Phase transition of granular superconducting films

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The phase transition from the normal state to the superconducting state of acicular granular films of niobium nitride has been studied experimentally. The transition has also been analyzed on the basis of percolation theory with fluctuations.

Granular structures are extremely common among superconducting materials. A microstructure of this sort prevails in many of the known superconductors: in *situ* volume composite superconductors, thin films of superconducting metals and compounds, and the ceramic metal-oxide high-temperature superconductors which were discovered in 1986. A convenient model material for studying granular systems is a single-phase film of niobium nitride synthesized by reactive cathode sputtering. Such films have fairly high critical parameter values and take the form of acicular grains separated by barriers.[1] The resistivity ρ of such films can be varied over a rather wide

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range by varying the deposition parameters. The values of ρ of the individual acicular grains are lower than the resistivity of the film as a whole by a factor of at least one or two orders of magnitude, so the system can be treated as a typical granular system.[2] A related feature is the semiconducting nature of the temperature dependence of the resistance of most films (it has been found that there is a relationship between the increase in the surface resistivity of the film at 300 K, $R_{\square 300} = \rho/d$, and the increase in $R_{\square 20}/R_{\square 300}$, where ρ is the resistivity, and d is the thickness of the film).

The weakness of the links between the grains must be taken into consideration in a description of the transition of granular structures to a superconducting state.[3] It should be kept in mind that there is a scatter in the properties of the barriers between grains in a film; in particular, there are a scatter in their thickness and thus a scatter in the resistance. In this case the transition of a granular film to a superconducting state does not end at the transition temperature of the grain material, T_{c0}, since a phase coherence among the individual grains is reached at various temperatures $T < T_{c0}$. These temperatures can be found by equating the energy of the links between grains, E_{ij}, to the thermal noise kT. At $T < T_{c0}$, the superconducting grains begin to combine into superconducting clusters, and only at T_c—the temperature at which an infinite cluster forms, which can be found by percolation theory[3]—does the electrical resistance of the film disappear completely. The change which occurs in the structure of an infinite cluster at $T < T_c$ has not been studied in previous experiments.

In this letter we report a study of phase transitions induced by the temperature

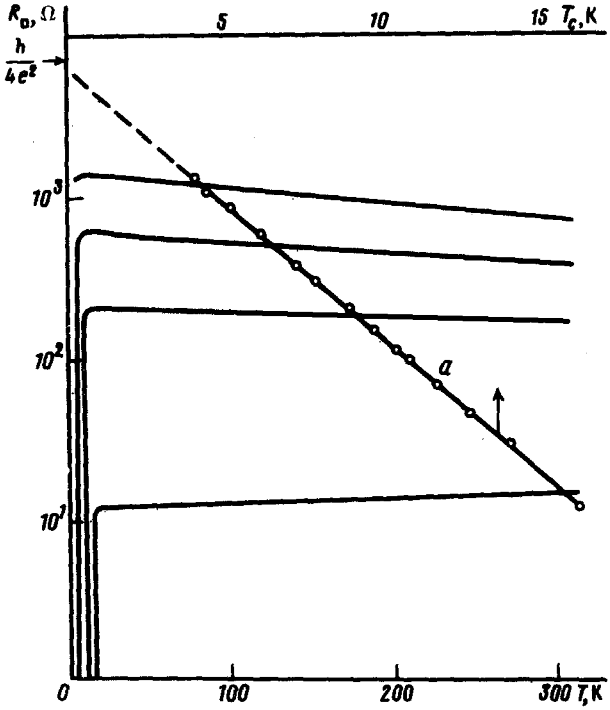

FIG. 1. $R_\square(T)$ and $T_c(R_{\square m})$ of granular niobium nitride films.

and the transport current in thin films of niobium nitride as a function of the resistivity of the films. Figure 1 shows $R_\square(T)$ over the range 4.2–300 K along with the values of $T_c(R_{\square m})$ of granular films of niobium nitride ($R_{\square m}$ is the maximum surface resistivity of the film). We see that T_c is an exponential function of $R_\square$ over a wide range of the latter, and an extrapolation of this function to $T_c = 0$ yields a value on the order of $R_\square = h/4e^2 = 6455\ \Omega$.

This limiting value of $R_\square$, at which a superconductivity is still possible, can be found from the resistive model of a Josephson junction represented as an RLC circuit.[4] Phase coherence in such a junction is possible if the uncertainty in the difference between the phases of the two banks does not exceed 2π. The phase difference can be found from the expression $\gamma = \gamma_0 + (2e/\hbar)Ut$, where U is the voltage across the junction, and t is the time. Assuming $U = 2eN/C$ (C is the capacitance, and $2eN$ is the charge at the junction), we have $\Delta\gamma \sim (4e^2/\hbar C)\Delta N t_0$ when we make the transition to uncertainties. In a parallel RLC circuit we would have $t_0 \sim RC$, and a phase coherence between the banks would be reached only at $R < h/4e^2$ (with $\Delta N = 1$). A value of $R_\square$ close to that found here has been observed in previous experiments on granular metal films; specifically, it has been observed as the limiting value at which a superconductivity is still possible.[5]

