

## Effect of Dissolved Manganese on Superconductivity of Pure and Impure Indium

M. F. MERRIAM\*

*University of California, San Diego; La Jolla, California*

AND

S. H. LIU AND D. P. SERAPHIM

*IBM Watson Research Center, Yorktown Heights, New York*

(Received 24 April 1964; revised manuscript received 22 May 1964)

The superconducting critical temperature of indium decreases by  $\sim 70^\circ\text{K}$  per unit resistance ratio,  $\rho_{4.2}/\rho_{273}^\circ\text{K}$ , when doped with manganese. The addition of a third element, lead or tin, (just a few percent) progressively decreases the effect of the manganese and eliminates the effect completely when the mean free path is decreased to  $\sim 500 \text{ \AA}$ . The data are explained on the basis of the Korringa model for the resistivity-minimum phenomenon found in dilute transition-metal solutions. It is assumed that the scattering of the conduction electrons undergoes a resonance (presumably caused by the localized moments) of width  $\sim 1^\circ\text{K}$  at the Fermi surface. The effect disappears when enough nonparamagnetic impurity is added to make the width of the electron energy levels large compared to that of the resonance. The technique and the model (if correct) opens a new way for investigating the resonance model for paramagnetic impurities.

### INTRODUCTION

THERE is abundant evidence<sup>1-4</sup> that dissolved paramagnetic impurity can strongly depress the transition temperature of a superconducting solvent, if the solvent metal is such that the impurity remains paramagnetic when dissolved, i.e., retains a localized moment. Such a situation is easily realized experimentally in the transition metals and in lanthanum, where paramagnetic impurities are easily dissolved. More trouble is encountered in the nontransition metals since solubilities of magnetically active impurities (e.g., Cr, Mn, Fe, Co, Ni or rare earth) are usually low. Boato *et al.*<sup>5</sup> have studied the depression of  $T_c$  of aluminum by Fe, Cr, and Mn, and more recently<sup>6</sup> have observed a strong depression of  $T_c$  in zinc containing dissolved Mn. In the aluminum case, the solute atoms apparently lower  $T_c$  only through a reduction of electronic mean free path<sup>7,8</sup>; [i.e.,  $\partial T_c/\partial(1/l)$  is similar for Mn and nonparamagnetic solute].<sup>9</sup> This is evidence that Mn does not have a localized moment in Al. Several experiments<sup>1,3,4</sup> have used metastable films, in which the superconducting solvent metal and the paramagnetic solute are codeposited on a cold (liquid-He

cooled) substrate, so that "solubilities" far in excess of equilibrium may be achieved.

Our experiment was designed to measure the dependence of  $T_c$  of bulk In on Mn concentration, for small concentrations of dissolved Mn, and to determine whether this dependence would be modified if the electronic mean free path in the indium were shortened by dissolving a magnetically neutral nontransition metal impurity. We were able to dissolve sufficient Mn for our purposes and we did, in fact, observe both the  $T_c$  depression caused by Mn and its mean-free-path dependence. The latter effect (mean-free-path dependence of the  $T_c$  depression arising from a paramagnetic solute) has not been observed until now. Mn depresses  $T_c$  of In rather strongly (unlike the case of Al) leading to the inference that it does carry a localized moment in In, but this has not been directly checked by measurement of other properties.

### EXPERIMENTAL

#### Samples

We encountered considerable difficulty in dissolving Mn in In, and we were not able to dissolve very much. Our troubles were further compounded by the very strong tendency of Mn to combine chemically with oxygen, which resulted in the formation of considerable manganese oxide precipitate. The presence of this precipitate was inferred from the large discrepancy between the total manganese content as determined from chemical analysis and the solute concentration inferred from residual resistivity measurements. The ferromagnetic compound<sup>10</sup>  $\text{Mn}_3\text{In}$  was not present in our samples. It would have been detected, even in the ppm range, in the course of magnetic moment determinations performed on the samples at cryogenic temperatures.

\* Experimental work performed while a summer visitor at IBM Watson Research Center, Yorktown Heights, New York.

<sup>1</sup> F. Reif and M. A. Wolf, *Phys. Rev. Letters* **9**, 315 (1962).

<sup>2</sup> B. T. Matthias, H. Suhl, and E. Corenzwit, *Phys. Rev. Letters* **1**, 93 (1958); *Phys. Chem. Solids* **13**, 156 (1960).

<sup>3</sup> K. Schwidtal, *Z. Physik* **158**, 563 (1960).

