Electron-tunneling observation of localized excited states in superconducting manganese-doped lead

J.-K. Tsang and D. M. Ginsberg
Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801
(Received 11 April 1980)

We have made electron-tunneling measurements on a dilute, superconducting lead-manganese alloy. A well-defined structure was observed in the ac-conductance–voltage curves, indicating excited states within the BCS energy gap. These states were partially accounted for by Shiba theory when spin-dependent *s*-, *p*-, and *d*-wave scattering were included. The phase shifts used in doing that were the results of band calculations. The experimental data also show the existence of a broad background density of states in the energy gap, which cannot be accounted for by the theory.

In a recent paper[1] we reported the tunneling observation of a band of localized states in quench-condensed films of dilute, superconducting indium-manganese alloys. The tunneling characteristics were measured for aluminum–aluminum oxide–alloy sandwiches. The results were compared with calculations based on Shiba's theory[2] of superconductors containing magnetic impurities. This theory predicts that the exchange interaction between the conduction electrons and the magnetic impurity spins should generate a band of excited states in the BCS energy gap if only *s*-wave scattering is considered. This band is located around an energy denoted by $\epsilon_0\Delta$, where Δ is the superconducting order parameter. On the inclusion of *p*- and *d*-wave scattering,[3] additional bands should appear at the energies $\epsilon_1\Delta$ and $\epsilon_2\Delta$. The values of ϵ_0, ϵ_1, and ϵ_2 depend on the strength of the exchange interaction. We treated the ϵ's as adjustable parameters. The values of these parameters which produced the best fit were in good agreement with the results of band calculations[4] and with thermal-conductivity measurements.[5]

We have now made measurements on lead-manganese samples with similar techniques,[1] and have compared the results with Shiba's[2] theory.

The experimental details are the same as those we reported previously[1] except that the lead-manganese films were made by flash evaporation.[6] This was required because of the difference in the vapor pressures of lead and manganese.[7] The pure lead samples were made in the same way so that a direct comparison could be made with the alloy samples. The lead-manganese alloys were prepared as described earlier[5] from 99.999% pure lead and 99.99% pure manganese. After the evaporation of the aluminum film onto a *z*-cut quartz substrate and the partial oxidation of the aluminum, the alloy film was fabricated by evaporating pellets, each with a mass of 3 mg or less. One to three pellets were dropped at a time into a molybdenum boat held at 1100 °C. (The boat had previously been outgassed at 1400 °C.) Both of these temperatures were measured by an optical pyrometer. Each pellet evaporated in 3 to 5 s, adding about 20 Å or less to the film thickness. The temperature of the substrate holder was kept below 2.5 K during the entire evaporation process. We made tunnel junctions of Pb-Mn with three different manganese concentrations; 25, 69, and 202 at. ppm. The good homogeneity of each alloy sample was confirmed by the width (10 to 90% of the normal-state resistance) of the resistive transition, which was less than 12 mK. The width of transition of the pure lead sample was 7 mK. For each concentration, three tunnel junctions were made simultaneously. In each run the three junctions showed essentially the same characteristics. We only report the results on the sample with 69 at. ppm manganese since similar conclusions would be drawn from the characteristics of the other samples.[8]

The earth's magnetic field was canceled to less than 15 mG by three pairs of coils during the experiment. We have determined that the application of a magnetic field of approximately 2 G, oriented perpendicular to the sample film, produced no observable changes in the sample's tunneling characteristics.

The I-V characteristic of a tunnel junction for lead with 69 at. ppm manganese is shown, together with that of a junction for pure lead, in Fig. 1. For these two samples, there is a sizable difference between the bias voltages at which the cusp occurs, and also between the bias voltages at which the main rise occurs. The gap parameter for the aluminum counterelectrode in either sample is one half of the difference between the voltage at the main rise and the voltage at the cusp, and the sample of pure lead evidently had an aluminum counterelectrode with a smaller gap parameter than did the alloy sample. This difference corresponds to a lower measured transition temperature for the aluminum electrode in

