Electronic thermal conductivity of superconducting lead-manganese and indium-manganese alloy films*

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Measurements have been made of the electronic thermal conductivity of quench-condensed films of lead-manganese and indium-manganese alloys. The results are compared with calculations based on Shiba's theory of superconductors containing magnetic impurities. For Pb-Mn, the value of ϵ_0 (the normalized position in the energy gap of the excited state associated with a single impurity) which was used earlier to explain tunneling measurements, is 0.55; this value is consistent with our data. For In-Mn, the value $\epsilon_0 = 0.85$ gives excellent agreement with our data.

I. INTRODUCTION

The sharp depression of the transition temperature and the marked changes in the other thermodynamic and the transport properties which are caused by magnetic impurities in superconductors have been of considerable interest in recent years, particularly because theoretical progress has been forthcoming in this area.[1,2] The effects of gadolinium impurity atoms are now rather well predicted by calculations based on the theory of Abrikosov and Gorkov (AG).[3] This theory, which uses the first Born approximation, is well suited to the case of gadolinium; the magnetic electrons, which are in the 4*f* atomic shell, are well shielded from the host metal's conduction electrons, and therefore interact only weakly with them. Magnetic electrons in impurity atoms which are found among the 3*d* elements are less well shielded, and therefore interact more strongly with the conduction electrons. It is therefore not surprising that the predictions of the AG theory do not account quantitatively for the influence of the 3*d* magnetic impurities.

The theory of Shiba,[4,5] which was elaborated by Rusinov,[6] goes beyond the first Born approximation. In fact, it is an "exact" calculation, except that it treats the impurity spin classically. This theory has accounted for some, but by no means all, of the observed effects; this situation has been reviewed recently both for quench-condensed films[7] and for the bulk samples.[8]

Theoretical work by Müller-Hartmann and Zittartz (MZ),[2] which is based on the Nagaoka decoupling approximation, is also "exact," i.e., it also takes into account multiple scattering of conduction electrons from impurity atoms, but the MZ theory treats the impurity spins quantum mechanically. The validity of this theory is presumably limited[8] to temperatures which are at least as large as the Kondo temperature T_K. In the limit where T_K/T is very small, the MZ theory, together with the pole approximation,[9] reduces to that of Shiba and AG. The extent to which the MZ theory agrees with experimental data has been reviewed recently.[7,8]

In order to help cast light on some of the still puzzling features of superconductors with 3*d* magnetic impurities, we have measured the electronic part of the thermal conductivity of lead-manganese and indium-manganese films. We chose manganese as the impurity because it has the largest spin of all the 3*d* elements. Its effect on the transition temperature of lead[10] and indium[11,12] is known to be very large. The films were quench condensed to prevent precipitation of the impurities, to decrease the phonon part of the thermal conductivity,[13,14] and to provide a short electron mean free path, which slightly lessens the likelihood of interactions of impurity spins with each other.[15-17] The results are compared with the theory of Shiba; Leon and Nagi[18] showed how to do this after part of our measurements were made. There is at present no way to compare our results with the MZ theory.

Measurements similar to ours have been made by Petersen.[19] He compared his thermal conductivity results on Pb-Mn and In-Mn alloys with the calculation of Ambegaokar and Griffin,[20] which is based on the AG theory. We have not tried to fit his data to Shiba's theory, since the scatter in his data is much greater than in ours, and since our samples were produced under conditions where the substrates were colder. Our results agree with his within the scatter of the data, except perhaps for our most highly doped Pb-Mn sample. (The thermal conductivity data for bulk Zn-Mn alloys obtained by Sanchez[21] are in good agreement with the AG theory up to a manganese concentration of 8.4 ppm.)

The parameter of interest is the ratio K_{es}/K_{en} of the electronic part of the thermal conductivity in the superconducting state to that in the normal

state. In order to calculate[18] theoretical values of that ratio according to Shiba's theory, one needs to know the transition temperatures of the alloy (T_c) and the pure host metal (T_{c0}), the order parameter of the pure host metal at absolute zero (Δ_0), and the parameter ϵ_0, which is $1/\Delta_0$ times the energy around which a band of impurity-associated states is formed within the host metal's energy gap. It is evident that $0 \leq \epsilon_0 \leq 1$. According to Shiba's theory, ϵ_0 is given by

$$\epsilon_0 = \left| \frac{1 - (\frac{1}{2}\pi JSN_0)^2}{1 + (\frac{1}{2}\pi JSN_0)^2} \right|, \quad (1)$$

where J is the exchange constant, S is the impurity spin, and N_0 is the electron density of states at the Fermi energy. In the weak magnetic limit, $JSN_0 \ll 1$, ϵ_0 approaches 1, and Shiba's theory reduces to the AG theory.

