Investigation of the magnetic scattering in a superconductor by the tunnel-effect method

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We have investigated the tunnel systems Al—Al_2O_3—M—Sn with impurity metals (M) of the 3d group (Cr, Mn, Fe) on the barrier boundary on the superconductor side, at concentrations less than 10^{16} atm/cm^2. We have observed that the presence of magnetic impurities destroys the superconductivity in a certain region of radius r_s around the impurity atom. In the limit of low concentrations, the values of r_s are 2.6±0.5, 3.6±0.5, and 2.8±0.5 Å for Fe, Cr, and Mn, respectively.

1. Much attention has been paid recently to superconductors with magnetic properties.[1] Most investigations of this type, however, were performed on alloys. In this case the measurements of T_C and of the specific heat, as well as tunnel measurements, yield characteristics that are spatially averaged. Investigations of the spatial variation of the order parameter are confined mainly to studies of the "proximity" effect in a superconductor + magnetic metal system. In this case both measurements of T_C and tunnel measurements[2-5] performed on the superconductor side yield information on the properties of the superconductor far from the magnetic atoms at distances on the order of ξ_0. On the other hand, investigations of the scattering of electrons by magnetic impurities by the tunnel-effect method, which could yield information on the behavior of the superconductor near the magnetic atom, are limited mainly to normal metals[6].

We have previously attempted[7] to investigate the properties of a superconductor near magnetic atoms by determining the change produced in the tunnel characteristics when a magnetic impurity is deposited on the barrier on the superconductor side. It was observed that the presence of an Fe impurity on the barrier boundary leads to a decrease of the singularities of the tunnel characteristics without noticeable smearing or displacement of the characteristics. We present here the results of further study of tunnel systems with magnetic impurities. The study objects were tunnel systems of the type Al—Al_2O_3—M—Sn, where M is a controllable admixture of a metal from the 3d group (Fe, Cr, Mn).

2. The samples were prepared by evaporating the metals in vacuum. A diagram of the sample is shown in Fig. 1. The metals were condensed through a system of moving screens on a glass substrate kept at $T \sim 300°K$. After condensing the aluminum film (~1000 Å thick), a BaF_2 layer was deposited (also ~1000 Å thick). The insulating layer is essential to prevent the edges of the Al and Sn films from affecting the characteristics of the tunnel junction. The insulator layer had windows measuring ~1 mm^2, through which the tunneling took place. After depositing the BaF_2, the Al film was oxidized in an atmosphere of air at pressure ~0.02 atm for 1–2 min. The impurity was deposited on the oxidized aluminum film, after which a tin film ~3000 Å thick was condensed. The resistances of the junctions obtained in this manner ranged from 10 to 100 Ω. During the evaporation time, the vacuum in the system was not worse than 10^{-6} Torr. The aluminum and tin were evaporated from tungsten coils. The metals Fe and Cr were evaporated from

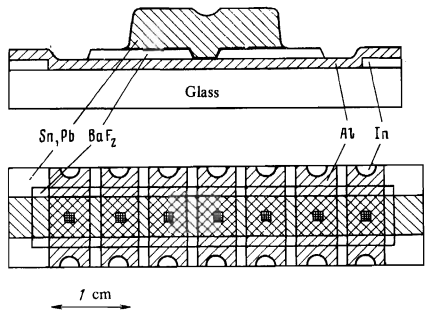

FIG. 1. Diagram of sample.

wires made of this material, 99.99% pure; the Mn and BaF_2 were evaporated from tantalum vessels.

The film thickness d, as well as the amount of impurity on the barrier boundary, was estimated from the amount of evaporated metal, assuming the source to be isotropic. To measure the amount of evaporated impurity metal, a quartz radio balance was used, located near the evaporator. The balance was similar to that described by Sorokin[8] and contained two quartz resonators of natural frequency 10 MHz. The presence of these two resonators, maintained under identical conditions, has reduced the effect of heating, although not completely. The sensitivity of the balance was determined from the total frequency drift and from the evaporator weight loss, and amounted to $\sim 7 \times 10^{-8}$ g/Hz. The accuracy with which the amount of matter on the barrier was measured was $\sim 10^{14}$ at/cm^2.

We investigated tunnel systems with impurity concentration N on the barrier boundary up to 10^{16} at/cm^2. At the same time, a series of eight samples were prepared, of equal film thickness but with differing impurity contents. The range of variation of the amount of impurity over the series was from 1.5 to 2 times.

