Superconductivity and negative magnetoresistance in amorphous In_2O_x films

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The superconducting transition and the negative magnetoresistance of amorphous indium oxide were studied as samples were changed reversibly between insulating and metallic states by thermal treatment. All the observations can be adjusted if we assume that a gap at the Fermi level appears in the insulating state due to the superconducting interaction, and that this gap is destroyed by the magnetic field. © *1995 American Institute of Physics.*

Amorphous indium oxide (am-In_2O_x) can be transformed by influencing it comparatively slightly from an insulating state (I-) to a metallic state (M-). Since this material exhibits a superconducting (S-) state, the problem of (S–I) transition also arises. This determines the stable interest in am-In_2O_x (Refs. 1–5).

We have in fact a poor description of both S- and I- states near the (S–I) transition. They both are affected by inhomogeneity of the material. This usually is assumed to be an annoying factor which masks the evolution of the properties near the transition. We intend here to use the properties of macroscopically inhomogeneous high-resistance materials as a guide in an attempt to understand the nature of the transition.

It is known that the resistance of a macroscopically inhomogeneous material in the S-state can be essentially larger than that in the normal state.[6–8] This can be easily explained by considering the model of a granular metal in which the main contribution to the resistance comes from the carrier tunneling between the grains. When the grains become superconducting at the temperature $T=T_c$, a gap Δ appears in the energy spectrum at the Fermi level, a number of quasiparticles in the grains freeze out, and the one-particle tunnel current decreases. If, in addition, the Josephson current is absent under these conditions, because of damping by the quantum fluctuations, for example,[9,10] an exponential factor will appear in the resistance:

$$R(T) \propto \exp(\Delta/T). \tag{1}$$

The magnetic field H increases the conductivity enormously by destroying the gap in the grains. This is one of the mechanisms of the gigantic negative magnetoresistance[8] (NMr: we use the lower case r for the abbreviation in order to avoid confusing it with nuclear magnetic resonance). Apparently, this type of the S-response takes place rather often in high-resistance inhomogeneous materials.[11] In particular, it was seen in granular films of In_2O_x (Ref. 12) and Al_2O_x (Ref. 13).

One may wonder what happens with this anomalous S-response (the resistance increases exponentially, while the temperature in zero magnetic field and the gigantic

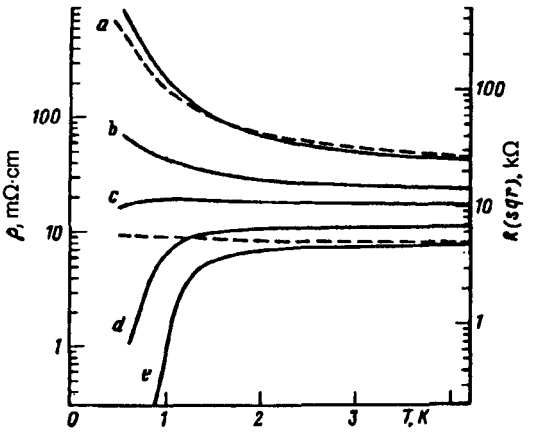

FIG. 1. Resistivity of a am-In_2O_x film at different stages of the heat treatment (states $a-e$). Solid lines—In zero field, dashed lines—in a 7-T field.

NMr decrease) when the typical size of the structure decreases. By decreasing the grain size we can achieve, at least mentally, a crossover from the granular metal to the insulator with long-range fluctuations of the random potential or even to one with random impurity centers. The question is whether the Cooper pairs can survive and become localized and what is the role of the Cooper interaction in the insulators. Note that an experimental study of the possibly localized Cooper pairs were performed by Paalanen and co-workers only on the am-In_2O_x films.[3] From the analysis of the $R(H)$ curves at temperatures below the S transition, they came to the conclusion that localized pairs do exist. Below we present additional arguments in favor of this conclusion.

This investigation was motivated by the arguments presented above. Assuming that the am-In_2O_x films are quasihomogeneous, we analyzed the evolution of the transport properties of a film along the row of its successive states spanning the $M-I$-transition. Special attention was paid to the trace relations between the S-transition and NMr. Except for the following two distinctions, we have repeated the experiments described in Ref. 4:

a) we used thinner films than those in Ref. 4, $\approx$200 Å; this modification allowed us to change their state reversibly;

b) we used higher magnetic fields, up to 8 T; however, even such fields turned out to be not high enough to saturate the NMr.

