Electron-tunneling observation of local excited states in manganese-doped indium

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We have measured the electron-tunneling characteristics of a dilute indium-manganese alloy. Well-defined structure was observed, corresponding to a band of local excited states within the energy gap. The measurements were made on two samples, and were quantitatively compared with the theory of Shiba and of Rusinov. We obtained good agreement of the tunneling data with the theory by taking into account only *s*-wave scattering of conduction electrons from the magnetic-impurity atoms. Even better agreement was obtained by including *p*- and *d*-wave scattering. Only by including these higher partial waves could we account for the magnitude of the observed depression of the transition temperature. The phase shifts used are in good agreement with band-theory values calculated recently.

I. INTRODUCTION

The classic theory of Abrikosov and Gorkov (AG)[1] is usually adequate to account for various properties of superconductors containing $4f$ magnetic impurities.[2] That theory uses the first Born approximation to treat the effect of the exchange interaction between the conduction electrons and the impurity atoms. Therefore it is valid only for weak interactions. Shiba[3] and then, independently, Rusinov[4] calculated the effect of the interaction exactly except that they treated the spins as being classical. This theory predicted one or more[5] bands of local excited states within the energy gap. If one takes into account only *s*-wave scattering of the conduction electrons by the impurity atoms these states form a single band, with its position characterized by a parameter ϵ_0, which depends on the strength of the exchange interaction.

The theory of Shiba and of Rusinov should apply to superconductors containing magnetic impurities from among the $3d$ elements of the Periodic Table, which have an interaction with the conduction electrons which is not weak. The earliest tunneling experiment on superconducting alloys with $3d$ magnetic impurities, by Woolf and Reif,[6] showed that the density of states inside the energy gap was larger than predicted by the AG theory, but the concentration of magnetic impurity was too large for a well-defined band to be formed. The tunneling conductance curves for Pb-Mn alloys have been successfully explained by Chaba and Nagi[7] by using the Shiba-Rusinov theory with $\epsilon_0 = 0.55$. However, a similar analysis[8] of In-Fe data[6] showed poor agreement with the theory.

Dumoulin *et al.*[9] used tunneling measurements to observe distinctly the predicted band within the energy gap. They used low-concentration Cu-X (X = Mn, Cr, Fe) and Au-Fe alloys. In these experiments, the proximity effect was involved. The analysis of these data therefore relies on the theory of the proximity effect, which has not been developed quantitatively for samples containing magnetic impurities. Levin *et al.*[10] similarly observed this band by using ion-implanted Pb-Mn and Sn-Mn samples. However, the impurity concentration was not uniform, and this provides a further obstacle to a quantitative analysis of the results, which has not been overcome.

Thermal-conductivity measurements[11] indicated a value $\epsilon_0 = 0.85$ for In-Mn and are consistent with $\epsilon_0 = 0.55$ for Pb-Mn. On the other hand, measurements[12] of the specific-heat jump at the transition temperature indicated that the Shiba-Rusinov theory is not accurate very near the transition temperature, although improvement over the AG theory was found.

We have attempted to utilize the inherent simplicity and sensitivity of superconductor-insulator-superconductor tunneling experiments to provide direct information about the density of states of an In-Mn alloy. We have used a very low concentration of impurities so that the expected tunneling currents would be very small at low voltages. The observation of low tunneling currents there then provided an indication that there was very little leakage current.[13]

II. EXPERIMENT

Our tunnel junctions were fabricated by first evaporating aluminum onto a piece of Z-cut quartz substrate at room temperature. Three strips of aluminum films were made in this way for each run. They were then exposed to the room air for about 60 seconds to form an oxide layer tunnel barrier. The substrate was then cooled to 1.1 K before quench

TABLE I. Sample characteristics.