According to Hansen's data[9], at room temperature Cr, Mn, and Fe are not dissolved in Sn and produce no intermetallic compounds. The absence of intermetallic compounds from overlapping Fe and Sn films prepared at room temperature is confirmed by the results of Tsuya[2].

The influence of mutual diffusion on the tunnel characteristics was verified by us experimentally. Annealing of samples with Cr, Mn, and Fe impurities for 10 hours at room temperature in an He atmosphere did not lead to a change in the tunnel characteristics of the junctions.

d_N, Å	d_S, Å	T_c, °K	α	τ_S, 10^{-14} sec
		Iron		
1.46	550	2.71	21	2
1.5	680	2.98	16	2.5
1.53	800	3.12	15	2.6
1.53	930	3.26	15	2.5
1.53	1000	3.31	14	2.6
1.5	1040	3.35	13	3
2.1	540	2.21	22	2.5
2.2	670	2.63	20	2.3
2.2	800	2.82	20	2.2
2.3	920	3.01	15	2.7
2.2	1030	3.13	13	3
		Chromium		
28	670	2.[illegible]	[illegible]	5.3
28	820	2.[illegible]	[illegible]	4.3
28	950	3.[illegible]	[illegible]	4.4
28	1020	3.14	[illegible]	4.3
28	1060	3.[illegible]	[illegible]	4.2

In the experiment we usually measured the R—V characteristics of the junctions ($R \equiv dV/dI$). A modulation circuit similar to that described in[10] was used for the measurements. The modulation signal applied to the junction did not exceed 10 μV. The measurements were made in the temperature range 4.2—1°K. From the characteristics plotted at $1°K < T_c$ Al, we were able to assess the quality of the tunnel junctions.

The influence of the Sn-film dimensions was also verified experimentally. The thickness of the Sn film (~3000 Å) was so chosen that the tunnel characteristics of the Al—Al_2O_3—Sn—Fe junctions did not differ from the characteristics of the Al—Al_2O_3—Sn junctions at the largest impurity concentrations.

The presence of a potential barrier due to various impurities on the interface between the magnetic impurity and the superconductor weakens, naturally, the influence of the magnetic impurities on the superconductivity. To estimate the quality of the impurity-superconductor boundary, measurements were made of T_c of Sn films of thickness smaller than indicated above, placed in contact with a layer of magnetic metal. The film parameters and the measured values of T_c are listed in the table. In the calculation of the thickness, we used the density values for bulk material. The table lists also the values of the parameter $\alpha = \hbar/2\pi k T_c \tau_S$, which enters in the modified equations of the theory of de Gennes and Werthamer[5]. A comparison of the results with the data of[2,5] shows that the interface in our case was pure enough and the contact between the magnetic metal and the superconductor was good.

3. Figure 2 shows typical R(V) characteristics of Al—Al_2O_3—Fe—Sn junctions with varying amounts of Fe on the barrier boundary, obtained at T = 1°K. With increasing Fe concentration, the characteristics of the junction change from curves of the S—I—S type (curve 1) to curves of the S—I—N type (curve 5). No noticeable smearing or shift of the singularities is observed. The singularity at $V = \Delta_{Sn} - \Delta_{Al}$ disappears before the singularity at $V = \Delta_{Sn} + \Delta_{Al}$, and cannot be seen on the curves of Fig. 2. The character of variation of the singularities can be more distinctly traced in the Fe-Pb system[7], where they are strongly separated in terms of voltage.

Figure 3a shows the dependence of the energy gap of the (Fe + Sn) superconductor near the barrier. Up to the highest Fe concentrations, the change of the gap does not exceed 5%.