The pair-breaking parameter α, which is needed for the calculation, is calculated from T_c and T_{c0} by using the relation[5]

$$\ln(T_c/T_{c0}) = \Psi(\tfrac{1}{2}) - \Psi(\tfrac{1}{2} + 0.1404\alpha T_{c0}/\alpha_{cr} T_c), \quad (2)$$

where Ψ is the diagamma function and

$$\alpha_{cr} = \tfrac{1}{2}\Delta_0. \quad (3)$$

In performing the calculations, the measured value of Δ_0 is used everywhere, including Eq. (3). This procedure scales the order parameter Δ in the alloy, and provides a needed correction of the theory to take strong electron-phonon coupling into account.[22]

II. EXPERIMENTAL PROCEDURES

A. Measurement of thermal conductivity

Our experiment employed basically the same equipment and techniques as those used previously in this laboratory to measure the thermal conductivity of In-Gd and Pb-Gd alloys.[23] The substrate was a circular piece of Dupont Kapton H-film, 0.005 cm thick. A heater was attached to the center of it. Heat flowed radially outward to the edge of the substrate, which was clamped to the sample holder. The H-film substrate provided a strong smooth support and a low-background thermal conductance. During the condensation of the sample film onto the substrate, the heat of condensation and the radiant heat absorbed by the substrate were conducted away by liquid helium, which was in direct contact with the substrate.

Some changes were made in the experimental techniques. Silver was deposited by evaporation onto the H-film to form two circular isotherms instead of the four isotherms which were used previously. The inner isotherm was a disk with a radius of 1.505 cm. The outer isotherm was a ring which extended from a radius of 1.905 cm out to the edge of the substrate. The part of the sample film for which the thermal conductivity was measured was located in the gap between the inner and outer isotherms. Carbon resistance thermometers were attached with General Electric GE7031 varnish to the outer edge of the inner isotherm and to the inner edge of the outer isotherm.

Thermal conductivity measurements were made by a steady-state method. The temperature of the outer isotherm was regulated by standard techniques of electronic feedback control. With the heater off, the temperature of the inner isotherm (T_{off}) was measured. Then the heater was turned on, and the heater power was adjusted to raise the temperature of the inner isotherm by an amount $\delta T = T_{on} - T_{off} \simeq 100$ mK. When steady state was reached, T_{on} and the power dissipated in the heater ($\dot{Q}$) were determined. The thermal time constant for the experiment varied from about 7 sec at 1.7 K to 70 sec at 7.2 K. Measurements of the background thermal conductance of the substrate (before the film was condensed on it) were made at 17–25 different temperatures.

To a first approximation, the thermal conductance was equal to

$$k_0(T_{av}) = \dot{Q}/\delta T, \quad (4)$$

where

$$T_{av} = \tfrac{1}{2}(T_{off} + T_{on}). \quad (5)$$

In fact, k_0 is the thermal conductance for some temperature in the interval between T_{off} and T_{on}, but not exactly for T_{av}. Cappelletti and Ishikawa[24] have shown that the thermal conductance k at T_{av} is given by

$$k(T_{av}) = k_0(T_{av}) - \sum_{n=1}^{\infty} k^{(2n)}(T_{av}) \frac{(\frac{1}{2}\delta T)^{2n}}{(2n+1)!}, \quad (6)$$

where $k^{(2n)}(T_{av})$ is the $2n$th derivative of k with respect to T, evaluated at T_{av}. We used Eq. (6) as follows: A polynomial in the temperature, of degree 2, was fitted to the function $k_0(T_{av})$. Using the polynomial to calculate the values of $k^{(2n)}(T_{av})$, a better approximation for $k(T_{av})$ was calculated by using Eq. (6). This process was repeated until the change in $k(T_{av})$ was less than one part in 10^6 for all the temperature values. Usually only one or two iterations were needed to accomplish this. The entire process was then repeated, using polynomials of degree 3, 4, etc., until the scatter of the experimental values from the polynomial fit was a minimum. For the bare substrate, a fifth-degree polynomial usually provided the best fit. For the substrate plus sample film, a fourth-degree polynomial usually provided the best fit to

the superconducting-state points, and a third-degree polynomial usually gave the best fit to the normal-state points.