Sample	Material	C (atomic ppm)	T_c (K)	T_{c0} (K)	Thickness (Å)	$\frac{2\Delta(0,0)}{kT_{c0}}$	Material	T_c (K)	Thickness (Å)	Junction resistance (Ω)
A	In	0	4.489 ±0.010	· · ·	1250 ±100	1.80 ±0.01	Al	· · ·	520 ±40	890 ±3
B	In-Mn	22	4.197 ±0.004	4.28 ±0.01	1400 ±150	1.80 ±0.03	Al	1.410 ±0.025	1450 ±100	45.8 ±1.0
C	In-Mn	22	4.653 ±0.005	4.76 ±0.01	780 ±20	1.80 ±0.03	Al	2.150 ±0.015	2090 ±20	23.2 ±1.0

condensing a cross strip of pure indium or indium-manganese alloy onto the substrate, forming three junctions. This was done by evaporating the alloy from a single-ingot source, prepared as described previously,[11] in a molybdenum boat held at 1110 °C. At that temperature, indium and manganese have the same vapor pressure,[14] so fractional distilation of the material does not occur. During this evaporation, the substrate temperature was 2 K, and the system pressure was $\sim 10^{-6}$ Torr.

In determining the sample's tunneling characteristics, current was fed through the junction from a low-impedance source, and I-V curves were traced on an X-Y recorder. A typical sweep rate was about 0.05 to 0.1 second per microvolt. The noise across the junction was kept below 15 μV peak to peak by properly grounding and shielding the equipment. The first derivatives of the I-V curves were also taken, using a 1-kHz ac signal which had an amplitude of 15 to 25 μV peak to peak. These first-derivative curves were useful in accurately locating the structure on the I-V curves. The three junctions made simultaneously in each run showed the same characteristics.

Four-terminal measurements were made on the tunneling sample's indium or indium-manganese film to obtain the resistance as a function of temperature, from which the transition temperature T_c was determined. T_c is taken as the temperature at which one half of the normal-state resistance is restored. The resistive transitions had a width (10% to 90% of the normal-state resistance) of only ≤ 35 mK, indicating good sample homogeneity. T_c for the aluminum films in each sample is also determined by a resistance measurement. The values for T_c are listed in Table I.

The temperature of the sample was kept below 5 K throughout each run to prevent precipitation of manganese atoms out of the indium, or to provide a pure indium film which would be directly comparable to the alloy films. The temperature was electronically regulated to achieve a stability of ± 1 mK at most temperatures. The earth's magnetic field was cancelled to < 10 milligauss. The tunneling data were obtained at a temperature of 1.1 K.

III. RESULTS AND ANALYSIS

I-V curves for two In-Mn samples, together with a typical pure indium run are shown in Fig. 1. The expected band of impurity-associated states in the alloy is evident; it is located between the cusp and the main rise which one always expects to observe in a measurement of electron-tunneling current in a superconductor-insulator-superconductor sample.

Our analysis was based on equations in the litera-

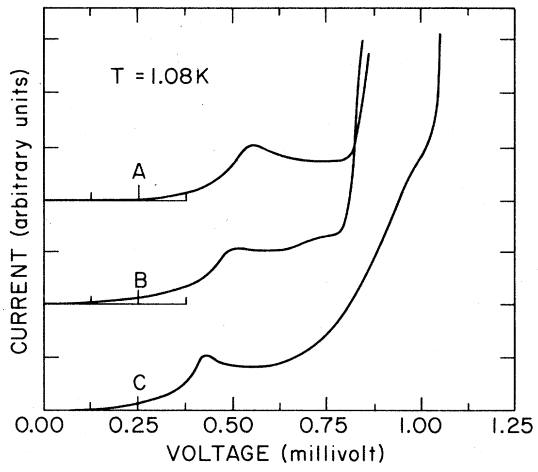

FIG. 1. I-V characteristic curves, obtained at a temperature of 1.1 K. Sample A is a pure indium sample. Samples B and C are composed of indium with 22 atomic parts per million (ppm) of manganese.

