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Observation of localized excited states in superconducting chromium-doped indium

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We have measured the electron-tunneling characteristics of a dilute, superconducting indium-chromium alloy. The *I-V* curve showed a structure corresponding to bands of localized states as predicted by Shiba's theory with *s*, *p*, and *d* waves included. The phase shifts used in fitting the theory to the data were the results of a band-theory calculation. We have also used these phase shifts to calculate the electron thermal conductivity, and find good agreement with previous experiments.

In two previous papers, our group reported the observation of states associated with manganese atoms which were introduced into films of indium[1] and lead.[2] The tunneling characteristics were measured for aluminum-aluminum oxide-alloy junctions, and the results were compared with Shiba's theory.[3] We have continued this line of experiments, and we report here the observation of similar states in quench-condensed films of indium doped with chromium.

Shiba's theory predicts that the exchange interaction between the conduction electrons and the magnetic atoms will generate a band of states in the Bardeen-Cooper-Schrieffer (BCS) gap, located around an energy $\epsilon_l\Delta$ for each value of the orbital angular momentum l. The values of the ϵ_l's depend on the strength of the exchange interaction. In the previous papers, contributions from *s*, *p*, and *d* waves ($l=0,1,2$) were included, and the values of ϵ_l which had been calculated from band theory produced a good fit to the tunneling data and thermal conductivity data.

The experimental details of this work are very similar to those used previously.[1] Three aluminum films were evaporated onto a crystalline quartz substrate, and were then oxidized by exposing them to moist oxygen for four to ten minutes. After cooling the substrate from room temperature to 1.1 K, the In-Cr alloy was deposited onto the aluminum oxide by flash-evaporating alloy pellets, each adding about 10 Å to the film thickness. The pellets were dropped a few at a time into a tungsten boat held at 1500 °C, as measured by an optical pyrometer (the boat had previously been outgassed at 1750 °C). The pellets had been prepared as described earlier[4] from 99.999% pure indium and 99.999% pure chromium. The temperature of the substrate was held at or below 2.5 K throughout the evaporation, and was kept at a low temperature throughout the experiment. In this way, three junctions were made simultaneously.

Two successful runs on In-Cr were completed, so a total of six junctions were made, and their *I-V* characteristics were measured. In each run, all three junctions showed nearly identical characteristics. We report here on the results from only one junction. For comparison, junctions were also made with pure (99.999%) indium. For this case, the indium was evaporated from one piece in a tungsten boat. Shown in Table I are the characteristics of the two junctions discussed here, including the transition width (10–90 % of the normal-state resistance). The earth's magnetic field was cancelled as in our previous measurements. The temperatures listed in Table I refer to the NBS-65 temperature scale.

The experimental *I-V* tunneling curves for pure indium and for indium doped with 18 ppm chromium are shown by the solid curves in Figs. 1 and 2. In Fig. 1, the upper curve is for pure indium, and the lower three are all for the same In-Cr sample. The In-Cr curve was corrected for a small leakage current that was present; the leakage current near zero-bias voltage was 5.5% of the normal current (our second set of In-Cr junctions showed similar leakage currents). Also shown in Fig. 1 are the theoretical fits to the data. The top two fits were calculated from a BCS density of states, while the bottom two were calculated from a Shiba density of states using an algorithm

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TABLE I. Sample Characteristics.

Material	c (at. ppm)	T_c (K)	T_{c0} (K)	Transition Width (mK)	Thickness (Å)	$2\Delta(0,0)/kT_{c0}$	Material	Thickness (Å)	Junction resistance (Ω)
In	0	4.245 ±0.005	4.245 ±0.005	84	992 ±37	3.790 ±0.005	Al	725 ±24	249 ±3
In-Cr	18	4.218 ±0.005	4.30 ±0.03	44	474 ±63	3.950 ±0.03	Al	589 ±15	9443 ±100

described previously.[1] The parameter $2\Delta(0,0)/kT_{c0}$ of the alloy and that for the aluminum were varied so that the cusp at voltage $(\Delta_1-\Delta_2)/e$ and the main rise at $(\Delta_1+\Delta_2)/e$ in the I-V curve occurred at the voltages indicated by the experimental data. The ratio T_c/T_{c0} was then varied to give the chromium-associated bands