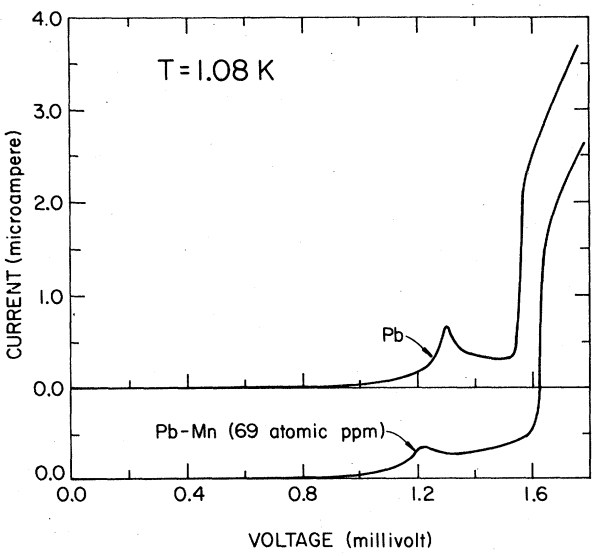

FIG. 1. Tunneling I-V characteristic curves of lead and of lead with 69 at. ppm manganese at a temperature of 1.08 K.

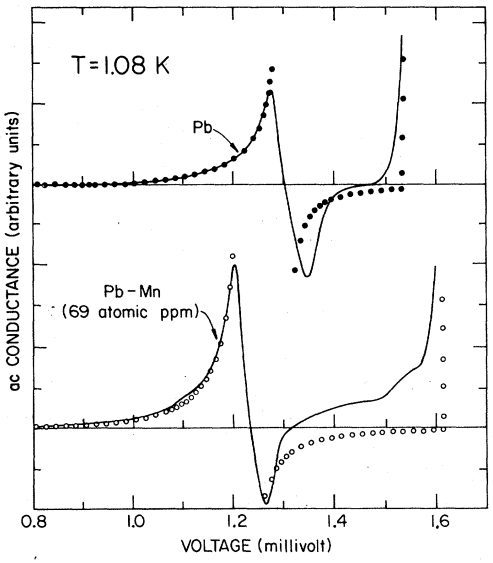

FIG. 2. The solid curves show the ac conductance as a function of the bias voltage of lead and of lead with 69 at. ppm manganese at a temperature of 1.08 K. The circles show the corresponding BCS theoretical conductances.

the former sample, as listed in Table I. (In this work and in our previous article,[1] temperatures less than 4.2 K refer to the T_{58} scale; those larger than 4.2 K refer to the NBS-65 scale.)

On the original chart recording for the alloy, one can see a small but unmistakable indication of a well-defined band of states in the BCS energy gap, just below the main current rise at $(\Omega_{G1}+\Omega_{G2})/e$, where Ω_{G1} and Ω_{G2} are the energy-gap widths for Pb-Mn and Al, respectively. (For the very small magnetic impurity concentration used in this experiment $\Omega_{G1}\cong\Delta_1$, where Δ_1 is the superconducting order parameter in the Pb-Mn alloy. Our calculations in this paper and in the previous paper[1] do not set $\Omega_{G1}=\Delta_1$, however.) To obtain a better indication of this band of states, we measured directly the ac conductance, dI/dV. The dI/dV vs V curves for these two samples are shown in Fig. 2. The curve for the alloy resolves distinctly a band of states near the voltage $(\Omega_{G1}+\Omega_{G2})/e$. The same band of states generates the bump in the curve below the cusp at $(\Omega_{G1}-\Omega_{G2})/e$, by tunneling of thermally excited quasiparticles. BCS theory, corrected for strong coupling effects, provides a reasonably good fit to the pure lead curve, except for the expected smearing of the gap edges. But the theory produces a poor fit to the Pb-Mn curve for voltages between the cusp at $(\Omega_{G1}-\Omega_{G2})/e$ and the main rise at $(\Omega_{G1}+\Omega_{G2})/e$. (The calculated curves were normalized so that they match the experimental curves at 1.8 mV.) As in our previous experiment,[1] the reduced order parameters $\Delta(0,0)/kT_{c0}$ for aluminum and for lead or the alloy were allowed to be adjustable to reproduce the voltages at which the cusp and the main rise were observed. The resulting value for the reduced order parameter of the alloy is listed in Table I, along with the other parameters of interest.

TABLE I. Sample characteristics.