ture.[3,4,7,15] The equation

$$\ln\left(\frac{T_c}{T_{c0}}\right)=\psi\left(\frac{1}{2}\right)-\psi\left(\frac{1}{2}+\frac{pT_{c0}}{4\gamma T_c}\right) , \quad (1)$$

where T_c is the transition temperature of the alloy, T_{c0} is the transition temperature of pure indium, $\gamma=1.781$, and ψ is the digamma function, was solved for the reduced concentration $p=C/C_{cr}$, where C is the impurity concentration and C_{cr} is the critical concentration required to completely destroy superconductivity. This value of p was then used in solving Eqs. (6′) and (14) in Ref. 15 simultaneously for the reduced order parameter $\delta=\Delta(p,t)/\Delta(0,0)$, where $t=T/T_{c0}$. Then the density of states $N_s(\omega)$ of the alloy as a function of energy ω was obtained in terms of the normal-state density of states N_n (0) at the Fermi energy by solving the equation

$$\frac{\omega}{\Delta(p,t)}=U\left[1-\frac{p}{2\delta}(1-U^2)^{1/2}(\epsilon_0^2-U^2)^{-1}\right] , \quad (2)$$

for the normalized energy U and putting it into the equation

$$N_s(\omega)/N_n(0)=\mathrm{Im}[\,U(1-U^2)^{-1/2}] . \quad (3)$$

Only s-wave scattering of the conduction electrons from the impurity atoms is considered here, as usual. To find the tunneling current I as a function of the voltage V, the following integral was computed numerically

$$I\propto\int_{-\infty}^{\infty}\frac{N_{s1}(\omega+eV)}{N_{n1}(0)}\frac{N_{s2}(\omega)}{N_{n2}(0)}[f(\omega)-f(\omega+eV)]\,d\omega , \quad (4)$$

where the subscripts 1 and 2 refer to the indium-manganese alloy and the aluminum, respectively. The BCS density of states was used for the aluminum. The function $f(\omega)$ is the Fermi function.

To obtain the best agreement between the experimental and the theoretical I-V curves, the reduced gap parameters $2\Delta(0,0)/kT_{c0}$ for aluminum and for the alloy were allowed to be adjustable to reproduce the voltages at which the cusp at $\Delta_1-\Delta_2$ and the main rise at $\Delta_1+\Delta_2$ were observed. This was necessary to account for the fact that both aluminum and indium[16] have reduced gap parameters which are somewhat sample-dependent. [It is evident from Fig. 1 that Δ_2, the gap parameter for the aluminum, was considerably larger in sample C than in sample B, reflecting the larger value of T_c in sample C (see Table I). It is well known that aluminum films tend to vary widely. The cusp in the tunneling curve which occurs at $\Delta_1-\Delta_2$ arises from thermally excited quasiparticles. Therefore, during the tunneling measurement at a given temperature, the reduced temperature of the aluminum T/T_{c2} was lower for sample C than for sample B, and this produced a cusp at $\Delta_1-\Delta_2$ which was smaller for C than for B, as shown in Figs. 2 and 3.] Then both ϵ_0 and T_c/T_{c0} of the alloy were adjusted, since T_{c0} is also sample dependent in pure indium films.[16] (The resulting values of T_{c0} are listed in Table I.) The value $\epsilon_0=0.80$ could be determined to within 2 or 3% by matching the position of the structure due to the impurity-associated local states. The ratio T_c/T_{c0} was adjusted so that the structure had the correct width. The best fits for the two indium-manganese samples are shown in Figs. 2 and 3. In the limited temperature ranges (1.08–1.40 K for sample B and 1.08 to 1.90 K for sample C) in which the structure of interest could be observed, we detected no significant temperature dependence of ϵ_0. But its value becomes rapidly more difficult to determine as T is increased.

