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Electron-tunneling search for bound states in superconducting manganese-doped aluminum

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It has been predicted that the virtual bound states localized at Mn atoms in bulk samples of Al-Mn alloys in the normal state will yield an observable band of bound states below the gap edge of the alloy when it is cooled and becomes superconducting. We present reasons why we believe that such bound states would be too broad to be seen in such samples but might be present in quench-condensed films. We have used electron-tunneling measurements to look for these bound states in superconducting, quench-condensed, Al-Mn alloy films, but have not found them. We believe our results indicate that the manganese atoms are nonmagnetic and that any bound states that exist must be too broad to be seen in this tunneling experiment.

In previous papers[1-3] our group has reported the observation of localized states associated with the presence of magnetic atoms in superconducting thin films. Structure due to these states was seen below the main rise in the I-V and dI/dV characteristics of superconductor-insulator-superconductor tunnel junctions. Using similar techniques, we now have looked for localized states due to localized, nonmagnetic virtual bound states (resonant states) in a superconductor. We report here the results of a tunneling experiment on manganese-doped aluminum.

Manganese does not have a long-lived magnetic moment in bulk aluminum but lies somewhere between magnetic and nonmagnetic. The $3d$ electrons of the Mn atoms are associated with resonant states of width Γ. The quantity $\pi\Gamma$ is comparable in magnitude to the splitting U of the up- and down-spin states[4] in Anderson's description[5]; the atoms will, therefore, be in the spin-fluctuation regime.[4] The resulting contribution to the resistivity of Al-Mn alloys varies as $1-(T/T_0)^2$ at low temperatures, where the spin-fluctuation temperature T_0 of Al-Mn is 530 K.[6] At superconducting temperatures ($T \ll T_0$), Mn should form nonmagnetic virtual bound states. Salomaa and Nieminen[7] predict that bound states within the energy gap should form in superconductors containing such nonmagnetic virtual bound states. (They used the $U=0$ resonant-level model.) They report that a band of states similar to that due to magnetic atoms should be observed in the tunneling characteristics. Among the systems they recommend investigating to observe such states is Al-Mn.

However, it is possible that any virtual bound states that are present in normal-state Al-Mn alloys are very broad. Grüner[8] has shown that the virtual bound state has an effective width Γ/η, where η is an enhancement factor which can be calculated in the Hartree-Fock approximation. One can also obtain Γ/η from the observed normal-state magnetic susceptibility,[8] yielding a value of 80 meV. This width is much greater than the superconducting order parameter $\Delta \cong 1.76kT_c$. It seems to us that such a broad state in the normal metal would be unlikely to result in a well-defined band of states in the superconducting metal, and would, therefore, be unobservable in our tunneling experiment. (Leaving aside the question of the breadth of this band, Salomaa and Nieminen have noted that if $\Gamma \gg \Delta$, the expected band of states in the superconductor would be too close to the gap edge to be resolvable.)

We have made quench-condensed films for our samples because the needed concentrations of manganese probably exceed the solubility at room temperature.[9] It is possible that quench-condensed films doped with magnetic atoms behave differently from the same alloys in bulk form. (This is known to be the case for In-Mn alloys; the bulk samples are nonmagnetic[10,11] but the quench-condensed films are magnetic.[12]) Therefore, we do not know what $\pi\Gamma/U$ is for quench-condensed Al-Mn alloys, and could not predict whether our Al-Mn films would be magnetic in the normal state or what the width of any virtual bound states might be. The shape of the expected band of states below the superconducting gap edge is different for the case where the dopant atom is magnetic in the normal state than for the case where it is nonmagnetic but forms a virtual bound state there[7]; therefore a tunneling experiment might distinguish between these two possibilities. (An additional way of telling whether the manganese atoms in aluminum are magnetic or whether

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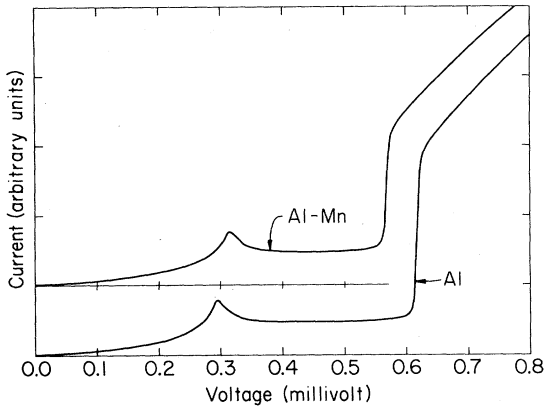

FIG. 1. *I-V* characteristics for the two tunnel junctions discussed here. The upper curve is for the 40-ppm Al-Mn sample at $T=1.07$ K; the lower curve is for the pure Al sample at $T=1.08$ K. The upper curve is shifted upward for clarity.