Material	C (at. ppm)	T_c (K)	T_{c0} (K)	Thickness (Å)	$\frac{\Delta(0,0)}{kT_{c0}}$	Material	T_c (K)	Thickness (Å)	Junction resistance (Ω)
Pb	0	7.204 ±0.005	· · ·	1260 ±40	2.30 ±0.01	Al	1.236 ±0.030	1520 ±25	305 ±3
Pb-Mn	69	7.193 ±0.005	7.22 ±0.01	2440 ±70	2.30 ±0.01	Al	1.595 ±0.025	680 ±15	404 ±5

In fitting the data on Pb-Mn to Shiba's theory, we also allowed T_{c0}, the transition temperature of pure lead, to be adjustable while holding T_c fixed. Lead films have approximately the same transition temperature as bulk lead,[9] however. Therefore T_{c0} should be adjusted only slightly in fitting the data. Shiba's theory with s-wave scattering alone, i.e., with only one band of impurity states, around $\epsilon_0\Delta_1$, failed to provide a satisfactory fit to the experimental data on the alloy sample without using an unreasonably high value for T_{c0} (above 7.35 K). In other words, the observed bump in the tunneling conductance has a magnitude which is much too large to be consistent with the theory if only s-wave scattering is included.

One can reasonably bring band theory to our aid, since quench-condensed lead films are known to be crystalline, rather than amorphous.[10,11] The band calculations[4] give four sets of values of the ϵ's for the four possible atomic configurations of manganese impurities. Among them, only two sets predict reasonably well the amount of depression of the transition temperature. The corresponding configurations are $(3d^5$, all +; $4s^2)$ and $(3d^6, 5+, 1-; 4s, 1+)$, where $n+$ and $n-$ refer to n electron spins in the + or − direction, respectively. The corresponding ϵ's have these values: I: $\epsilon_0=0.985$, $\epsilon_1=0.967$, and $\epsilon_2=0.970$; and II: $\epsilon_0=0.959$, $\epsilon_1=-0.680$, and $\epsilon_2=0.990$, respectively. We used these values to calculate the densities of states of the alloy which are shown in Fig. 3. The corresponding theoretical ac conductance curves are shown in Fig. 4 with dashed curves. These theoretical curves account partially for

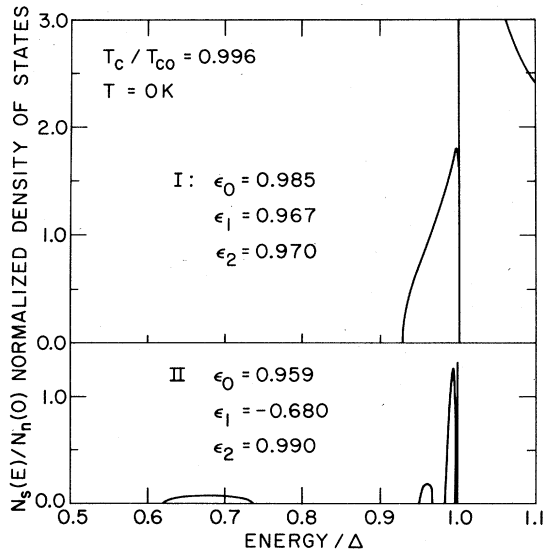

FIG. 3. The normalized density of states for lead-manganese as a function of energy, calculated using Shiba theory with two sets of values for ϵ's obtained from band calculations.

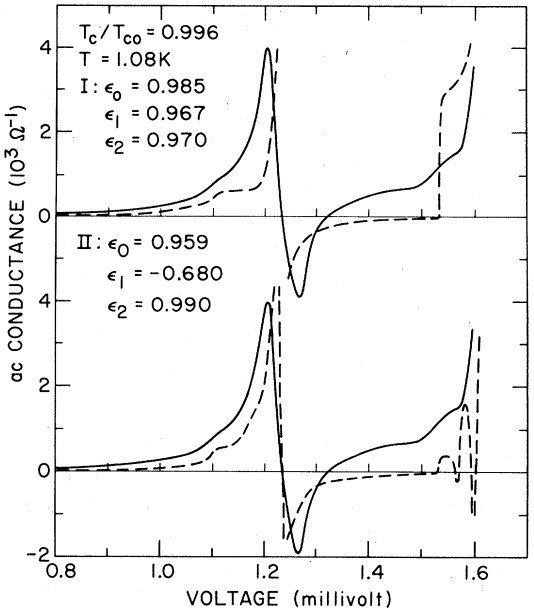

FIG. 4. The solid lines are the experimental dI/dV vs V curves for the lead-manganese sample at 1.08 K. The broken curves show the theoretical results generated from the two densities of states shown in Fig. 3.

the structure near $(\Omega_{G1}+\Omega_{G2})/e$, but they deviate from the experimental curve substantially in most of the voltage range between $(\Omega_{G1}-\Omega_{G2})/e$ and $(\Omega_{G1}+\Omega_{G2})/e$. The data indicate a broad background of states in the corresponding range of energies. The width of this background is more than an order of magnitude bigger than that which would be expected from quasiparticle lifetime effects, as observed by Dynes *et al.*[12]

We have tried to fit the broad background of states and the rest of the experimental data by a theoretical curve calculated with all three parameters ϵ_0, ϵ_1, and ϵ_2 arbitrarily adjustable. We found it impossible to obtain a better fit to the experimental data, however. We speculate that agreement with theory might be better if the effect of the magnetic fields generated by the magnetic impurity atoms were taken into account. The samples were type-II superconductors, of course. Alternatively, the difference between the experimental results and the theory may arise from the location of manganese atoms at more than one type of crystal site in the lead, where they might have more than one atomic configuration.

