Resistance anomalies and negative magnetoresistance in a regular 3D lattice of superconducting nanostructures

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Regular 3D lattices of superconducting nanostructures of the variable-thickness-bridge type have been prepared by using indium to fill voids in a crystallographically ordered insulating matrix. The matrix was modified by molecular lamination of TiO_2 on its interior surface. The $R(T, H)$ dependence was measured. The $R(T)$ curve exhibits two successive resistance anomalies as the temperature is lowered. These anomalies are associated with a negative behavior of the magnetoresistance.

The transport properties of low-temperature superconductors of reduced dimensionality are subject to the simultaneous effects of the superconducting order, quantum corrections to the conductivity, and thermal fluctuations.[1] The formation of superconducting nanostructures with dimensions comparable to the coherence length and of ensembles of such structures leads to further complications of the behavior of these systems because of interfacial and collective effects. Among the latter are resistance anomalies[2,3] and oscillations of the magnetoresistance.[4] Experimental studies of individual nanostructures have shown that a condition for the occurrence of a spike in the resistance at a temperature slightly above the superconducting transition temperature T_c is the development of nonequilibrium processes at S–N junctions, which result from a modulation of T_c along the current flow direction. A condition for the observation of this anomaly is that the contacts lie in a nonequilibrium region. By building up an ensemble of such nanostructures one can, on the one hand, increase the net strength of nonequilibrium effects and, on the other, obtain new effects due to interactions of the nanostructures in the ensemble.

Large regular ensembles of superconducting nanostructures (up to 10^{12} in a sample) can be produced by inserting a superconductor into the voids of porous crystalline insulating matrices.[5,6] The result is a composite material, produced by forcing molten metal into a porous insulating matrix consisting of identical silicate balls packed in an hcp lattice (this is the structure of precious opal). As a result, the metal forms a 3D network which, by virtue of the crystallographically ordered structure of the opal, can be represented as a 3D lattice of grains which are coupled with each other.[7] Any current path in this material is a zigzag-shaped channel in the form of an alternation of large and small interpenetrating grains. The size of the large grains, d_1, corresponds to the diameter of the sphere inscribed in a void of the matrix; the size of the small grains is d_2. The smallest intersection dimension is d_3 (a straightened channel is shown in Fig. 1a). These dimensions are related by a strict geometric

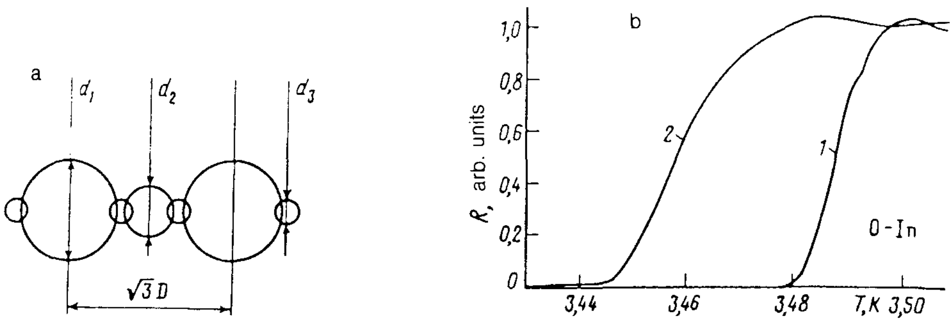

FIG. 1. a—Schematic diagram of a current channel in O–In; b—shape of the resistive transition O–In on the basis of (1) the original matrix and (2) the modified matrix.

relation to the diameter D of the silicate balls forming the opal (D is in the interval 200–400 nm; the scatter is no more than 5% in one sample). As the individual nanostructure in such an ensemble we can adopt an element $-d_1$–d_3–d_2–d_3- with a $d_1:d_3:d_2:d_3=2.7:1:1.5:1:2.7$ modulation of the transverse dimension of the current channel. The material produced by filling the voids in the opal with indium (O–In) has a drawn-out transition because of the size dependence $T_c(d)$ of the transition of indium, consisting of three stages, with T_{ci}'s corresponding to the geometric dimensions d_i of the components of the nanostructure.[8]