The use of a thermal gradient as large as 100 mK was a departure from our previous procedure[23] of using a 30-mK gradient. Even larger thermal gradients can be used if k is independent of δT. We made measurements by using gradients of 10, 30, 100, and 300 mK, and found no significant difference in the resulting values of k.

Each experimental run began with the measurement of the substrate's thermal conductance. This was done for every sample, in contrast to the procedure used in our earliest work.[12] Then the sample film was condensed onto the cold (4 K or less) substrate. Next, the carbon thermometers were calibrated against a germanium standard resistance thermometer. The sample was then heated to 9.5 K for at least 12 h, so residual helium gas could be pumped out of the sample holder. This allowed the sample to anneal at a higher temperature than the temperature range where its thermal conductivity would be measured. Finally, the total thermal conductance of the sample and substrate was measured. The thermal conductance of the substrate, obtained from the polynomial fit, was substracted from the value for the sample and substrate, and the difference was taken to be the thermal conductance of the sample film itself. The thermal conductivity of the sample film was obtained by dividing its thermal conductance by $2\pi d/\ln(r_0/r_i)$, where d is the sample's thickness and where r_i and r_0 are its inner and outer radii (1.505 and 1.905 cm, respectively).

B. Sample preparation

Each sample film was produced by evaporating small pellets containing a mixture of lead and manganese or indium and manganese. Each of these pellets weighed 6 mg or less. They were cut from ingots of the mixtures. The Pb-Mn and In-Mn mixtures were dilutions of master mixtures. The Pb-Mn master mixture was prepared by melting together 99.999%-pure lead and 99.99%-pure manganese in a tantalum crucible. The crucible and its contents were put in a rf induction furnace in an evacuated bell jar. They were heated to 1000 °C for 5 min and then quenched in a stream of helium gas. The resulting ingot was mechanically mixed by repeated rolling and folding between sheets of tantalum.

Each dilute alloy was made by remelting appropriate quantities of the master alloy and the pure lead in a sealed evacuated quartz capsule. The melt was removed from an oven just above the melting point of lead, shaken vigorously, and quenched in water. The ingot was removed from the quartz capsule and soaked in hydrofluoric acid, if necessary, to remove all of the quartz. Then it was mechanically mixed by pressing and folding it.

dc arc emission spectroscopy showed that the dilute alloys contained 25-at.-ppm copper, less than 50-at.-ppm iron, and no detectable amounts of tantalum or other transition-metal impurities.

For each run a piece of dilute alloy was cut into pellets. These were loaded on a conveyor belt. During evaporation of the sample film, they were dropped one or a few at a time into a hot molybdenum or tungsten boat.

The In-Mn master mixtures were made in a similar way, using 99.999%-pure indium and 99.99%-pure manganese and a Vycor, rather than quartz capsule in a resistively heated furnace. The dilute mixture was made by repeatedly pressing and folding together the pure indium and a piece of the master mixture.

C. Data analysis and uncertainties

The normal-state thermal conductivity was not measured below the transition temperature T_c. To obtain the desired ratio K_{es}/K_{en}, the normal-state values which were obtained above T_c were used to make an extrapolation to the lower temperatures. The normal-state thermal conductivity of the samples (K_n) did not exhibit the simple behavior $K_n = AT$ of electrons which are scattered by impurities and other point defects. There was a small, but noticeable, phonon contribution to the normal-state thermal conductivity.

The expected temperature dependence of the phonon contribution depends on the type of phonon scattering mechanism. Diffuse boundary scattering of phonons gives rise to a T^3 dependence. Scattering of phonons from dislocations of uniform density yields a T^2 dependence. Taken as a whole, the data did not favor either a T^2 or a T^3 dependence, but rather one which was in between them. Therefore the normal-state data from each film were fitted to two curves, of the form $K_n = AT + BT^2$ and $K_n = CT + DT^3$. For each temperature below T_c, this yielded two values for the reduced electronic thermal conductivity K_{es}/K_{en}. The reported value of this ratio is the average of these two. The uncertainty due to this averaging procedure, together with estimated standard deviations from random errors, are indicated by the error bars shown in the figures.