<sup>4</sup> W. Opitz, *Z. Physik* **141**, 263 (1955).

<sup>5</sup> G. Boato, G. Gullinaro, and C. Rizzuto, *Phys. Letters* **5**, 20 (1963).

<sup>6</sup> G. Boato, G. Gallinaro, and C. Rizzuto, *Rev. Mod. Phys.* **36**, 162 (1964).

<sup>7</sup> G. Chanin, E. A. Lynton, and B. Serin, *Phys. Rev.* **114**, 719 (1959).

<sup>8</sup> E. A. Lynton and D. McLachlan, *Phys. Rev.* **126**, 40 (1962). [See also the theoretical explanation of D. Markowitz and L. P. Kadanoff, *ibid.* **131**, 563 (1963).]

<sup>9</sup> The measurements of F. T. Hedgcock, W. B. Muir and E. E. Wallingford, [*Can. J. Phys.* **38**, 376 (1960)] demonstrate no resistivity minimum in Al containing Fe or Mn.

<sup>10</sup> K. Aoyagi and M. Sugihara, *J. Phys. Soc. Japan* **17**, 1072 (1962).

Master alloy samples were prepared from COMINCO or ASARCO indium and Johnson-Matthey electrolytic manganese, nominally 99.999% and 99.99% pure, respectively. The indium and the small chip of manganese were placed together in a clean quartz tube connected to a vacuum system. The system was evacuated to  $10^{-5}$  mm Hg, and the indium was melted. The tube was then sealed off and the contents were heated sufficiently so that the manganese was attacked by and became dissolved in the molten indium. Temperatures between 400 and 1100°C were used; the lower temperatures were found to be more satisfactory. Stirring of the melt was accomplished either by heating the stationary tube with an induction furnace or by placing the tube in a rotating resistance furnace. The melt was allowed to cool to a few hundred degrees centigrade and quick frozen by plunging it into water, without breaking the quartz tube. After removing the tube either mechanically or chemically (dilute HF), the ingot was sectioned. The transition temperature and residual resistance ratio of wires extruded from each of several sections were checked, in order to verify that the macroscopic spatial distribution of the solute was uniform in the ingot. This was always found to be the case.

Many samples were prepared from master alloys by dilution with In, Sn, or Pb. In such cases, the chunks of master alloy and pure metal were melted together in the rotating furnace at a temperature just above the melting point. Some of the dissolved manganese inevitably came out of the solution and converted to oxide precipitate during this process. Correction could be made for this since all samples of each batch based on a particular master alloy received the same heat treatment (time and temperature) and a control sample (no In, Sn, or Pb added) was included in each batch. All samples were presumed to have suffered the same dissolved manganese loss as the control sample. With this single correction, the data on the samples diluted with pure indium became consistent, i.e., the solute concentrations implied by the dilution ratios were those inferred from the resistance ratios.

### Measurements

All samples were extruded into wires and the resistance at 300, 77, and 4.2°K was measured by a conventional four-wire method. Superconducting transition temperatures were also determined in this way, using a Keithley 150AR voltmeter. Noise and thermals set a lower detection limit of about  $10^{-7}$  V. The temperature was determined from the He<sup>4</sup> vapor pressure, using the 1958 scale, as measured with a large mercury manometer and a Wild cathetometer. Correction was made for the self field of the measuring current (50 mA). Head corrections (which were generally an order of magnitude smaller than the effect to be measured) were made only for the measurements on In-Mn-Sn alloys.

A number of samples were also measured magnetically in the manner described previously,<sup>11</sup> by cutting up the wires into short lengths and dropping the sample bundle from one coil into another, both coils being connected to a ballistic galvanometer. A large Garrett solenoid in the nitrogen Dewar, coaxial with the sample wire segments and the signal pickup coils, provided a magnetic field of up to 1400 G. A complete curve of sample magnetization versus field could be traced out and the transition temperature determined by noting the critical fields observed at several temperatures just below  $T_c$  and extrapolating to zero field. All transition temperatures obtained in this way agreed with those obtained resistively; on this evidence the resistive  $T_c$  was accepted for all samples. The magnetization transitions appeared quite broad for the In-Mn alloys, but sharpened substantially as the Sn or Pb concentration was increased. Some trapped flux (a small fraction of the maximum moment) was noted, presumably because of the oxide precipitate.