The porosity of the matrix—the diameter of the pores and the extent to which they are isolated from each other—can be altered by depositing an additional layer of insulator on the interior surface of the matrix. In the case of a uniform deposition of a layer of insulator on the interior surface of the matrix, the ratio $d_3:d_{1,2}$ will obviously decrease. We have made use of this circumstance to control the properties of an ensemble of superconducting nanostructures, by weakening the intergrain coupling in a matrix modified by the deposition of several layers of TiO_2 on the interior surface of the opal by the method of molecular lamination.[9] The method used here corresponds best to the problem at hand, of achieving a uniform decrease in the void size while maintaining an identical geometry of the voids, but the result of the use of this method for overgrowing inner voids in a narrow-pore material requires a special study by electron microscopy.

Rectangular samples with dimensions of $3\times1\times0.5$ mm, in which the cross section was reduced to half its value in the central region, were prepared for the measurements. Four Ag contacts were grown on the samples by an electrochemical technique, in the form of bands intersecting the broad face. The samples were oriented perpendicular to the axis of a solenoid which generated a field up to 200 Oe. The ac resistance was measured at a frequency of 130 Hz under current-source conditions with subsequent lock-in detection. The resistance of the samples in the normal state near the transition was a few times 10^{-4} Ω. There was no shielding against the geomagnetic field.

To determine the role played by the matrix (changes in the relative dimensions of

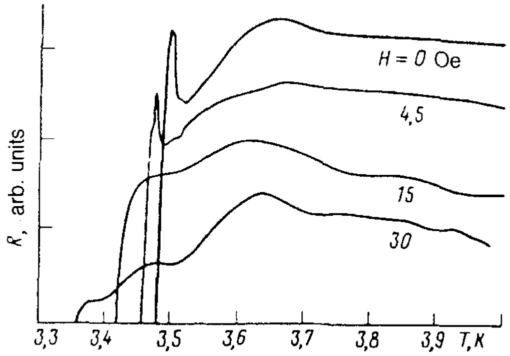

FIG. 2. Change in $R(T)$ near the transition due to the magnetic field (the curves are displaced with respect to each other along the ordinate axis. The curve labels are the magnetic fields in oersteds.

the grains and the bridges and, possibly, in the nature of the scattering by the surface as the result of the deposition of the TiO_2 layer) in shaping the $R(T)$ dependence, we compared the shape of the transitions of samples (Fig. 1b) on the basis of the original matrix (curve 1) and an overgrown matrix (curve 2). It turns out that each sample goes through an anomalous increase in resistance just before the transition to the superconducting state. The modification of the matrix causes (curve 2) an increase in the amplitude of the resistance anomaly just before the sharp decay in the resistance (from 4% to 5.5%), the occurrence of yet another anomaly (Fig. 2), an increase in the width of the transition, and a decrease in T_c. The latter fact runs contrary to the tendency for T_c of In to increase with decreasing size. The decrease in T_c of O–In is apparently being caused by not only a size dependence but also a weakening of the Josephson coupling of the grains in the lattice[10] and an increase in the role of thermal fluctuations with a decrease in grain size. Evidence for changes in the size of the In grains comes from the decrease in the shift of T_{cd3} in a field $H=30$ Oe, from 0.22 K to 0.175 K (as determined from the shift of the dR/dT peak). This feature corresponds to a decrease in the dimension d_1 by a factor of 1.26 (because of the linear T_c–d relationship[8]). This behavior corresponds to the deposition of a TiO_2 layer with a thickness of about 10 nm.