The temperature of the inner isotherm thermometer could be measured to a precision of 50 μK. Power dissipation in the sample heater could be measured to 0.01% or better. The largest uncer-

tainty in the measurement of k_0 arose from drift in the regulating temperature of the outer isotherm. This drift was kept to less than 0.1 mK. The scatter in the data from the polynomial fit to the thermal conductance of the substrate was typically 0.08%. For Pb-Mn, the sample thermal conductance in the normal state was about 10% of the substrate thermal conductance. For In-Mn, the sample thermal conductance was about the same size as that of the substrate.

III. RESULTS

The resistive transition of each film was measured *in situ* by a four-terminal determination of the electrical resistance. The resistive transition width, defined to be the width of the temperature range over which the resistance rose from 10% to 90% of its normal-state value, was always less than 100 mK for the Pb-Mn samples. For the In-Mn sample, it was 21 mK.

Figures 1–4 show the reduced electronic part of the thermal conductivity K_{es}/K_{en} versus temperature for all of the samples. The theoretical curves were calculated according to the Shiba theory by using the method of Leon and Nagi,[18] as discussed in Sec. I. The curves with $\epsilon_0 = 1.0$ are identical to the results of the AG theory. Since Chaba and Nagi[25] showed that the value $\epsilon_0 = 0.55$ accounts for the tunneling data of Woolf and Reif on Pb-Mn alloys,[26] curves for that value of ϵ_0 are shown in Figs. 1–3.

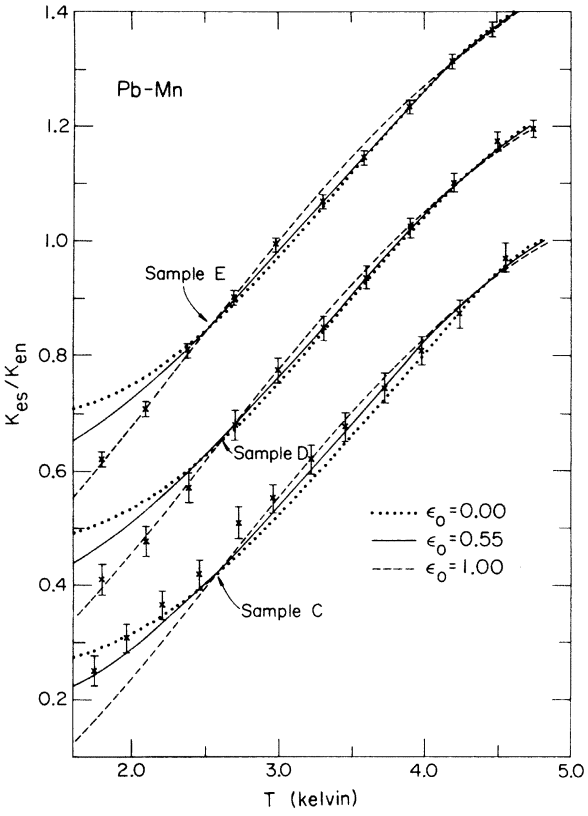

FIG. 2. Electronic thermal conductivity ratio versus temperature for Pb-Mn samples *C*, *D*, and *E*. The data for samples *D* and *E* are shifted upward by 0.2 and 0.4, respectively, for clarity.

