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SUPERCONDUCTIVITY AND NEGATIVE MAGNETORESISTANCE IN AMORPHOUS In_2O_x FILMS

V.F.Gantmakher[1)], *M.V.Golubkov*

Institute of Solid State Physics RAS

142432 Chernogolovka Moscow Region, Russia

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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 suppose 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.

Amorphous indium oxide (am-In_2O_x) can be transformed by a comparatively soft influence from an insulating (I-) to a metallic (M-) state. As this material exhibits a superconducting (S-) state too, the problem of ($S-I$)-transition arises in addition. This determines the stable interest to am-In_2O_x [1-5].

As a matter of fact, we have 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 supposed to be an annoying factor which masks the evolution of properties near the transition. We intend here to use the properties of high-resistance macroscopically inhomogeneous materials as a guide in attemps to understand the nature of the transition.

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

$$R(T) \propto \exp(\Delta/T). \qquad (1)$$

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 lower case for the last letter of the abbreviation to avoid confounding with nuclear magnetic resonance). Apparently, such type of the S-response takes place rather often in high-resistance inhomogeneous materials [11]. In particular, it was seen at granular films of In_2O_x [12] and Al_2O_x [13].

One may wonder what happens with this anomalous S-response (exponential increase of the resistance while decreasing of the temperature in zero magnetic field and the gigantic NMr) when the typical sizes of the structure decline. By decreasing the grains dimensions, we can achieve, at least, mentally, crossover from

[1)]e-mail: gantm@issp.ac.ru

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 experimental investigation of the possibly localized Cooper pairs was performed by Paalanen et. al. just on the am-In_2O_x films [3]. From analysis of the $R(H)$ curves at temperatures below the S-transition, they came to the conclusion that localized pairs do exist. Below we add addition arguments in favour of this conclusion.

From what was said above, the motivation of this investigation follows. Assuming that the am-In_2O_x films are quasihomogeneous, we analyzed the evolution of transport properties of a film along the row of its successive states spanning the $(M - I)$-transition. The special attention was paid to trace relations between the S-transition and NMr. In essence, we repeated the experiments described in [4] with two distinctions:

a) we used thinner films than in [4], approximately 200 Å; this allowed to change their state reversibly;

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

High-resistance films were prepared in the Racah Institute of Physics in Jerusalem by electron-gun evaporating high-purity In_2O_3 onto glass substrates in a vacuum chamber with oxygen atmosphere [1]. They had thickness 200-250 Å. Their resistance in the initial state reached 10 MOhm at liquid helium temperatures. After aging in air at room temperature during several months, their resistance reduced by two orders of magnitude but their low-temperature conductivity remained to be activated. 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 an initial one.

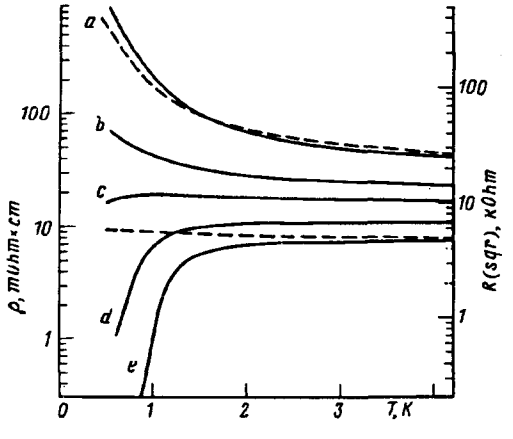

Fig.1

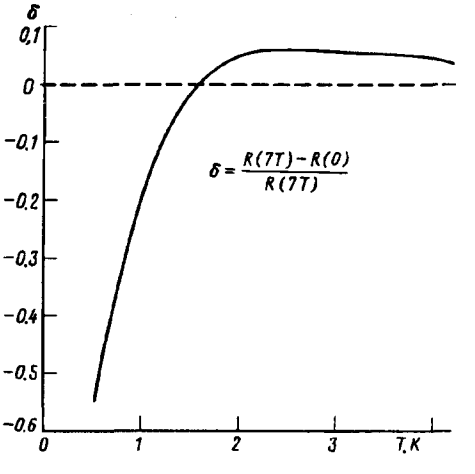

Fig.2

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 – in 7 T

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

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 some rather restricted interval but by softer treatment than in [14].