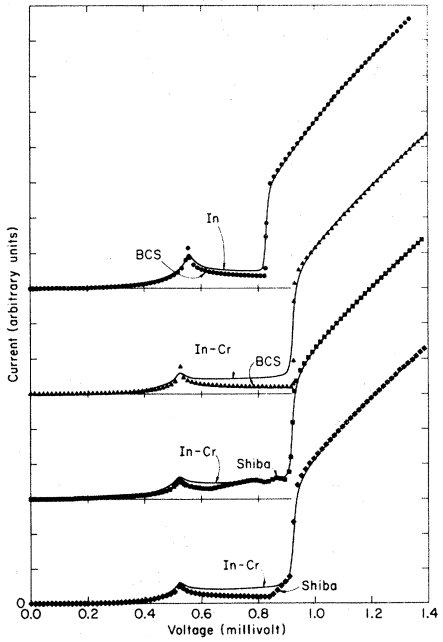

FIG. 1. Top solid curve shows the experimental I-V characteristics for pure indium at $T=1.09$ K. The lower three solid curves show the I-V characteristics for indium doped with 18-ppm chromium at $T=1.08$ K. The upper two curves are fitted with the I-V characteristics generated by a BCS density of states, and the lower two are similarly fitted by using the two densities of states shown in Fig. 3. The third fit from the top corresponds to atomic configuration no. 1 and the fourth to configuration no. 2. All of the fits are normalized to match the data at a voltage of 1.3 mV. The upper three curves are vertically offset for clarity.

about the proper shape, since T_{c0} for the In-Cr film was not known.[1]

A band-theory calculation[5] gives two possible sets of values for ϵ_l for chromium atoms in indium, corresponding to the two possible electronic configurations: $3d^5 4s$ (all $+$) and $3d^5(5+)4s$ $(1-)$, where $n+$ and $n-$ refer to n electron spins pointing in the $+$ and $-$ directions, respectively. The ϵ_l values for these two configurations are as follows. For no. 1,

$$\epsilon_0=0.8944,\quad \epsilon_1=0.7289,\quad \epsilon_2=0.9885\ ,$$

and for no. 2,

$$\epsilon_0=0.9715,\quad \epsilon_1=0.9398,\quad \epsilon_2=0.9938\ .$$

The density of states for each set of ϵ_l's is shown in Fig. 3. The theoretical points near the third I-V curve from the top in Fig. 1 were calculated for configuration no. 1; those near the fourth I-V curve were calculated for configuration no. 2.

It is clear from Fig. 1 that configuration no. 1 gives the better fit to the data. Fig. 2 shows an enlarged plot of the low-bias region of the upper three sets of curves in Fig. 1. In the alloy data, just before the main rise at $(\Delta_1+\Delta_2)/e$ there is a distinct rise which is absent from the pure indium data. This rise is also present in the I-V curve generated from configuration no. 1. In the theoretical curve, the s and p bands are clearly distinguishable, while in the experimental data they seem to be smeared together. There is also a broad background in the data just after the $(\Delta_1-\Delta_2)/e$ cusp which is not present in the theoretical curves. This discrepancy was also shown by the published data on In-Mn and Pb-Mn alloys.[1,2] As mentioned there, the effect of the magnetic field generated by the impurity atoms may be important in explaining this feature of the data.

To bring out the details of the tunneling characteristics, we also measured the ac conductance

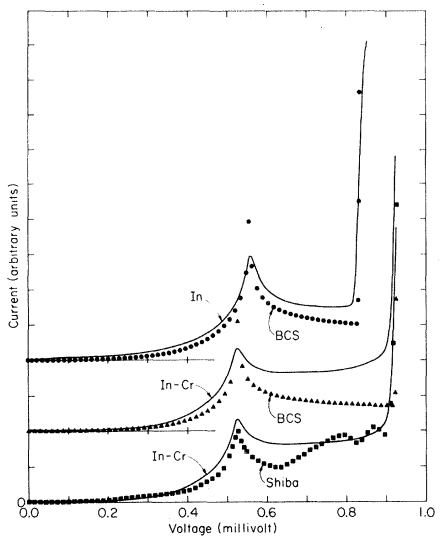

FIG. 2. Low-bias voltage region of the first three sets of curves shown in Fig. 1. The upper two curves are vertically offset for clarity.