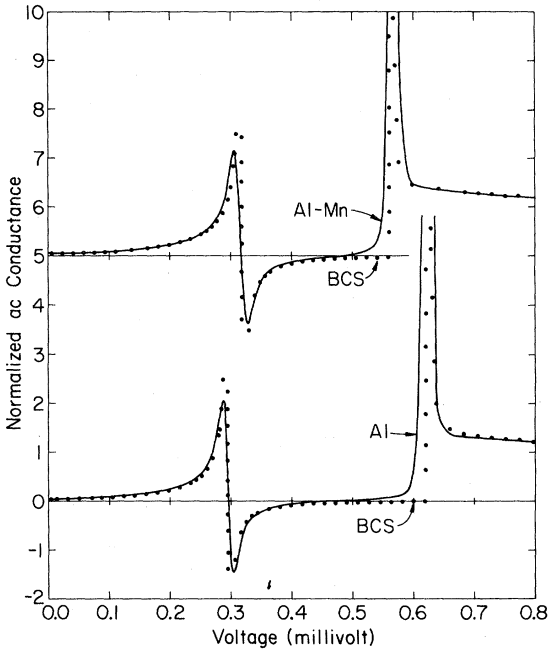

FIG. 2. Solid curves show the normalized ac conductances at $T=1.07$ K for the 40-ppm Al-Mn sample (upper curve) and the pure Al sample (lower curve). The points near the curves show the theoretical ac conductance generated from a BCS density of states. The experimental curves have been corrected for a small leakage current, as is explained in the text. The upper curve is shifted upward for clarity.

they introduce virtual bound states in the films is by the shape of the T_c—vs—Mn concentration curve.[4] Unfortunately, T_c of aluminum films is sample dependent, as is well known, so we cannot determine the depression of T_c in Al-Mn alloy films due to the addition of Mn.) We had hoped to warm up our films to room temperature and then cool them down again for more tunneling measurements, but the junction resistances became too large to give us useful data.

The desired concentration of Mn was determined as follows: For each Mn atom present in the host metal, one bound state should be formed, assuming s-wave scattering only. In a plot of the normalized density of states $N_s(\omega)/N_n(0)$ vs ω/Δ for one spin direction and one type of quasiparticle (electronlike or holelike), each Mn atom should contribute $\frac{1}{4}$ of a state. The superconducting order parameter Δ is approximately equal to the energy-gap width for our small concentrations of Mn. The area of the impurity band, α, in the normalized density-of-states plot can be expressed in terms of the number $[N_n(0)\Delta]$ of normal-metal states below Δ and the fraction of Mn atoms, n, in the sample by $\alpha N_n(0)\Delta=$number of bound states$=n/4$. Using $N_n(0)=0.286$ states/eV atom as deduced from specific-heat measurements on bulk Al samples[13] and a transition temperature of 3 K (a typical value for quenched-condensed Al films), we obtain $\alpha=7.6\%$ for $n=40$ ppm. A band with this large a normalized area should be easily seen. (If scattering of higher-order partial waves is included in the theory, α would be even larger.[14]) On the other hand, a Mn concentration of 40 ppm should be small enough so that almost all the Mn atoms are far apart and do not in-

TABLE I. Junction characteristics. T_{c1} is the superconducting transition temperature of the sample material and T_{c2} is that of the Al counterelectrode at junction C, which is the one with the characteristics plotted in this paper.

Sample material	C (at. ppm)	T_{c1} (K)	Transition width (K)	Sample thickness (Å)	$\frac{\Delta_1(0)}{kT_{c1}}$	T_{c2} (K)	Counterelectrode thickness (Å)	Junction resistance (Ω)
Al-Mn	40	2.901 ±0.01	0.125	163±21	1.77 ±0.03	1.263 ±0.01	763±22	260±3
Al	0	2.945 ±0.01	0.127	119±12	1.82 ±0.03	1.438 ±0.01	500±24	707±7

TABLE II. Sample energy-gap widths at $T=1.08$ K.

Sample material	Junction label	Gap width $\cong\Delta$ (meV)
Al-Mn	*A*	0.416±0.003
	B	0.440±0.003
	C	0.441±0.003
Al	*A*	0.444±0.003
	B	0.455±0.003
	C	0.457±0.003

teract with each other.[15] We have made samples with n equal to 20 and 40 ppm, and report here the results of the 40-ppm sample. (The more dilute sample gave data leading to the same conclusions.)

A master alloy of Al with 3550 ppm Mn was prepared from 9.265 g of 99.999%-pure Al wire[16] and 0.0672 g of 99.9%-pure Mn platelets.[17] The metals were heated in a Ta crucible by an rf induction furnace in a vacuum system at a pressure of less than 2×10^{-5} Torr until the Al had melted and had been stirred rapidly for 30 sec. The power was then shut off, and He gas was admitted to the system. The ingot was cut out of the crucible, etched in HCl, pressed thin under 2.2×10^{8} Pa of pressure, and cut into pieces. The pieces were diluted with pure Al, using the same procedure to produce alloys of 20 and 40 ppm Mn in Al, each of which was later cut into small pellets (~2 mg) for flash evaporating. Several pieces of each dilute alloy were chemically analyzed, and the concentrations agreed with those calculated from initial weights of the materials to within the accuracy of the analysis. A pure Al ingot was similarly prepared and was used to make a sample for comparison.