### Interpretation of Data

Our experiment consisted essentially of measuring  $T_c$  as a function of impurity concentration for pure indium samples. For the In-Mn samples, as mentioned earlier, direct chemical analysis was not useful for determining the concentration of dissolved Mn, because of the presence of oxide precipitate. Consequently, residual resistance measurements were relied upon to provide an index of solute Mn concentration. The data are all presented as a function of the quantity  $\rho$ , where  $\rho = R_{4.2}/(R_{273} - R_{4.2})$  (subscripts refer to degrees Kelvin). The value of  $R_{273}$  was obtained from the experimentally measured quantity  $R_{300}$ , using the reported<sup>12</sup> value of  $R_{300}/R_{273} = 1.128$ . The resistance ratio is expected to be proportional to impurity concentration for solid solutions as dilute as ours, but the In dilution experiments (diluting a master alloy with pure indium) provide objective evidence in any case. In all the dilution experiments, the results indicated a reduction in solute Mn concentration, as inferred from the resistance ratio, of the amount expected on the basis of the amount of In added. Our dissolved Mn concentrations corresponded to inverse resistance ratios ( $\rho$  values) of from  $0.4 \times 10^{-3}$  to  $1.6 \times 10^{-3}$ . These correspond to direct resistance ratios of from 2500 to 625. The approximate actual concentrations may be estimated from the case of Al-Mn, where the proportionality constant between  $\rho$  value and Mn concentration is known.<sup>5</sup> The In lattice is rather similar to Al, so some correspondence might be expected. On this basis we would estimate our Mn concentrations to range from 1 to 10 ppm. Even if our crude estimates were low by

<sup>11</sup> D. P. Seraphim, F. M. d'Heurle, and W. R. Heller, Appl. Phys. Letters **1**, 93 (1962).

<sup>12</sup> G. K. White and S. B. Woods, Rev. Sci. Instr. **28**, 638 (1957).

an order of magnitude, we are still dealing with an extremely dilute solution.

The (impurity limited) mean free path in a metal at low temperatures can be deduced<sup>7</sup> from the resistance ratio, the absolute resistivity at 273°K, and the ac surface conductivity in the limit of the anomalous skin effect. Using the value of Dheer<sup>13</sup> for this last quantity, and the value of White and Woods<sup>12</sup> for the ice-point resistivity, we find, for indium  $l^{-1} = 1.40 \times 10^6 \rho$  (cm<sup>-1</sup>). This result is independent of the nature of the solute and is, of course, invalid if solute atoms interact with each other to any appreciable degree. However, there is no reason to doubt its applicability for any of our alloys.

The impurity-limited mean free path of electrons in indium is easily adjusted experimentally by dissolving small amounts of Sn or Pb in the indium. The Mn concentration in our samples was so small that it did not appreciably affect  $l$  in the In-Mn-Pb or In-Mn-Sn alloys. There is no evidence that the third element (the Sn or Pb) was removing any Mn from solution, and the fact that the results obtained are essentially independent of the nature of the third element constitutes evidence, admittedly not conclusive, against this possibility. The experiment was performed with both Sn and Pb for precisely this reason.

RESULTS

The measured values of  $T_c$  plotted as a function of  $\rho$  for the In-Mn samples are shown in Fig. 1. A certain amount of scatter is apparent; this is not surprising in view of the metallurgical difficulties and the rather expanded scale for  $T_c$ . The magnitude of the rate of  $T_c$  depression with increasing Mn concentration is large,

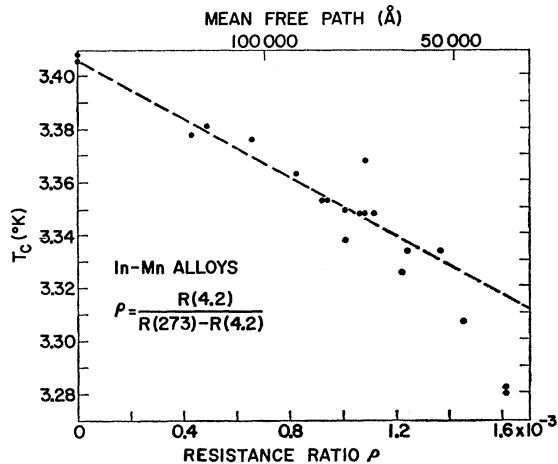
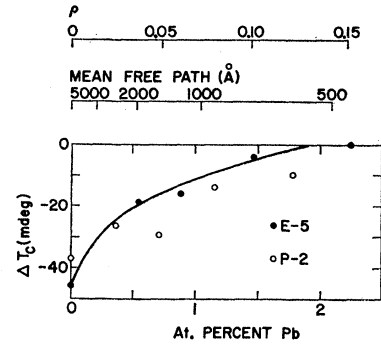


FIG. 1. Superconducting transition temperature of indium containing dissolved manganese in the extremely dilute range. Manganese concentration is proportional to  $\rho$ . The apparent non-linearity at the highest manganese concentrations may or may not be real.