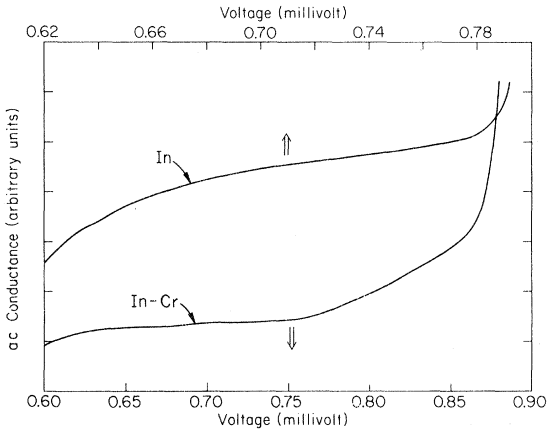

FIG. 4. Top curve shows the ac conductance data for pure indium at $T=1.09$ K. The bottom curve is for In-Cr at $T=1.05$ K.

(dI/dV) for pure indium and for the alloy, and the results are shown in Fig. 4. Only the region between the cusp at $(\Delta_1-\Delta_2)/e$ and the main rise at $(\Delta_1+\Delta_2)/e$ is shown. Each curve was calculated by averaging four separate measured curves to decrease noise. The curves shown were scaled so that the distance from the flat region [between $(\Delta_1-\Delta_2)/e$ and $(\Delta_1+\Delta_2)/e$] and the top of the main rise beginning at $(\Delta_1+\Delta_2)/e$ is the same for both of these samples. The two curves have different shapes; the chromium doping causes the rise right below $(\Delta_1+\Delta_2)/e$. Unfortunately, we were unable to distinguish the individual bands.

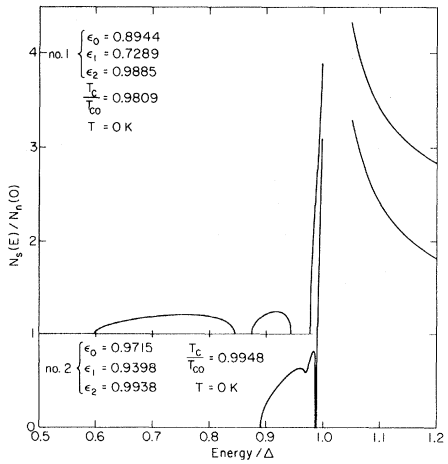

FIG. 3. Normalized density of states for chromium-doped indium as a function of energy, calculated from Shiba's theory with the two sets of ϵ_l's obtained from band-theory calculations for two possible atomic configurations for the chromium atom. The upper plot is shifted up by one unit for clarity.

The impurity concentration required by the theory to produce the best fit to the data from configuration no. 1 is 13.13 ppm, which deviates from the actual alloy concentration of 18 ppm (we used $N_n(0)=0.358$ states/eV atom as deduced from specific-heat measurements[6]). The initial slope of the depression of the transition temperature due to impurities is 45.6 K/at.%. This is lower than the value of 72.2 K/at.% predicted by the theory for configuration no. 1,[5] and also lower than the value measured previously of 65 K/at.% for samples of higher concentration.[7] Our samples may have had a lower concentration of chromium than we thought, but this would not affect our conclusions.

Summing up, we have found that the behavior of superconducting chromium-doped indium can be fitted to Shiba's theory, if we go beyond s waves and include p waves and d waves, and if we choose one of the two proposed electronic configurations of the chromium atom. The necessity of including these higher waves is also demonstrated[8] by incompatibility between transition-temperature data and predictions of s-wave-only theory.

It is useful to consider the electron thermal conductivity of an In-Cr alloy, which has been measured previously.[4] We have recalculated the ratio of the thermal conductivity in the superconducting state to that in the normal state for Przybysz and Ginsberg's In-Cr sample. Our calculated curve, using configuration no. 1, agrees with calculated values[4] for s waves only ($\epsilon_0=0.7$) to within approximately 1%. Therefore the values calculated

from configuration no. 1 also agree well with experiment.

Müller-Hartmann and Zittartz (MHZ) have proposed a theory[9] of magnetic atoms in superconductors which, in contrast to Shiba's theory, takes into consideration the quantum-mechanical nature of the impurity atom spins. Their theory, in the pole approximation, predicts a density of states, $N_s(E)$, at $T=0$, which is identical to that of Shiba's theory in the case where s-wave scattering only is present. We may speculate that higher partial waves could be put into the MHZ theory, and that the resulting $N_s(E)$ at $T=0$ would again agree with Shiba's theory. As the temperature approaches T_c, the two theories would have to diverge, however, since they do so when s-wave scattering only is present. The specific-heat jump ΔC at T_c has been measured, and differs from that predicted by Shiba. The experimental values[10] of ΔC for In-Cr and In-Mn alloys are not in agreement with Shiba's theory, but are in the range of values allowed by the theory of MHZ. In short, MHZ's theory may be more successful than Shiba's theory as T approaches T_c.

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