The theoretical density of states of the alloy at $T=1.08$ K which provided the best fit for sample B is shown in Fig. 4. That used to fit sample C was nearly identical; only the value of T_c/T_{c0} was slightly lower (see Table I). The expected effect of the local states at voltages just below $\Delta_1-\Delta_2$ was observable in the first-derivative curves for both B and C. Its roughly determined position agrees with the theory.

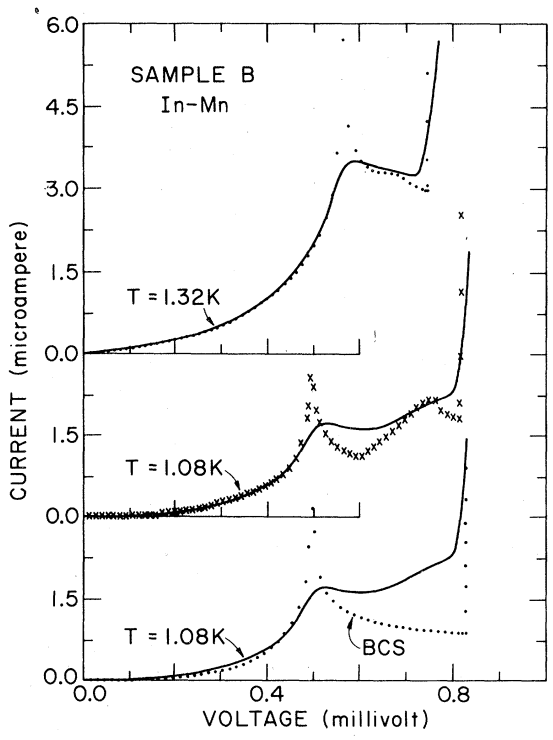

FIG. 2. Solid curves show the experimental I-V curves of sample B. The points show the corresponding theoretical results according to Shiba's theory with only s-wave scattering. For comparision, the bottom curve is shown with the theoretical results for the concentration $C=0$.

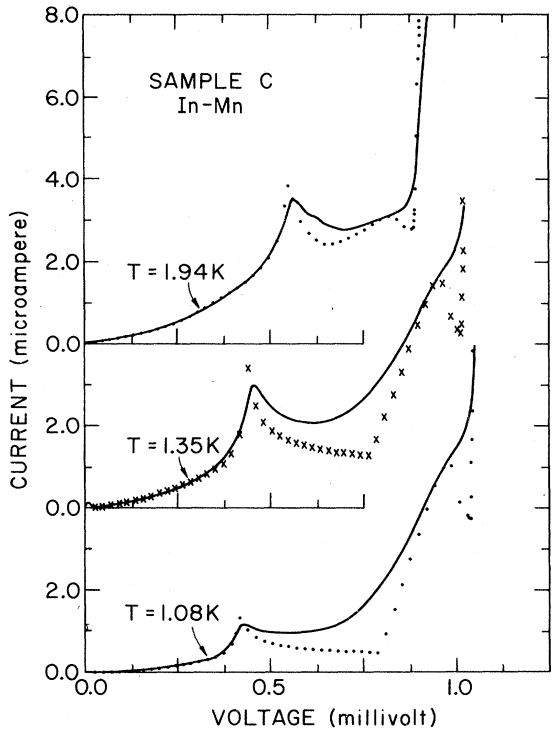

FIG. 3. Solid curves show the experimental I-V curves of sample C. The points show the corresponding theoretical results according to Shiba's theory with only s-wave scattering.