Figure 2 shows the change in $R(T)$ upon the imposition of an external magnetic field. In the temperature interval 3.2–4.2 K, $R(T, H=0)$ has two anomalies, roughly equal in amplitude: a spike in the resistance with a half-width of 0.02 K [this is the low-temperature anomaly (LTA)] and a broad maximum at high temperatures (HTA). There is a slight increase in the resistance beginning at 4.2 K. When an external magnetic field is imposed, the transition shifts down the temperature scale, the LTA decreases in amplitude, and it eventually disappears at $H > 10$ Oe. The HTA, in contrast, undergoes essentially no change in amplitude or position in the external field. As the field is increased, several other irregularities appear on the $R(T)$ curve; these irregularities are indistinguishable in the absence of a field.

At measurement currents from 3 to 30 mA, we observe no changes in the $R(T)$ curves. When the measurement current is increased by yet another two orders of magnitude, however, both of these anomalies disappear completely, although there is essentially no change in $T_c(R=0)$.

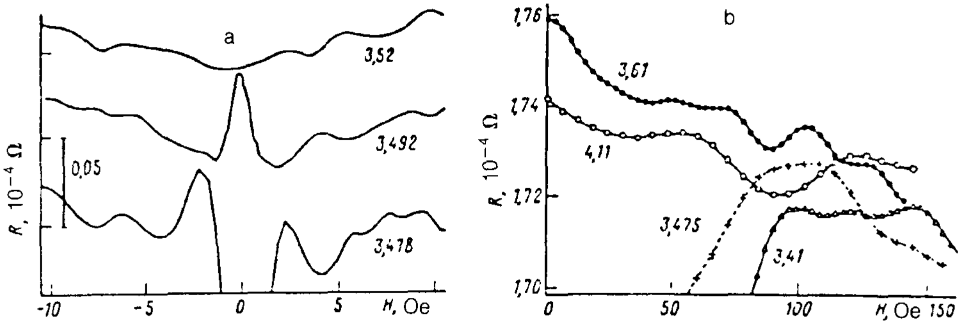

FIG. 3. a—Change in the magnetoresistance in the low-temperature region (the curves are shifted along the ordinate axis); b—high-temperature resistive anomalies. The curve labels are the temperatures.

The suppression of the LTA in a weak field should be seen as a descending region of the resistance in the *R–H* coordinates near a zero field (Fig. 3a; the central curve was recorded at the temperature corresponding to the LTA). This anomaly persists as a spike in the resistance at lower temperatures, at which the resistance in a zero field has already decreased (the lower curve in Fig. 3a).

The LTA which we observe is similar to the resistive anomalies which have been explained on the basis of a discrepancy which arises between the numbers of quasiparticles and Cooper pairs at an S-N boundary upon a superconducting transition of reduced-dimensionality entities which contain two components whose T_c's differ by at least a few percent.[2,3] A characteristic feature of these anomalies is that they are suppressed in very weak fields, on the order of a few oersteds. There is also an interpretation of the anomalies at the boundary of the transition of inhomogeneous superconductors as an artifact resulting from a redistribution of the current flowing through the sample due to an anisotropy of T_c when the current contacts and the potential contacts do not lie on a common line.[11] Without completely ruling out such a contribution, which would be possible because of imperfections of the contacts, we should point out that this effect would probably be negligible in the case of the linear arrangement of the electrodes in Refs. 2 and 3 and in our own experiments. Furthermore, an anisotropy would be incapable of explaining the entire set of properties accompanying the anomaly. The O–In system has three characteristic T_{ci}'s, corresponding to transitions in the three constituents of its nanostructures:[8] As the temperature is lowered, there is first a transition of the d_3 constrictions to a superconducting state; then comes a transition of the d_3–d_2–d_3 regions; and the transition of the overall system is finally completed by the transition of the d_1 grains. As the temperature is lowered, S-N boundaries of two types correspondingly arise. Analogously, the $R(T)$ anomalies of O–In, which are highly subject to the effect of the external magnetic field [the LTA and the irregularities on the $R(T)$ curves], can also be explained as manifestations of a deviation from equilibrium at the set of S–N boundaries in the interior of the material. The presence of a clearly expressed LTA, with an amplitude precisely the same as in the case of the anomalies of the individual nanostructures studied in Refs. 2–4, is evidence that the elements of the nanostructures in the ensemble have identical dimensions. The appearance of several irregularities on the $R(T, H)$ curve is due to the polycrystalline structure of the material which was prepared;[7] this polycrystalline structure means a variety of orientations of the crystallites with respect to the magnetic field.