<sup>13</sup> P. N. Dheer, Proc. Roy. Soc. (London) A260, 333 (1961).

FIG. 2. Mean-free-path dependence of  $T_c$  depression caused by Mn in In-Mn-Pb alloys. E-5 and P-2 are two different master alloys used for the dilution experiments. The known  $T_c$  versus Pb dependence in In-Pb alloys has been subtracted out.

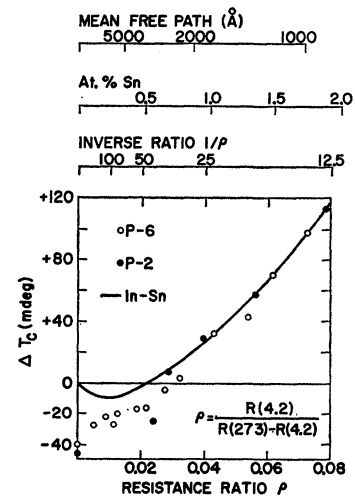


implying that the Mn carries a localized moment in In. The value of  $dT_c/d\rho$  is about 70°K, compared with 2.25°K for<sup>5</sup> Al-Mn, where the Mn does not carry a localized moment and 65–70°K reported<sup>6</sup> for Zn-Mn, where it does.<sup>14</sup> Attempts by the Franklin Institute Group to detect a localized moment in some of our In-Mn samples by direct susceptibility measurement were unsuccessful,<sup>15</sup> but this is not surprising considering the probable low dissolved Mn concentration and high oxide background. The data of Fig. 1 suggest a stronger than linear depression of  $T_c$  at the higher Mn concentrations, but this cannot be regarded as established. The stronger than linear dependence rests on only a few data points, and these are near the upper limit of Mn solubility, where the experimental difficulties are most severe.

Attempts to repeat Fig. 1 with In-Fe were unsuccessful. We were not able to dissolve measurable amounts of iron. Experiments with other paramagnetic solutes were not attempted.

In Figs. 2 and 3 we show, in somewhat different plots, the mean-free-path dependence of the  $T_c$  depression

FIG. 3. Mean-free-path dependence of  $T_c$  in In-Mn-Sn alloys. P-6 and P-2 are two different master alloys from which the samples were made by dilution. The dependence of  $T_c$  for In-Sn alloys is shown for comparison. The progressively diminishing (with decreasing mean free path) effect of Mn on  $T_c$  is apparent.



<sup>14</sup> F. T. Hedgcock and W. B. Muir, J. Phys. Soc. Japan 16, 2599 (1961).

<sup>15</sup> F. T. Hedgcock (private communication).

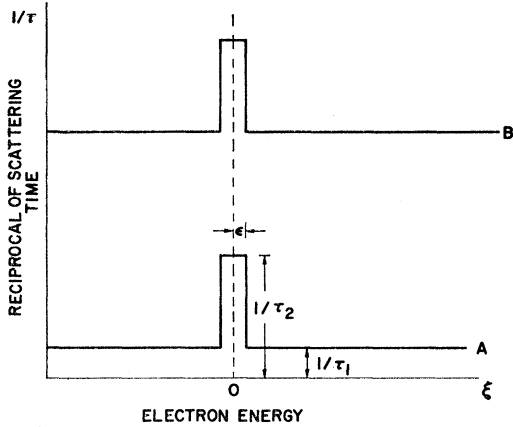


FIG. 4. A schematic plot of the inverse scattering time of the conduction electrons as a function of the electronic energy. The curve A illustrates our resonant scattering model in absence of nonmagnetic impurities. The curve B shows the effect on the scattering time when nonmagnetic impurity is added.