Figure 4 shows a plot of the tunnel conductivity

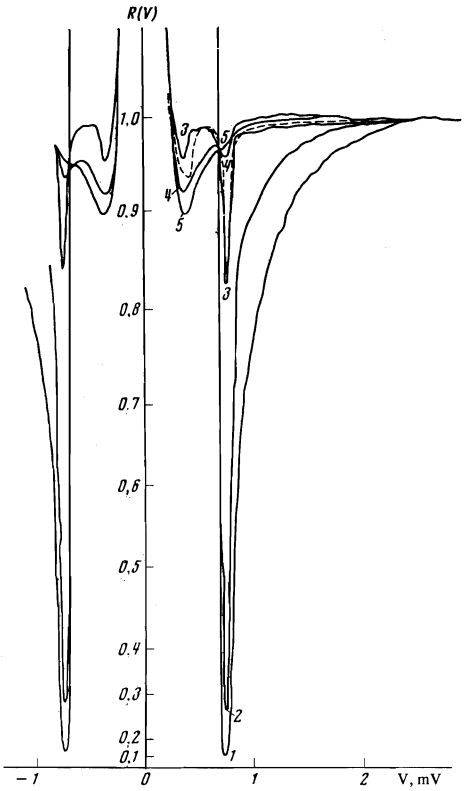

FIG. 2. Plots of dV/dI against V for Al—Al_2O—Fe—Sn junctions with various Fe concentrations (in 10^{15} at/cm²): 1—pure tin, 2—1.3, 3—1.8, 4—2.5, 5—3.2.

$\sigma(0)/\sigma(\infty)$ at V = 0 against the temperature in logarithmic coordinates. For a tunnel junction consisting of a normal metal, an insulator, and a BCS superconductor, the conductivity was calculated[11] at $T \sim T_c$, viz., $(1 - \sigma(0)/\sigma(\infty)) \sim (1 - T/T_c)$. As seen from Fig. 4, addition of the Fe impurity on the barrier boundary shifts the plots without changing their slope.

This behavior of the R(V) plots can be described by assuming the existence of two parallel tunnel currents I_S and I_N,[7] where I_S is the tunnel current in the Al + superconductor system, and I_N the tunnel current in the Al + normal metal system. The conductivity per unit surface of the junction consists correspondingly of two parts:

$$\sigma(V) = \sigma_S(V) + \sigma_N(V),$$

with the ratio of σ_S to σ_N dependent on the impurity concentration. The dashed curve in Fig. 2 was calculated in accordance with this model at a value $\sigma_N/\sigma_S|_{V>\Delta_{Sn}} = 39$. The described behavior of the R(V) characteristics can be represented as destruction of the superconductivity on a certain part f of the barrier surface. If it is assumed now that the barrier transparency does not depend on the presence of impurity atoms on the barrier, and that the density of states in the "normal" region is equal to the density of states in normal tin, then we can calculate the tunnel conductivity

$$\frac{\sigma(V)}{\sigma(\infty)} = \frac{1-f(N)}{\rho_S(V)} + \frac{f(N)}{\rho_N(V)}.$$

Here ρ_S and ρ_N are respectively the resistivities of junctions of the type Al—Al_2O_3—Sn and Al—Al_2O_3—N (where N is the "normal" metal), with $\rho_S(V) = \rho_N(V) = 1$ at $V \gg \Delta_{Sn}$. By measuring the function $\sigma(V)$

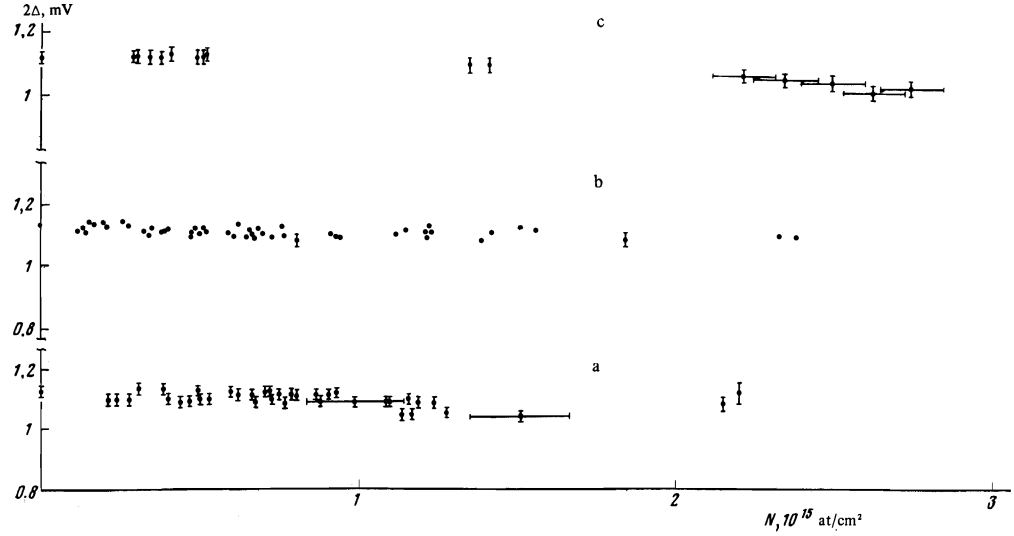

FIG. 3. Superconductor energy gap for the systems Fe-Sn(a), Cr-Sn(b), and Mn-Sn (c).