The impurity concentrations required by the theory to produce the amount of depression of the transition temperature corresponding to the densities of states shown in Fig. 3 are

I: $C=37$ at. ppm and II: $C=11$ at. ppm ,

respectively. [Here we have used $N_n(0) = 0.6363$ states/(eV atom) as obtained by specific-heat measurements.[13]] Both of these values of concentration deviate from the actual concentration in making the sample, which is 69 at. ppm. The initial slope of the depression of the transition temperature by the impurities is 3.9 K/at.% in this sample. This is considerably lower than the value 21 K/at.% obtained previously[14] from samples having much higher concentrations. Our samples may have had a lower concentration of manganese than we thought they had. This problem would not affect our main conclusions, however.

We attempted to fit the tunneling data of Woolf and Reif[15] on more highly doped Pb-Mn alloys, using the same sets of ϵ's. We were not able to do so. However, if we assumed the presence of a leakage current, proportional to the bias voltage, we could obtain better agreement, using these ϵ's. The fit was about as good as Chaba and Nagi[16] obtained with single fitting parameter $\epsilon_0 = 0.55$. Conductance due to the leakage had to be assumed to be as high as 35% of the normal-state conductance in order to obtain the better agreement using the values for ϵ's in set I, and 25% using the values in set II. Because of the high-impurity concentrations used by Woolf and Reif, the impurity bands were not resolved. It should be noted that their data were obtained from normal metal-superconductor tunneling, which has a much lower resolution than superconductor-superconductor tunneling does. The band of localized excited states in a Pb-Mn alloy has also been seen by Levin *et al.*,[17] but in an ion-implanted sample, in which the Mn concentration was known to be inhomogeneous, so that their results are difficult to compare with theory.

In conclusion, localized impurity states in Pb-Mn were observed in our experiment. The tunneling data disagree with Shiba's theory if one includes only *s*-wave scattering between the conduction electrons and impurities. When *p*- and *d*-wave scattering are included, the theoretical density of states agrees better with the experimental data.

ACKNOWLEDGMENT

This work was supported in part by the DOE under Contract No. DE-AC02-76ER01198.

[1]J.-K. Tsang and D. M. Ginsberg, Phys. Rev. B 21, 132 (1980).
[2]H. Shiba, Prog. Theor. Phys. 40, 435 (1968).
[3]D. M. Ginsberg, Phys. Rev. B 20, 960 (1979).
[4]A. B. Kunz and D. M. Ginsberg, Phys. Rev. B (to be published).
[5]J. X. Przybysz and D. M. Ginsberg, Phys. Rev. B 14, 1039 (1976).
[6]W. Opitz, Z. Phys. 141, 263 (1955).
[7]R. W. Roberts and T. A. Vanderslice, *Ultrahigh Vacuum and Its Applications* (Prentice-Hall, Englewood Cliffs, 1963), Chap. 3.
[8]J.-K. Tsang, Ph. D. thesis (University of Illinois, 1980) (unpublished).
[9]B. W. Roberts, J. Phys. Chem. Ref. Data 5, 581 (1976).
[10]H. Bulow and W. Buckel, Z. Phys. 145, 141 (1956).
[11]C. G. Granqvist and T. Claeson, J. Low Temp. Phys. 13, 1 (1973).
[12]R. C. Dynes, V. Narayanamurti, and J. P. Garno, Phys. Rev. Lett. 41, 1509 (1978).
[13]*American Institute of Physics Handbook*, 3rd ed., edited by D. E. Gray (McGraw-Hill, New York, 1972).
[14]N. Barth, Z. Phys. 148, 646 (1957).
[15]M. A. Woolf and F. Reif, Phys. Rev. 137, A557 (1965).
[16]A. N. Chaba and A. D. Singh Nagi, Nuovo Cimento Lett. 4, 794 (1972).
[17]H. Levin, H. Selisky, G. Heim, and W. Buckel, Z. Phys. B 24, 65 (1976).