density of states of electrons near each

impurity, giving rise to an anomalous scattering mechanism.

A general formula for the change in T_c is given by Zuckermann's equation (2.27) in terms of the number n_I of impurity atoms, of the half-width Γ of the virtual level, and of the energy E_d of the level, measured from the Fermi level. For the concentration range of interest in Al and Zn and for Γ not smaller than 0.1 eV, Zuckermann's equation reduces to

$$\Delta T_c=-(\tfrac{1}{2}T_{c0}n_I/N(0)\Gamma)[1+(E_d/\Gamma)^2]^{-1}\{\ln(2\gamma\Gamma/\pi kT_{c0})$$
$$+\tfrac{1}{2}\ln[1+(E_d/\Gamma)^2]-(1/q)\arctan q\}. \qquad (11)$$

T_{c0} is the critical temperature of the pure superconductor, $N(0)$ is the density of states at the Fermi level, γ is Euler's constant, and $q=(n_I/N(0)\Gamma+E_d^2/\Gamma^2)^{1/2}$. Now $(1/q)\arctan q$ is a very slowly varying function of n_I, its value being about 1, so that the change of T_c expected from Zuckermann's theory is negative and linear in the impurity concentration. This appears to be in qualitative agreement with the experimental results.

In order to check more quantitatively Zuckermann's theory, we calculate the ratio $\Delta T_c/\rho$. We observe that, on the basis of Anderson's model, the residual resistivity ratio ρ is expressed by

$$\rho\cong\tau_{273}/\tau=[\tau_{273}n_I/\pi\hbar N(0)][1+(E_d/\Gamma)^2]^{-1}, \qquad (12)$$

where τ is the relaxation time due to impurities[39] and τ_{273} is the relaxation time of the pure metal at 273°K. The other symbols were already defined. From (11) and (12) we derive

$$\Delta T_c/\rho\cong-8.5\hbar T_{c0}/2\Gamma\tau_{273}. \qquad (13)$$

The numerical factor 8.5 is the approximate value of the expression within curly brackets of Eq. (11), for $\Gamma\cong0.5$ eV. In a first approximation, this factor is insensitive to the values chosen for E_d or Γ, owing to the very large value of $2\gamma\Gamma/\pi kT_{c0}$.

Equation (13) tells us that, on the basis of Zuckermann's theory, the ratio $\Delta T_c/\rho$ depends on the impurities only through the half-width Γ of the virtual level. By comparing Eq. (13) with the experimental data given in the last column of Table III, we are faced with the conclusion that Γ depends remarkably on the particular transition metal impurity introduced in the host matrix. This fact is shown clearly by the Al alloys. By calculating Γ from (13), using the values of τ_{273} given by Fawcett,[40] Γ is found to be of the order of 0.1 eV for Zn alloys and to range from 0.1 to 1 eV for Al alloys, with a sharp minimum for Al-Mn.

These values of Γ are comparable to those recently derived by Klein and Heeger[41] for Be-Ni (0.4 eV) and

[38] E. Daniel, J. Phys. Chem. Solids 23, 975 (1962).

[39] See Ref. 35, Eq. (5.5).
[40] E. Fawcett, in The Fermi Surface, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960), p. 201.
[41] A. P. Klein and A. J. Heeger, Phys. Rev. 144, 458 (1966).

Cu-Ni (0.3 eV). However, a large variation of Γ along the row of the transition elements is hardly understandable in terms of the Friedel-Anderson picture of localized states.[17,30] Moreover, the derived values of Γ are too small in comparison with the expectations of Friedel and Anderson, who evaluate Γ to be 1 to 2 eV. With $\Gamma = 0.1$ eV, a splitting of the virtual level due to the crystalline field should also occur, a fact that has not been experimentally observed. Since the values of Γ derived from the experimental data on the basis of Zuckermann's theory seem to be questionable, we should like to conclude with the following remarks, which may be useful for future work on this subject:

(1) The Markowitz-Kadanoff type of analysis may not be correct in our case. This could happen if a logarithmic term is simulated by some additional effect of the virtual d level which is not taken into account by the present theory. Such a term might be brought about by additional anisotropy effects. An indication in favor of this criticism is given by the large variation of $\lambda_i \langle a^2 \rangle$ (see Table III).

(2) Zuckermann's theory is valid only in the absence of d-level degeneracy and of correlation effects. However, taking these effects into account seems to produce no substantial change in Eq. (13).[42]

(3) It is possible that the s-d admixture changes the effective electron-electron interaction leading to superconductivity.[43] Since this effect is likely to produce again a decrease of T_c, it should be added to Zuckermann's effect. The resulting values of Γ may then be sizably increased.

C. In-Mn and Sn-Mn

Two more systems remain to be discussed, namely In-Mn and Sn-Mn. We are not able to explain the results obtained for these two systems, in the framework previously outlined.

The case of In-Mn is very peculiar. It was recently shown by Hedgcock and Muir that in this system localized moments are not present.[44] The evidence presented is indirect, but quite convincing. In fact no resistance minimum was found and no negative magnetoresistance was detected. Unfortunately, magnetic susceptibility measurements were not conclusive, since undissolved manganese was present in their specimens. This evidence is confirmed by the measurements of the superconducting critical temperature carried out by us, and by Martin in a higher concentration range[23] (see Fig. 6). These measurements show that no linear decrease of T_c with concentration is present in this system; therefore the measurements do not support a preliminary claim by Merriam and Seraphim that