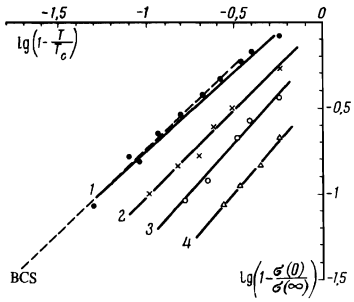

FIG. 4. Temperature dependence of the tunnel conductivity for Fe-Sn systems with different amounts of Fe (in 10^{15} at/cm^2): 1–0.44, 2–0.72, 3–0.88, 4–0.93.

$= 1/R(V)$ for various N we can determine the form of the function f(N). If $\Delta\sigma_S/\sigma_S(\infty) \gg \Delta\sigma_N/\sigma_N(\infty)$, then

$$f(N) = 1 - \frac{\Delta\sigma}{\sigma(\infty)} \Big/ \frac{\Delta\sigma_s}{\sigma_s(\infty)},$$

where $\Delta\sigma = \sigma(V) - \sigma(\infty)$.

Figure 5 shows a plot of $\ln(1 - f)$ against the impurity concentration on the barrier boundary for the Fe-Sn system. The dark circles were obtained for samples from the same series. Although the form of the function is determined in the general case by the structure of the impurity layer, we can make certain estimates in our case.

Since the substrate temperature during the deposition of the layer is lower than the recrystallization temperature of the Fe film ($\sim 0.4T_{melt}$) and since estimates of the critical dimensions for the nucleus in the formation of the Fe film on an Al_2O_3 substrate[12] yield $r_{cr} \sim 2$ Å (on the order of the dimension of the atom), we can assume that the migration of the atoms along the substrate is small. If it is assumed that each Fe atom produces around itself a normal region of area s, then the total area of the normal region produced by N iron atoms is $f(N) = 1 - \exp(-Ns)$[12]. We assume that the dimension of the normal region around the impurity atom does not depend on the impurity concentration and there is no migration of Fe atoms along the barrier. As seen from Fig. 5, this simple model describes adequately the experimental results obtained for the Fe-Sn system. The values of s and r_S determined in this manner are $s = 21.5 \times 10^{-16}$ cm^2 and $r_S = 2.6$ Å. A similar f(N) dependence was observed also for the Fe-Pb system[7,13].

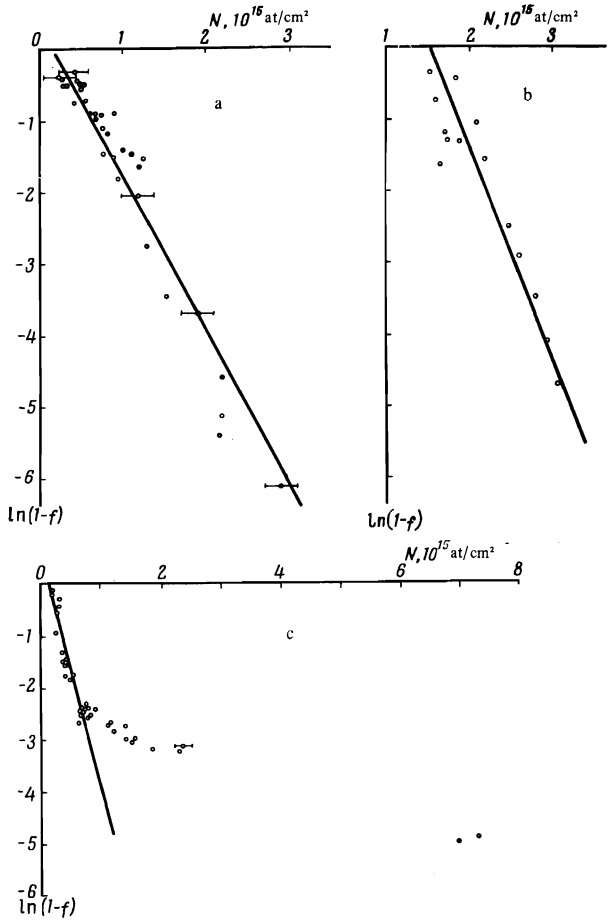

FIG. 5. Dependence of ln (1–f) on the impurity concentration for the systems Fe-Sn (a), Mn-Sn (b), and Cr-Sn (c).