( $\Delta T_c$ ) arising from the presence of the Mn. In Fig. 2 we plot the difference between the  $T_c$  measured for our In-Mn-Pb alloys and that reported earlier<sup>16</sup> for In-Pb alloys without Mn, in order to display the effect of the Mn. In Fig. 3 we plot our In-Mn-Sn data and compare with the In-Sn data previously reported.<sup>16</sup> In both cases (In-Mn-Pb and In-Mn-Sn) the ability of the Mn to depress  $T_c$  is seen to diminish progressively, disappearing completely for mean free paths of order 500–1000 Å. Though scatter in the data and differences between samples are present, there is no doubt about the validity of the essential result. Fortunately, the  $T_c$  variation of In containing dissolved Pb or Sn, is accurately known,<sup>16</sup> so the effect of the magnetically neutral solute may be subtracted out with confidence.

#### THEORETICAL INTERPRETATION

We argue that our results cannot be explained by the spin scattering theory of Abrikosov and Gor'kov.<sup>17</sup> In the first place, the suppression of the critical temperature is about an order of magnitude larger than what one expects from magnetic scattering, and secondly, according to Abrikosov and Gor'kov,  $\Delta T_c$  is independent of the amount of nonmagnetic impurities that may exist in the material. Therefore, a different model is necessary to explain our findings.

It is known that transition-metal impurities can give rise to: (a) the resistivity minimum<sup>18</sup>; (b) the anomalously high thermoelectric power<sup>19</sup>; and (c) the anomalous de Haas-van Alphen effect.<sup>20</sup> All these effects have

<sup>16</sup> D. P. Seraphim, C. Chiou, and D. J. Quinn, *Acta Met.* **9**, 861 (1961).

<sup>17</sup> A. A. Abrikosov and L. P. Gor'kov, *Zh. Eksperim. i Teor. Fiz.* **39**, 1781 (1960) [English transl.: *Soviet Phys.—JETP* **12**, 1243 (1961)].

<sup>18</sup> J. Koringa and A. N. Gerritsen, *Physica* **19**, 457 (1953).

<sup>19</sup> C. A. Dominicali, *Phys. Rev.* **117**, 984 (1960).

<sup>20</sup> F. T. Hedgcock and W. B. Muir, *Phys. Rev.* **129**, 2045 (1963).

been explained by the resonant-scattering model first proposed by Koringa.<sup>18</sup> It is assumed in this model that the scattering of the conduction electrons by the impurities undergoes a resonance when the electrons have nearly the Fermi energy. The origin of this resonance is not yet explained but seems to be associated with localized spin.<sup>18</sup> Adopting this *ad hoc* model to the present problem we assume that the scattering time has the following energy dependence:

$$\begin{aligned} \tau(\xi) &= \tau_1, & |\xi| > \epsilon, \\ \tau(\xi) &= \tau_2, & |\xi| < \epsilon, \end{aligned} \quad (1)$$

with  $\tau_2 < \tau_1$ ,  $\epsilon \sim 1^\circ\text{K}$ .<sup>18,20</sup> In the above expression  $\xi$  is the electronic energy measured from the Fermi level. The dependence of  $1/\tau$  on the energy is depicted in Fig. 4. For convenience, we ignore the spin-dependent part of the scattering interaction. The calculation of the change in  $T_c$  is very similar to that in Ref. 17 and is therefore omitted here. The result is

$$\begin{aligned} \frac{\Delta T_c}{T} &\cong 4\hbar^2 \epsilon \left( \frac{1}{\tau_2} - \frac{1}{\tau_1} \right) kT_c \\ &\times \sum_{n=0}^{\infty} \frac{1}{\omega_n [\omega_n + (\hbar/\tau_1)] [\omega_n + (\hbar/\tau_2)]}, \end{aligned} \quad (2)$$

where  $\omega_n = (2n+1)\pi kT_c$  and  $n$  is a positive integer. Since  $\tau_1$  and  $\tau_2$  are inversely proportional to the paramagnetic impurity concentration, the suppression of critical temperature is a linear function of the concentration.