It has been noted that it is necessary to go beyond s-wave scattering to explain the sharp depression of T_c with impurity concentration.[17] Shiba's theory has been generalized[4,5] to include higher partial wave scattering. In the case where only s-wave scattering is considered, with $\epsilon_0 = 0.80$ as obtained above, the

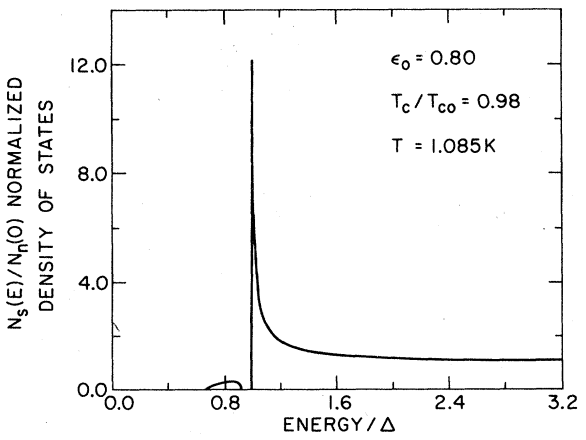

FIG. 4. Theoretical density-of-states curve which was used to calculate the theoretical current values shown in Fig. 2 for sample B.

theory gives for sample B

$$C_{cr} = \pi N_n(0)\Delta(0,0)/(1-\epsilon_0^2) = 2100 \text{ atomic ppm} \quad (5)$$

and for sample C

$$C_{cr} = 2350 \text{ atomic ppm}$$

which are approximately three times larger than the observed values[18–20] (about 700 atomic ppm). In doing this calculation, we use $N(0) = 0.358$ states/(eV atom), as deduced from specific-heat measurements.[21] With $p = 0.0279$ for sample B and $p = 0.0323$ for sample C, values which are determined to $\pm 15\%$, for sample B

$$C = pC_{cr} = 58.89 \text{ atomic ppm}$$

and for sample C

$$C = 75.96 \text{ atomic ppm} .$$

These are also approximately three times larger than the actual concentration we used in making the samples, which was 22 atomic ppm.

The discrepancies which we have just described can be removed by taking into account p-wave and d-wave scattering as well as s-wave scattering. In this way, parameters ϵ_1 and ϵ_2 enter the picture. In general,

$$\epsilon_l = \cos(\delta_l^+ - \delta_l^-) , \quad (6)$$

where $\delta_l^{\pm}$ is the phase shift for waves with orbital angular momentum quantum number l and spin up or down, respectively. A recent band-structure calculation[22] gives

$$\epsilon_0 = 0.962, \quad \epsilon_1 = 0.840,$$

and

$$\epsilon_2 = 0.991.$$

The calculated values of ϵ_0 and ϵ_2 were used together with an adjustable ϵ_1 to determine the density of states,[5] from which theoretical I-V curves were obtained. Because the additional parameters ϵ_0 and ϵ_2 are close to unity they have the effect of smearing the energy gap edge. Consequently, the peak at $\Delta_1 - \Delta_2$ in the calculated I-V curve is lowered and the sharp rise at $\Delta_1 + \Delta_2$ is broadened out, producing a better fit to the data, as shown in Figs. 5 and 6. (However, since smearing of various amounts is also observed in pure indium samples, the improvement here may be accidental).

When $\epsilon_1 = 0.80$ was used, reasonably good fits were obtained. This value of ϵ_1 is in good agreement with the theoretical value 0.84 which has been calculated.[22] With $\epsilon_1 = 0.80$, we have

$$C_{cr} = \pi N_n(0)\Delta(0,0)/\sum_l (2l+1)(1-\epsilon_l^2) = 611 \text{ atomic ppm} \quad (7)$$

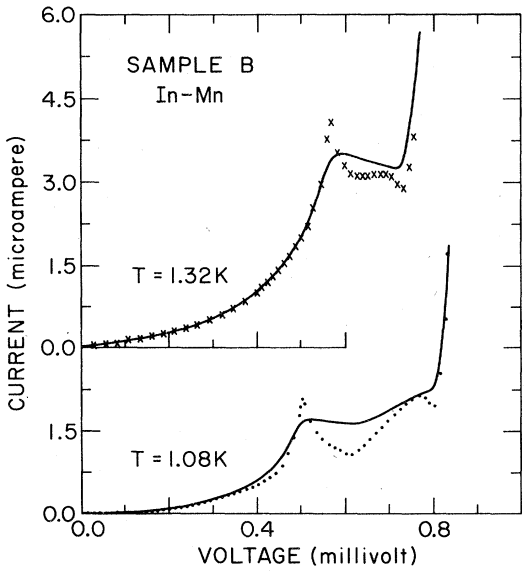

FIG. 5. Experimental I-V curves of sample B are compared with the results according to Shiba's theory with s-, p-, and d-wave scattering.