4. The tunnel characteristics obtained for the systems Mn—Sn and Cr—Sn did not differ from those shown in Fig. 2. The presence of these metals as impurities on the barrier boundary also leads to a decrease in the singularities of the tunnel characteristics, without noticeable smearing or shifts. Figures 3b and 3c show plots of the energy gaps of the superconductors Cr—Sn and Mn—Sn, respectively, determined from the positions of the minima of the R(V) curves plotted at

$T = 1°K$. Just as in the case of the Fe—Sn system, a small change of the gap, ~5%, is observed only at the largest concentrations. A reduction of the R(V) curves, similar to that performed earlier for the Fe—Sn system, is shown in Figs. 5b and 5c. As seen from Fig. 5b, a linear dependence of $\ln(1 - f)$ on N is observed also for the Mn—Sn system at Mn concentrations larger than 1.5×10^{15} at/cm^2. Up to these concentrations, the presence of Mn does not affect the tunnel characteristics. We attribute the presence of such a region ($<1.5 \times 10^{15}$ at/cm^2) to the systematic error in the determination of the Mn concentration from the readings of the quartz balance. Since the Mn was evaporated from a tantalum vessel, it was possible for the evaporator to become contaminated by the volatile impurities sublimated before the Mn, which produced a shift in the determination of the concentration. The value of r_s calculated for Mn is 2.8 ± 0.5 Å.

The dependence of $\ln(1 - f)$ on N, obtained for the Cr—Sn system, is much more complicated (Fig. 5c) and is not described by a simple linear relation. But the dimension of the normal region around the impurity atom, at low impurity concentrations, can be obtained from the value of df/dn as $N \to 0$. Estimates made in this manner yield for Cr a value $r_s = 3.6 \pm 0.5$ Å.

The appearance of an inflection on the $\ln[1 - f(N)]$ curve (Fig. 5c) can be attributed to at least two causes: 1) structural peculiarities in the formation of the Cr film, 2) decrease of the magnetic moment of the Cr atoms at large Cr concentrations on the barrier boundary.

It should be noted, however, that the arguments presented above for the Fe—Sn system are fully applicable also to Cr. When the Cr was evaporated, the substrate temperature was lower than the recrystallization temperature, and when the Cr film is produced the critical dimension of the nucleus is also of the order of the dimension of the atom. Consequently, the structure of the Cr layer should differ little from the Fe layer, and the observed difference seems to be due to a decrease of the magnetic moment of the Cr atoms.

It was shown in a number of studies[14-17] that the presence of a magnetic impurity in a superconductor leads to a spatial change in the order parameter. In this paper we approximate the spatial dependence of the order parameter by means of a simple step function

$$\Delta(r) = \begin{cases} 0, & r < r_s \\ \Delta_0, & r > r_s \end{cases},$$

and this appears to be a good approximation in the case of the Fe—Sn system. For the Mn—Sn and Cr—Sn system, possibly, one should use a more complicated function $\Delta(r)$. This yields, naturally different values of f(N) for the maxima and minima of the R(V) curves.

For Cr concentrations larger than 6×10^{14} at/cm^2, a discrepancy is observed between the values of f(N) obtained from different points of the curves. The values of f(N) obtained from the maximum of the R(V) curves at $T = 1.6°K$ are approximately 20% lower than those obtained from the minima of the curves obtained at $T \sim 1°K$, although an appreciable section (up to 6×10^{14} at/cm^2) and the overall course of the curves coincide. The obtained picture agrees qualitatively with that given in[15]. A detailed comparison is hardly meaningful, since Heinricks's theory[15] is confined to the region $T \sim T_c$ and makes no allowance for the Kondo effect and for the interaction between the impurities, which probably plays an important role in the investigated systems.

We observed in the studied systems in the normal state no attributes of giant anomalies at $V = 0$, which were attributed in a number of papers to electron scattering by magnetic impurities[18,19]. Thus, in the voltage region <10 mV of interest to us, the value of $\Delta R(V)/R(0)$ for the systems Cr—Sn and Mn—Sn did not exceed 8% at $N < 3 \times 10^{15}$ at/cm^2.

The junction resistance of the Fe—Sn system was independent of the voltage.

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