High-resistance films were fabricated in the Racah Institute of Physics in Jerusalem by electron-gun evaporation of high-purity In_2O_3 onto glass substrates in a vacuum chamber with oxygen atmosphere.[1] Their thickness was in the range 200–250 Å. Their resistance in the initial state reached 10 MΩ at liquid helium temperatures. After aging in air at room temperature for several months, their resistance decreased by two orders of magnitude but their low-temperature conductivity remained the same. The measurements described in this paper were performed with these aged samples; in this sense, the state a in Fig. 1 should be regarded as the initial state.

The resistance of am-In_2O_x is determined by two factors: disorder and chemical content, i.e., the x value in In_2O_x. The x value can be changed by some outer treatment.[14] We managed to change x reversibly, in a rather restricted interval, but by softer treatment than in Ref. 14.

Kept in an inert atmosphere or in vacuum at temperatures in the range 90–100 °C for 3–4 hours, the sample could be transformed from state a to state e (Fig. 1), with the surface resistivity at 4.2 K reduced from 25 kΩ to 4 kΩ. Kept in the presence of oxygen (for instance, in air) at 20 °C–40 °C, it could be brought back to a state close to state a. X-ray analysis confirmed that in all these transformations the film remained amorphous. Together with reproduction of the transport properties after such a cycle, this means that the disordered network made of indium atoms remains unaltered during these transformations. In particular, the appearance of the superconductivity does not depend on the appearance of indium clusters. The same conclusion was made earlier in Ref. 4.

It seems that equilibrium values $x<3$ of the oxygen concentration exist for the am-In_2O_x films, and that they depend on the temperature; the limiting value $x=3$ corresponds to low temperatures, where the time needed to approach the equilibrium becomes inaccessibly large. The magnitude $(x-3)$ determines the concentration of the electrons which are not bound by oxygen bonds.

Curves $a-e$ in Fig. 1 illustrate changes in the low-temperature transport properties of the film which accompany its transformation. Such set of curves usually interpreted as the $S-I$-transition.[15] Apart from the zero-field $R(T)$ curves, those in the field $H=7$ T for the two extreme states are plotted in Fig. 1 by the dashed lines. Note that NMr in the state a and superconductivity in the state e appears in the same temperature range—near 1.5 K.

The logarithmic scale in Fig. 1 conceals the magnitude of the NMr in the state e. That is why its relative magnitude

$$\delta=\frac{R(7\mathrm{T})-R(0)}{R(7\mathrm{T})}$$

is plotted separately in Fig. 2. This figure demonstrates the second important observation; namely, the relative value of the NMr increases rapidly with decreasing T, without a tendency to become saturated.

In Fig. 3, we show the field dependence of $R(H)$ at $T=0.5$ K for the set of different states. The S-transition in the M-states forced us to normalize the curves to $R(7\mathrm{T})$, instead of the more usual $R(0)$. Figure 3 shows the next two important features of the NMr. In addition to the sample becoming metallic, the NMr domain is pushed toward the higher magnetic fields, being swallowed up by the standard effect of destruction of the S-state by low and moderate fields. Note that the "standard effect," i.e., the positive derivative dR/dH, exists even in those states of the sample where there is no sign of the usual S-response (states a and b). The final point we wish to emphasize is that the relative value of the NMr continues to rise in our largest field, 8 T. It can be seen from the curves in Ref. 3 that the NMr is not saturated in a field of 10 T.

The low-field NMr in the variable-range-hopping regime has been well established experimentally.[16,17] The conventional explanations include the influence of the field on

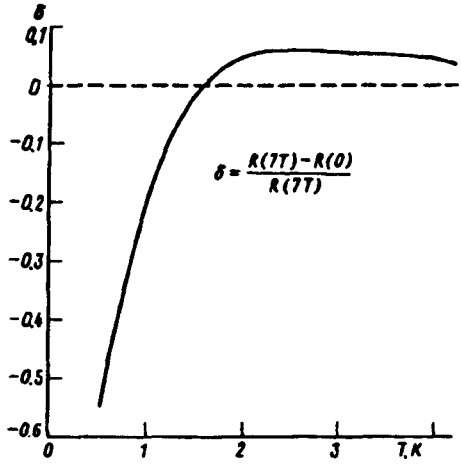

FIG. 2. Normalized magnetoresistance of the am-In_2O_x film in the state e.