To form the tunnel junctions three aluminum counterelectrodes were produced first by evaporating 99.999%-pure Al from a W filament onto a crystalline-quartz substrate in an evaporator at a pressure of less than 4×10^{-5} Torr. The aluminum films were placed into our cryostat. They were then exposed to air for 3 h in order to form the oxide tunnel barriers, and the cryostat was evacuated and cooled down to 1.2 K. In the cryostat, pellets of the Al or Al-Mn were then dropped, a few at a time, into a W boat (0.076 cm thick) held at 1500 °C. The boat had been previously outgassed at 1500 °C for 1 min. During the evaporation, the substrate temperature was held below 2.5 K, and the cryostat pressure remained below 5×10^{-6} Torr. In this manner, three junctions were simultaneously made, each with a square shape and an area of 2.3 mm^2. Data were then taken on the junctions, as described previously.[1] The temperature was held below 5 K throughout the experiment, to avoid precipitation of the manganese, and the earth's magnetic field was canceled to less than 15 mG. (The temperatures below 2 K refer to the T_{58} scale, and those above 2 K refer to the NBS-65 scale.)

At the boat's temperature of 1500 °C, the vapor pressures of Al and Mn are 10 and 180 Torr, respectively, so we calculate that all of the Al and Mn evaporated from the boat in not more than a few seconds. The Mn would evaporate more quickly than the Al, of course. The evaporation time of the pellets was visually observed, and the evaporation was allowed to proceed to completion before dropping additional pellets into the boat. For these reasons, we are certain there was Mn in the samples. In fact, our earlier work on In-Mn and Pb-Mn alloys[1,2] gave positive results for the effect of the Mn atoms, although the boat's temperature was approximately 400 °C lower for those alloys.

A single cusp should be seen in the I-V tunneling curve at a voltage $(\Delta_1-\Delta_2)/e$, where Δ_1 is the order parameter of the sample and Δ_2 that of the counterelectrode. (As expected, our quench-condensed films had higher values of the transition temperature and Δ than the Al counterelectrodes, which were deposited on a room-temperature substrate.) Our first eight runs produced either junctions of too low a resistance to be useful or junctions with I-V curves having double cusps. These junctions were prepared differently than those described above; the first aluminum evaporation was done in the cryostat, and the films were oxidized in pure oxygen of controlled humidity for times ranging from 10 min to 1.5 h. These unsuccessful junctions had areas of 0.58 mm^2. We do not know what caused the double cusps. They were observed in both pure and doped samples.

Returning to our successful junctions, Fig. 1 shows the I-V characteristics of one junction for pure Al (lower) and one junction for Al doped with 40 ppm Mn (upper). The normalized ac conductances along with theoretical fits for the same two junctions are shown in Fig. 2. The theoretical curves were generated from a BCS density of states, with Δ_1 and Δ_2 adjusted to match the observed positions of the cusp at $(\Delta_1-\Delta_2)/e$ and the main rise at $(\Delta_1+\Delta_2)/e$. The measured ac conductances which we show were corrected for the small leakage current that is visible in Fig. 1; the theoretical and experimental normalized conductances were made to agree at zero bias by subtracting a voltage-independent conductance from the measured conductances. The subtracted normalized conductance was 0.0185 for the pure Al sample and 0.0377 for the Al-Mn alloy.

Table I lists the characteristics of the two junc-

tions discussed. T_{c1} is the temperature at which the sample film reached 50% of its normal-state resistance. The transition width is defined as the temperature change required to increase the film's resistance from 10% to 90% of its normal-state resistance. T_{c2} is the temperature at which the cusp at $(\Delta_1-\Delta_2)/e$ in the I-V curve vanishes.

In both runs discussed here the sample's gap width varied from junction to junction. Table II lists the sample's gap width, determined from the I-V curve by using Rowell's construction,[18] observed in each junction of the two runs. As shown in Table I, the transition widths of the sample films are appreciable. Apparently, different regions of the film had different transition temperatures. Aside from the variation in energy-gap widths, the three junctions in each run had I-V and dI/dV curves with identical features when plotted as a function of ω/Δ. In both runs the data for junction C had slightly less noise than those of the other two junctions and are, therefore, presented here.

From Fig. 2 we see that a BCS density of states fits the pure and doped samples equally well. There is some rounding of the experimental curve, but there are no other deviations from BCS. We see no evidence for bound states introduced within the energy gap by the doping with manganese.

The fact that both pure Al and Al-Mn alloy films have the same density of states implies that all their thermodynamic properties will be identical when they are expressed in reduced units, i.e., all the properties scale with the order parameter. This is consistent with the critical-field measurements of Smith on bulk Al-Mn alloys.[19]

We conclude from our data that the manganese atoms in quench-condensed Al-Mn alloys are not magnetic because they apparently introduce no bound states in the energy gap. We believe that any nonmagnetic virtual bound states which are present in the normal state of these alloys are so broad that the resulting bound states in the superconductor are too broad to be seen in our experiment.

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