When a nonmagnetic impurity is introduced into this solid solution, the additional scattering reduces both  $\tau_1$  and  $\tau_2$  but the difference  $1/\tau_2 - 1/\tau_1$  remains constant. This effect is shown schematically in the upper curve of Fig. 4. It is readily seen from Eq. (2) that  $\Delta T_c$  must decrease with increasing amount of nonmagnetic impurity. The infinite series on the right-hand side converges very rapidly, so it may be well approximated by the leading term. This gives

$$\begin{aligned} \frac{\Delta T_c}{T_c} &\cong 4\hbar^2 \epsilon \left( \frac{1}{\tau_2} - \frac{1}{\tau_1} \right) \\ &\times \frac{1}{[\pi kT_c + (\hbar/\tau_1)] [\pi kT_c + (\hbar/\tau_2)]}. \end{aligned} \quad (3)$$

In the absence of nonmagnetic impurities  $1/\tau_1$  and  $1/\tau_2 \ll \pi kT_c/\hbar$ , the corresponding change in critical temperature,  $\Delta T_{c0}$  may be found by ignoring  $1/\tau_1$  and  $1/\tau_2$  in the denominator of Eq. (3). When a sufficiently large amount of nonmagnetic impurity is added, we may put  $1/\tau_2 \cong 1/\tau_1$  in the denominator and obtain

$$\begin{aligned} \frac{\Delta T_c}{\Delta T_{c0}} &\cong \left( 1 + \frac{\hbar}{\pi kT_c \tau_1} \right)^{-2} \\ &= (1 + A\rho)^{-2}, \end{aligned} \quad (4)$$

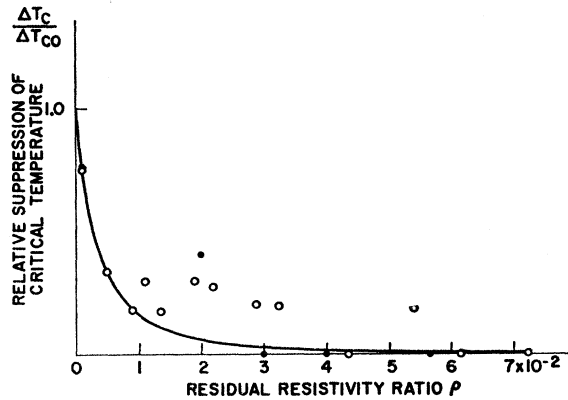


FIG. 5. Disappearance of the paramagnetic impurity effect in In as a function of resistivity contributed from nonparamagnetic impurity. Comparison between the predicted  $\Delta T_c$  versus  $\rho$  curve [Eq. (4)] with some experimental points taken from the In-Mn-Sn data of Fig. 3. The open and solid circles have the same meaning as in Fig. 3. The value of  $\Delta T_{c0}$  (the effect due to Mn alone) is chosen by matching the theoretical curve with the first experimental points on the left-hand side.

where  $\rho$  is the resistivity ratio,  $A$  is given by

$$A = \hbar / \pi k T_c \tau_{273^\circ}, \quad (5)$$

and  $\tau_{273^\circ}$  is the scattering time at 273°K. For indium,  $A$  is estimated to be around  $1.5 \times 10^2$ . In Fig. 5, the dependence of  $\Delta T_c$  on  $\rho$  is plotted along with some experimental points where the added nonmagnetic impurity is tin. In spite of the large scatter of the experimental points, the over-all agreement appears to be satisfactory. As another check, one can find from Eq. (4) that when  $\rho \cong 4 \times 10^{-2}$  the ratio  $\Delta T_c / \Delta T_{c0} \cong 0.02$ . Experimentally, this value of  $\rho$  does indeed correspond to the nonmagnetic impurity concentration at which

the paramagnetic impurity effect disappears. Physically, a small mean free path implies a large uncertainty in the electronic energy. When the width of the electron states becomes large compared with the width of the resonance, the resonance is smeared out and its effect vanishes. It is interesting to point out that this condition happens to coincide with the criterion that the material is a superconductor of the second kind. This is because the width of the resonance is of the same order of magnitude as  $kT_c$ .

The existing data do not allow us to determine all the parameters that enter the expression for  $\Delta T_c$ , particularly the expression for scattering time as a function of energy. A measurement of the resistivity anomaly of these materials would be very helpful.

#### CONCLUDING REMARKS

Since this is the first time the effect of paramagnetic impurities on superconductivity has been shown to be mean-free-path dependent, it is clearly desirable to follow up the phenomenon. The experimental difficulties in the In-Mn system were more severe than had been expected, and future investigations will probably be made in a different alloy system. Further investigations are also indicated to establish whether or not the effect occurs in transition metals (e.g., Mo, W) known to be sensitive to paramagnetic impurities.

#### ACKNOWLEDGMENTS

We would like to thank H. Suhl, B. T. Matthias, and F. T. Hedgcock for continued encouragement and stimulating comments, and A. C. Burgess for invaluable experimental assistance. One of us (Marshal F. Merriam) was partially supported by an AFOSR grant during the final portion of the work.