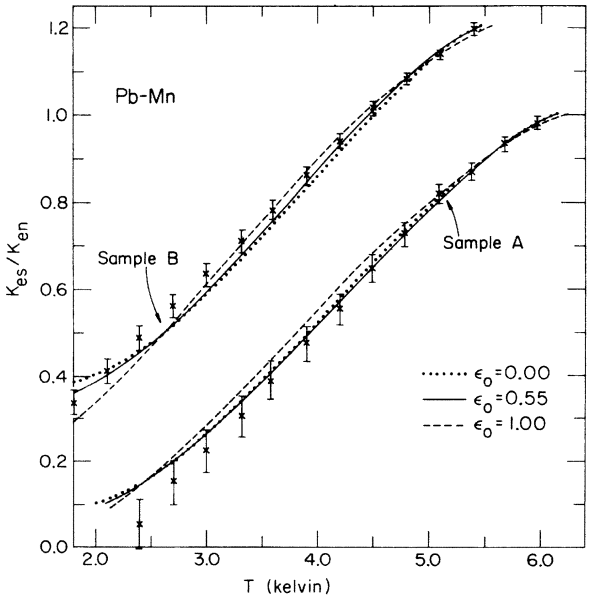

FIG. 1. Electronic thermal conductivity ratio versus temperature for Pb-Mn samples *A* and *B*. The data for sample *B* are shifted upward by 0.2 for clarity.

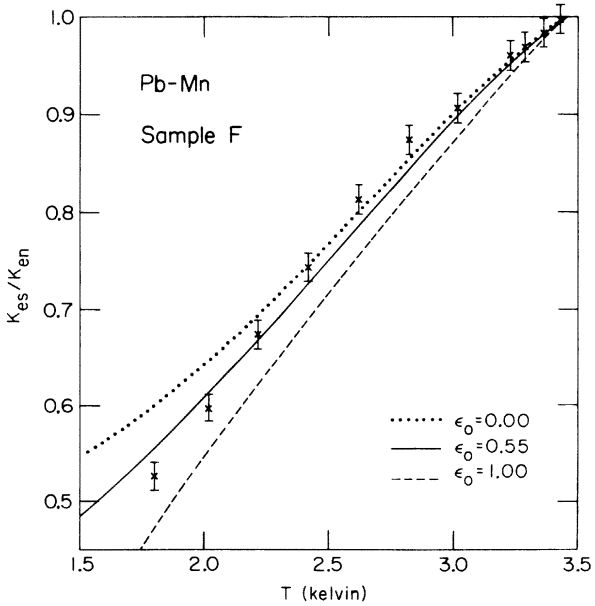

FIG. 3. Electronic thermal conductivity ratio versus temperature for Pb-Mn sample *F*.

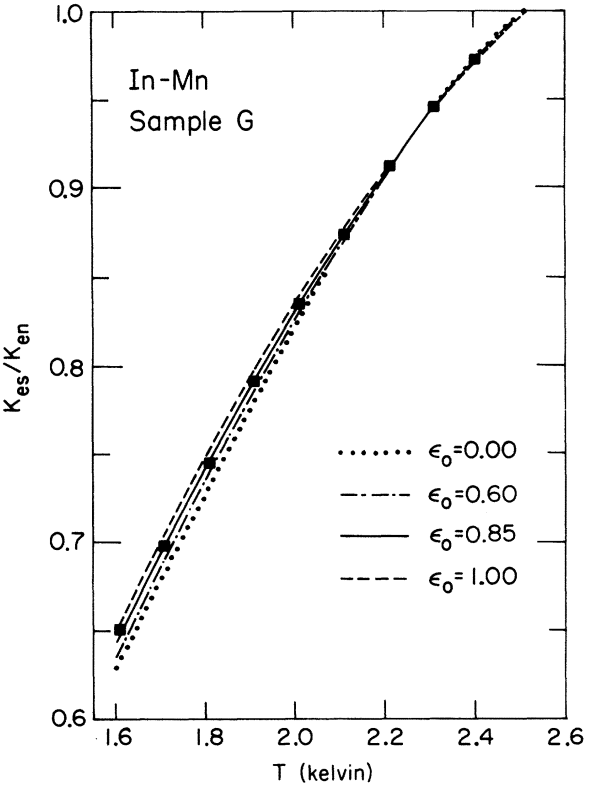

FIG. 4. Electronic thermal conductivity ratio versus temperature for In-Mn sample *G*. The vertical error bars are not indicated because they would be slightly smaller than the squares which indicate the data points.

In calculating the theoretical curves for the Pb-Mn samples, the value used for T_{c0} of pure quench-condensed lead was 7.176 K, which is an average of Mrstik's results.[27] The value used for the energy gap parameter in pure lead at $T=0$ was 1.335 meV, the value used by Chaba and Nagi[25] in fitting theory to the tunneling data of Woolf and Reif.