A distinctive feature of this material is that at temperatures corresponding to the anomaly region an equilibrium distribution cannot be established within the components of different sizes; as a result, there may be a summation of the effect over the entire sample. The typical size of the S-N region should be comparable to the grain size in this case. The distance over which an equilibrium distribution of quasiparticles and Cooper pairs is established should be greater than the grain size, while the coherence length $\xi = \sqrt{\xi_0 d_3}$ should not exceed it ($\xi_0 = 440$ nm is the coherence length in bulk In). In the opposite case, either an equilibrium normal state or an equilibrium superconducting state is established in the grains after the transition of the narrower parts of the nanostructure. In either case, no anomaly could be manifested in this mechanism. This circumstance can explain why there is no anomaly in the resistance in samples with a modest modulation of the channel cross section,[8] in which the dimension d_3 is not small enough to isolate the nanostructures in the ensemble (i.e., $\xi < d_1$). As a result, there are only slight changes in the properties of the superconductor along a channel. The current in O–In at $T_{cd1} < T < T_{cd3}$ is thus carried by both quasiparticles and Cooper pairs. This point is of importance for determining the nature of the penetration of magnetic flux into the lattice of coupled grains.

The HTA has no analog in other superconducting systems. Its low-temperature decay is due to a fluctuational pairing of quasiparticles, as is demonstrated by the positive course of the magnetoresistance in this temperature region (the upper curve in Fig. 3a). The increase in the resistance in the high-temperature part of the HTA with decreasing temperature may be due to either a localization of carriers in narrow channels (which are approximately 1D channels in terms of the nature of the conductivity) connecting grains or an analogous (in terms of the nature of the LTA) nonequilibrium process at S-N boundaries between superconducting bridges and normal grains. The material O–In apparently does not satisfy the conditions for carrier localization, since the resistance of the bridges is on the order of 1 Ω —much smaller than the quantum of resistance. The assumption that the HTA is associated with the superconductivity has a firmer basis since (*i*) the differential resistance of the sample at low currents at 3.7 K is slightly lower than the ohmic resistance, (*ii*) the position of the HTA corresponds to the size-governed T_{cd3} (for particles 10 nm in size we would have $T_c \simeq 3.9$ K), and (*iii*) the magnetic field required to shift T_{cd3} is considerably larger than the corresponding fields of the grains.[8] This circumstance could explain why there is no shift of the HTA in fields up to 30 Oe (Fig. 2). The region in which the HTA exists includes a negative behavior of the magnetoresistance over the entire temperature range studied (Fig. 3b): As the temperature is lowered, the slope of the $R(H)$ curve increases, and it reaches a maximum near the maximum of the LTA along the temperature scale. Furthermore, at $T < T_c$ ($H = 0$) a region of a negative magnetoresistance is also observed after the suppression of the superconductivity in O–In by the field.

The oscillations in the magnetoresistance observed on the $R(H)$ curves have certain periods and tendencies in their variation with the temperature. In the present experiments, however, these oscillations were smoothed out considerably in the course of the analysis of the results in order to demonstrate the larger-scale changes. We intend to devote a future study to analyzing these oscillations.

In conclusion we would like to stress that an increase in the depth of the geometric modulation of a current channel leads to the formation of a more clearly defined potential well and thus to a conversion of a nanostructure material into the category of an ensemble of interacting nanostructures.

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