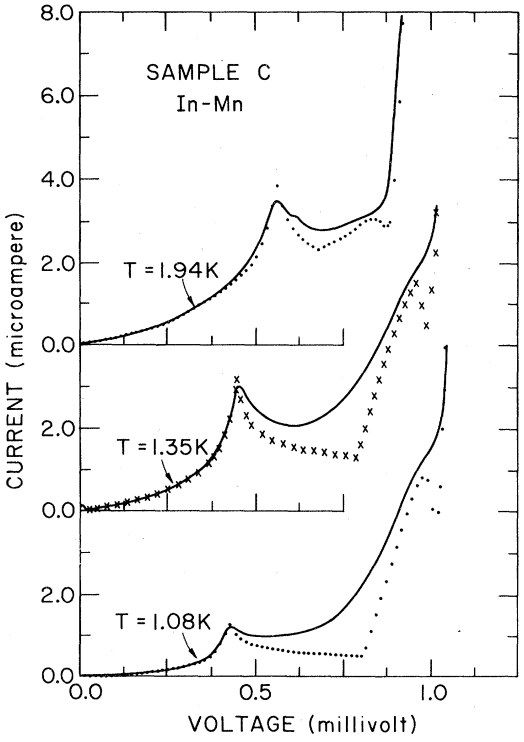

FIG. 6. Experimental I-V curves of sample C are compared with the results according to Shiba's theory with s-, p-, and d-wave scattering.

for sample B,

$$C_{cr} = 680 \text{ atomic ppm}$$

for sample C, and

$$C = 17.04 \text{ atomic ppm} ,$$

$$C = 21.98 \text{ atomic ppm} ,$$

for samples B and C, respectively. Both are in reasonably good agreement with the expected values, 700 and 22 atomic ppm, respectively, considering the uncertainty in determining the reduced concentration p.

The band of states observed for our samples appears to be more smeared out than theory predicts. This may be due to some nonideal property of the samples.

The theoretical values[5] of thermal conductivity[11] would be exactly the same with $\epsilon_0 = 0.80$ and $\epsilon_{l\neq 0} = 1$ as with $\epsilon_1 = 0.80$ and $\epsilon_{l\neq 1} = 1$, for a given value of T_c/T_{c0}. The thermal conductivity would be nearly the same with $\epsilon_0 = 0.962$, $\epsilon_1 = 0.80$, and $\epsilon_2 = 0.991$. Hence, the agreement between theory and the thermal conductivity measurements remains undisturbed when p-wave and d-wave scattering are included.

Finally, it should be noted that for sample C, an extra structure showed up at voltages just above $\Delta_1 - \Delta_2$ as the temperature was increased, as shown in Fig. 3. Its origin is not clear to us.

IV. CONCLUSIONS

The band in the density of states which is predicted by the Shiba-Rusinov theory is found in our samples. For the first time, our data provide an opportunity of quantitatively checking the theoretical shape of the band. Our tunneling measurements have been interpreted in terms of a model including only s-wave scattering, yielding $\epsilon_0 = 0.80 \pm 0.02$ for an In-Mn alloy. This is reasonably consistent with the value 0.85 obtained previously from thermal-conductivity data.[11] We have also interpreted the data with a model which includes p-wave and d-wave scattering, using theoretical values of the phase shifts. This inclusion of higher partial waves improves the agreement between theory and the tunneling data, and it also enables us to account for the magnitude of the observed depression of T_c caused by the magnetic impurity atoms.

ACKNOWLEDGMENTS

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