For the indium alloy films, T_{c0} and Δ_0 depend on the electron mean free path.[28] We used[23] the normal-state thermal conductivity to estimate the mean free path and therefore T_{c0} and Δ_0. The value for Δ_0 which we obtained in this way (0.684 meV) agrees within 2% with that of Reif and Woolf.[29] The value obtained for T_{c0} of quench-condensed pure indium was 4.087 K.

Shiba's theory was fitted to the results as follows: The reduced electronic thermal conductivity K_{es}/K_{en} was plotted as a function of T. To obtain the transition temperature, a curve passing through the data points near the transition was extrapolated slightly to the place where the reduced electronic thermal conductivity is equal to 1.0. Since the slope of the theoretical curve depends somewhat on the choice of ϵ_0, the transition temperature which was found to give the best fit of the theory to the data depended slightly on ϵ_0. Better discrimination of the transition temperature is possible if the thermal conductivity is measured at many temperatures near the transition. This was done for sample *F*. Each of the three points nearest the transition of that sample is an average of several data points. Smaller temperature intervals δT(30 instead of 100 mK) were used here to avoid overlapping the sharp change in the slope of the thermal conductivity curve at the transition temperature.

Table I lists characteristics of the films. The approximate transition temperature and the thickness of each sample are given. The transition temperature indicated by measurements of the electrical resistance was usually slightly higher than that indicated by the thermal conductivity curves, presumably because of sample inhomogeneity. For each sample, the difference between these two transition temperatures was 0.1 K or less except for sample *A*, for which it was 0.2 K. The film thickness was measured by optical interferometry,[30,31] using a film which was condensed onto a cold (less than 4 K) glass substrate which was near the sample substrate during the film condensation. For sample *C*, this could not be

TABLE I. Film characteristics. The parameters *A*, *B*, *C*, and *D* are discussed in Sec. II B.

Sample	Alloy	Impurity concentration[b] at. %	Approximate T_c	Film thickness (Å)	$K_n = AT + BT^2$ A (mW/cm K^2)	B (mW/cm K^3)	$K_n = CT + DT^3$ C (mW/cm K^2)	D (mW/cm K^4)
A	Pb-Mn	0.047	6.2	3703	0.3806	0.018 90	0.4508	0.001 26
B	Pb-Mn	0.079	5.5	2616	0.7350	0.025 42	0.8244	0.001 78
C	Pb-Mn	0.106	4.8	1700 [a]	1.3061 [a]	0.007 35 [a]	1.3265 [a]	0.000 65 [a]
D	Pb-Mn	0.109	4.7	1632	0.7446	0.015 76	0.7897	0.001 37
E	Pb-Mn	0.112	4.6	1651	1.0211	0.004 43	1.0331	0.000 40
F	Pb-Mn	0.16	3.45	1360	0.9842	0.025 56	1.0515	0.002 32
G	In-Mn	0.030	2.51	3898	3.6994	0.033 13	3.7563	0.004 73

[a] Estimate based on quantity of material evaporated.
[b] Estimated from the value of T_c indicated by the thermal conductivity data (Refs. 10 and 12).

done, and the film thickness listed for that sample is a rough estimate which could be in error by as much as a factor of 2. For the other samples, the thickness determinations are accurate to ± 100 Å.

Our results on In-Mn disagree with those which were obtained for a very thin sample five years ago in this laboratory,[12] in which the reduced electronic thermal conductance was much lower than the prediction of the AG theory, even when strong-coupling corrections are included.[23] The improvements which we have made in our techniques, outlined in Ref. 23 and in Sec. II A above, make the present data much more reliable. A deviation of only 2.5% in the thermal conductance of the substrate used in the earlier work from that of the substrates which were used at that time to measure the thermal conductance of the bare Kapton H-film would account for all of the discrepancy.

IV. CONCLUSIONS

Shiba's theory is in reasonably good agreement with our data. The value $\epsilon_0 = 0.55$ for Pb-Mn, which was obtained earlier from tunneling measurements, is consistent with our data. However, for some of the samples the data points at the lowest temperatures fall below the theoretical curves. This low-temperature discrepancy may not be reproducible, since it is seen in samples *D* and *E*, but not in sample *C*, and these three samples have approximately the same transition temperature. For In-Mn, the value $\epsilon_0 = 0.85$ gives excellent agreement with our data.

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