In-Mn carries localized moments,[45] the claim being based solely on the high value of $\Delta T_c / \rho$ found in this system. On the other hand, the experimental results cannot be explained in the framework of Zuckermann's and Markowitz and Kadanoff's theories, as for Al alloys and Zn alloys. If we plot $\Delta T_c / \rho$ versus $\ln \rho$, we find a very strong deviation from linearity, due to the very steep decrease of T_c with concentration in the dilute concentration range. Moreover, Zuckermann's model appears to be not applicable, since in this alloy ρ / c is small, pointing to no virtual level present at the Fermi surface.[20]

A way to explain the results is to assume that something peculiar happens to the alloy in the dilute range. This is not apparent from residual resistivity measurements since ρ is linearly dependent on concentration from about 10 to 2000 ppm. However, it may be possible that the Mn atoms occupy special positions in the lattice in the dilute concentration range—for example, they lie along dislocations or near other defects—and that in these positions the formation of localized moments is favored. The superconductivity could then be strongly affected at low concentrations (an initial dT_c / dc as high as several hundreds may be expected) but would be much less affected in the high concentration range, when the special positions of the lattice are all occupied. Unfortunately, no data are available for the nearby dilute solid solutions In-Cr and In-Fe, which are very difficult to prepare in bulk form.

Also, the results for the Sn-Mn system need an explanation. The ρ / c ratio is in this case very high, so that the Mn is certainly dissolved. A virtual state should be present at the Fermi level. Moreover, the smoothing out of gap anisotropy is very clear when "normal" impurities are added to tin.[10] We cannot understand why the critical temperature seems to be not affected at all by the addition of Mn atoms.

Finally, we should like to compare our results on In-Mn and Sn-Mn with those obtained in thin films by the Göttingen group.[1] As mentioned in the Introduction, this group found that addition of Cr, Mn, and Fe gives rise to a linear decrease of T_c with concentration in thin films of In, Sn, Pb, and Bi. The values of $-dT_c / dc$ for In-Mn and Sn-Mn are 53 and 69, respectively. These thin films behave as if in them the impurities are indeed associated with localized magnetic moments. This finding was later confirmed by the measurements of Reif and Woolf,[4] who found gapless superconductivity in In-Fe and Pb-Mn, a result which can be explained only if free spins are present in the superconductors.

The behavior of the bulk solid solutions appears to be definitely different from that of low-temperature deposited thin films. In bulk In-Mn and Sn-Mn systems

[42] M. J. Zuckermann (private communication).
[43] We should like to thank Dr. A. Blandin for having brought this point to our attention.
[44] F. T. Hedgcock and W. B. Muir, Phys. Letters **14**, 11 (1965).

[45] M. F. Merriam and D. P. Seraphim, Bull. Am. Phys. Soc. **8**, 613 (1963) and Colgate Conference on Superconductivity [see Rev. Mod. Phys. **36**, 164 (1964)].

we have no indication that magnetic moments are formed. The same should be true for all dilute solid solutions of iron-group metals in In, Sn, and Pb, if we believe that the Friedel-Anderson model is right and applicable to these systems. In fact, trivalent and tetravalent metals should give rise to a large *s-d* admixture effect, owing to the high value of the Fermi energy and no splitting of the virtual *d* state should occur, even in the most favorable case of Cr and Mn impurities.

Since both theory and experiment support the fact that substitutional transition metal impurities should not give rise to localized moments in bulk In, Sn, and Pb, we think that the results of the Göttingen group can be understood only by assuming that in thin films deposited at low temperature the transition metal atoms place themselves in positions favorable for the appearance of magnetic moments. This could happen if the metal matrix is locally so loose, that the electron concentration is strongly diminished, or if the transition metal atoms group themselves in such a way as to give local resultant magnetic moments. In any case, the peculiar situation of localized moments in thin films is shown also by the much lower value of $-dT_c/dc$ obtained by the Göttingen group as compared with those found by us in **Zn**-Mn and **Zn**-Cr. If we maintain that the *s-d* exchange integral *J* causing the depression must be large in these alloys (owing to the *s-d* admixture effect), the low values of $-dT_c/dc$ found in thin films are difficult to explain in terms of the standard theory,[6-9] which assumes a random distribution of atomic spins.

D. In-Pb-Mn

The measurements on **In**-Pb-Mn alloys were carried out because of a claim by Merriam *et al.*,[46] that the addition of lead destroys the ability of Mn to depress the critical temperature of In. We took particular care in preparing the alloys, since the small amount of manganese to be used can be easily oxidized by oxygen contained in the original metals. The data in Table II

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[46] M. F. Merriam, S. H. Liu, and D. P. Seraphim, Phys. Rev. **136**, A17 (1964).

show that there is no dramatic effect on the critical temperature. The small change observed varies linearly with Pb concentration. No effect seems therefore to be produced by the lead atoms on the ability of Mn to depress the critical temperature of In. The result of Merriam *et al.* may have been fortuitous. It is likely that in their specimens the manganese was oxidized and therefore taken away from the system by the addition of nonoutgassed base metals.

5. CONCLUSIONS

We have studied the critical temperature of several bulk dilute solid solutions of transition metals in Al, Zn, In, and Sn. When localized magnetic moments are present, the critical temperature decreases linearly with concentration, in agreement with theory. If magnetic moments are not present, the critical temperature is affected by two principal factors: the effect of virtual levels lying across the Fermi surface, which gives rise to an approximate linear decrease of the critical temperature, and the effect of mean free path, which gives rise to the main part of the observed downward curvature in the plot of T_c versus *c*, through the smoothing out of gap anisotropy. This picture does not appear to be applicable to **In**-Mn and **Sn**-Mn systems, but we feel that more data should be obtained on In and Sn base alloys before reaching any conclusion on this point. No localized moments are present in these alloys in the bulk form; this result differs from what was found in low temperature deposited thin films, where localized moments are stabilized by a still unknown mechanism.