the interference of different tunnel trajectories[18,19] and changes of the density of states at the Fermi level.[20] However, the interference NMr occurs in comparatively low fields, below

$$H_i \approx \Phi_0 / r^{3/2} \xi^{1/2}, \tag{2}$$

where Φ_0 is the quantum flux unit, r is the hopping distance, and ξ is the localization length. These fields are on the order of 1 T. In two dimensions, the character of the NMr

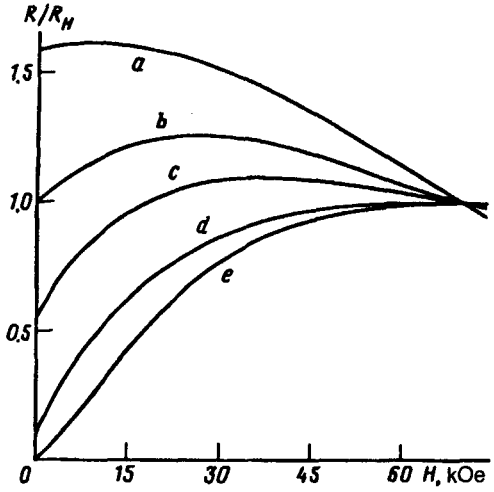

FIG. 3. Field dependence $R(H)$ normalized to R (7 T) in different states of the sample. $T=0.5$ K.

in films with long-range random potential is slightly different,[21] but the typical field turns out to be even lower than H_i; an estimate such as (2) contains the typical long period of the random potential, $L \gg r$.

The attempts to explain the NMr in high magnetic fields within the frame of the ideas of the hopping and tunnel conductivity have therefore not been very successful. The spin degree of freedom leads to a positive magnetoresistance in the hopping conductivity.[22,23] Imagine then that there is an energy gap at the Fermi level of our insulator, and that the magnetic field destroys it. This would explain the experimental observations, in the first place, the rise of δ with decreasing temperature. This explanation justifies approaching the problem from the standpoint of superconductivity.

The idea that pairs of carriers can be localized at the impurity centers, and that this localization can result in a gap in the spectrum of one-particle excitations was discussed long ago by Anderson,[24] without referring to the superconductivity. The Cooper interaction can compensate for the Hubbard energy and promote the localization.

However, the carriers of a Cooper pair can be localized at different centers. The Coulomb interaction leads to a soft Coulomb gap at the Fermi level in the insulators[25] and to a dip in the metals.[26] The gap in the insulators comes from the redistribution of the carriers over the centers, i.e., it has a classical origin. It became clear recently that the dip at the Fermi level in metals appears not only in the quantum limit, but also in the classical limit.[27] This shows the root cause of the resemblance between these effects.

The Cooper interaction leads to the hard gap in metals. The redistribution of the carriers over the impurity centers of an insulator can also produce a hard gap (see the polaron effects in Ref. 25). The critical field in the superconductivity which destroys the S gap completely is

$$H_{c2} \approx \Phi_0 / 2\pi\xi_{sc}^2, \tag{3}$$

where the coherence length ξ_{sc} can be treated as the pair dimension or as the interaction distance. The lower limit 10 T for the field, which still does not saturate NMr will then give the upper limit of 50 Å for ξ_{sc}, i.e., for two electrons which form a pair and which localize at different centers. Note that judging from this estimate, we deal with a 3D, not 2D, material.

Next argument comes from the temperature dependence $R(T)$ in zero field.[5] Near the M–I-transition on the insulating side, the resistance is simply activated, i.e., it follows Eq. (1) at liquid helium temperatures.

Another sort of argument comes from the formal similarity of what was described above to the behavior of the S-response of inhomogeneous two-phase alloys:[8,11] NMr rising against the background of the exponential increase of R, competition between different components of the S-response displayed by superposition of negative and positive magnetoresistances which have different field dependences. Since all these features in two-phase alloys result from the superconducting gap Δ, it seems natural to expect the existence of a similar gap in this material. The main difference from the experiments described in Refs. 8 and 11 is that the S-transition temperature T_c is not well defined and not fixed in am-In_2O_x. But the principal attributes of the superconductivity, such as the

Cooper interaction and the gap in the density of states, can exist without a sharp S-transition.

In conclusion, NMr appears in am-In_2O_x in the same temperature range as the S-transition, it persistently increases with decreasing temperature, and it does not saturate in a 10-T field. All these observations can be explained assuming that the Cooper interaction leads to a gap in the density of states in the insulating state of the am-In_2O_x, and that the total decay of this gap occurs in magnetic fields larger than 10 T.

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