Kept in an inert atmosphere or vacuum at 90° C - 100° C during 3-4 hours, the sample could be transformed from state a to state e (Fig.1) with resistivity per square at 4.2 K reduced from 25 kOhm to 4 kOhm. Kept in the presence of oxygen (for instance, in air) at 20°C - 40°C it could be brought back to a state near to state a. X-ray examination 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 emergence of the superconductivity is not conditioned by appearance of indium clusters. The same conclusion was made earlier in [4].

It seems that equilibrium values $x < 3$ of oxygen concentration exist for the am-In_2O_x films and 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 $a - e$ on Fig.1 illustrate changes in the low-temperature transport properties of the film which accompany its transformation. Such set of curves is usually interpreted as the $(S - I)$-transition [15]. Apart of zero-field $R(T)$ curves, those in the field $H = 7\,\mathrm{T}$ for the two extreme states are plotted on the Fig.1 by dashed lines. Note that NMr in the state a and the superconductivity in the state e emerge in the same temperature range – near 1.5 K.

The logarithmic scale on 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 the Fig.2. This figure demonstrates the second important observation, namely, rapidly rising relative magnitude of the NMr with reducing T, without any tendency to saturation.

In Fig.3, we display the field dependence of $R(H)$ at $T = 0.5\,\mathrm{K}$ 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 more usual $R(0)$. Fig.3 shows next two important features of the NMr. Along with the sample becoming metallic, the NMr domain is pushed toward the higher magnetic fields being swallowed up by the standard effect of demolishing of the S-state by low and moderate fields. Note that the "standard effect", i.e. the positive derivative dR/dH, does exist even at those states of the sample where there is no signs of the usual S-response (states a and b). The final observation we want to emphasize is that the relative magnitude of the NMr went on rising in our largest field 8 T. It can be seen from curves in [3] that NMr does not saturate in 10 T as well.

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

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 of the order of 1 T. In two dimensions, the character of NMr in films with long-range random potential is slightly different [21] but the typical field turns to be even lower than H_i ; the estimate similar to (2) contains the typical long period of the random potential $L \gg r$.

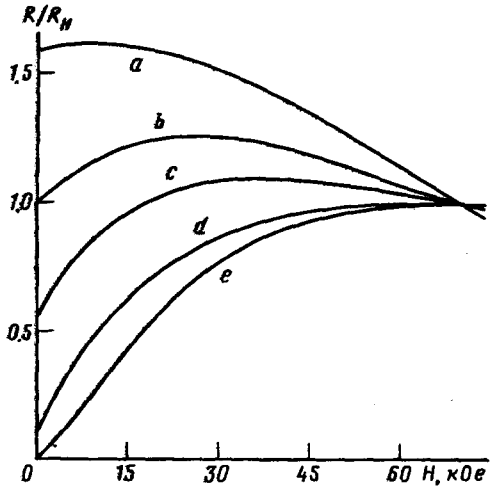

Fig.3. Field dependence $R(H)$ normalized to $R(7\,\mathrm{T})$ in different states of the sample. $T = 0.5\,\mathrm{K}$

So, the attempts to explain the NMr in high magnetic fields remaining in the frame of the ideas of the hopping and tunnel conductivity are not very successful. Spin degree of freedom leads to 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 reducing the temperature. This justifies the approach to the problem from the side of superconductivity.

The idea that pairs of carriers can be localized on the impurity centers and that this localization can result in the 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 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 re-distribution of the carriers over the centers, i.e. has the classical origin. It became clear recently that the dip at the fermi-level in metals appears not only in the quantum limit but in the classical limit as well [27]. This brings root cause of the resemblance between these effects.

The Cooper interaction leads to the hard gap in metals. And the re-distribution of the carriers over the impurity centers of an insulator can also produce a hard gap (see polaron effects in [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 distance of the interaction. Then the lower limit 10T for the field which still does not saturate NMr gives the upper limit 50 Å for ξ_{sc}, i.e. for two localized at different centers electrons forming a pair. Note that judjing from this estimate we deal with $3D$, not with $2D$, 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 on 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 dependence. As all these features in two-phase alloys result from the superconducting gap Δ, it seems natural to expect existence of a similar gap in this material. The main difference from the experiments described in [8,11] is that the S-transition temperature T_c is not well-defined and fixed in am-In_2O_x. But principal attributes of the superconductivity, such as Cooper interaction and the gap in the density of states, can well exist without a sharp S-transition.

In conclusion, NMr appears in am-In_2O_x at the same temperature range as the S-transition, persistently increases with reducing the temperature and does not saturate in the field 10T. 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 full decay of this gap occurs in magnetic fields larger than 10T.

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