It should be noted that as the resistance of the film in its normal state increases, there is an increase in the width of the superconducting transition (Fig. 1). There are two possible reasons here: an increase in the contribution of fluctuations to the conductivity and a percolation nature of the transition. A circumstance which should be taken into account here is that at $T > 20$ K the resistance $R(T)$ of films having a wide transition is of a semiconducting nature and can be approximated extremely accurately by the expression $R = R_0 \exp(T_0/T)^{1/3}$, which is typical of a 2D hopping conductivity (R_0 and T_0 are constants). Making use of this fact, we see that a calculation of 2D superconducting fluctuations in accordance with Ref. 6 yields a good description of the region of the superconducting transition found experimentally, nearly down to T_c,

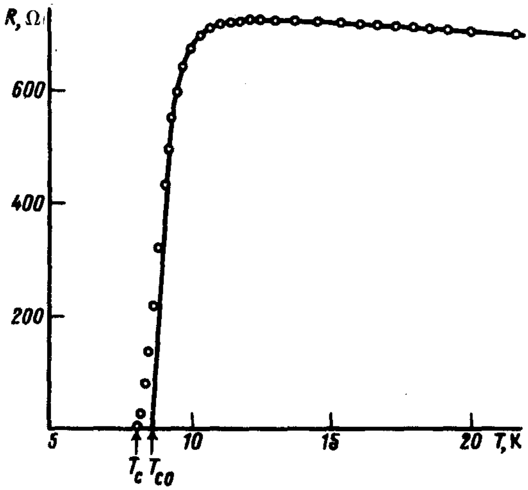

FIG. 2. Theoretical curve and experimental points of the $R(T)$ dependence for one of the niobium nitride films.

and we can estimate T_{c0}, the temperature of the superconducting transition of the grain material (Fig. 2). The resistive transition terminates at a temperature T_c which is only 0.2–0.5 K below T_{c0}, in good agreement with an estimate found by applying percolation theory to this system.

In an effort to learn about the phase transition region at $T < T_c$ we studied the field and temperature dependence of the critical currents of the films. We know[7] that when there is regularity in the structure of granular superconductors, one can observe a periodicity in plots of R, T_c, and I_c versus the magnetic field, with a period $\Delta H \approx \Phi_0/S$, where S is an area element of the periodic structure in the plane perpendicular to the field ($S \approx L^2$, where L is the difference between critical links in the film). In fact, oscillatory features with a period ranging from 250 to 800 Oe have been observed previously[8] on the $I_c(H)$ dependence for niobium nitride films. The oscillation period was found to increase with increasing degree of granularity (the field was directed perpendicular to the surface of the film). An estimate of the value of $L = (\Phi_0/\Delta H)^{1/2}$ at 4.2 K yields 100–300 nm for the films studied; this figure is on the order of several times the size of a grain. In other words, at $T \ll T_c$ the films is a branched current-conducting network with an average cell size on the order of ten grains.

In order to learn about the structure of the infinite cluster at $T < T_c$ we studied the dependence $I_c(H)$ at various temperatures. All of the curves exhibit the oscillatory features described above. The period of the oscillations remains constant over a certain temperature range and decreases rapidly toward T_c. Figure 3 shows the behavior $I_c(T)$ (line a) and $L(T)$ (line b) calculated from the experimental values of $\Delta H(T)$ for one of the samples. We see that there is a characteristic temperature $T_{c1} < T_c$ at which the rapid decrease in the cell size L and the nonlinear increase in $I_c(T)$ terminate simultaneously.

In summary, the phase transition from the superconducting state to the normal state of a granular film occurs over an extremely wide temperature range, in which

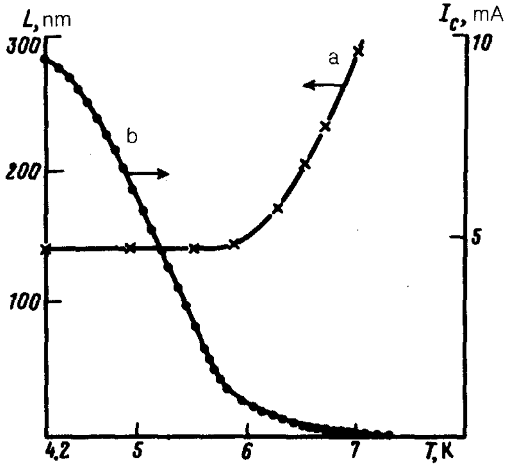

FIG. 3. a—$I_c(T)$; b—$L(T)$, for one of the niobium nitride films.

there are three characteristic regions. At $T > T_{c0}$, superconducting fluctuations play a governing role, while at $T = T_{c0}$ the individual grains go superconducting. In the interval $T_c < T < T_{c0}$ the superconducting clusters grow from weakly linked individual grains to the point that they form an infinite cluster, and a zero-resistance state is established at T_c. This is not the end of the phase transition, however: The grains become attached to the infinite cluster as the temperature is lowered, and at T_{c1} they form a branched current-conducting network with a typical cell size on the order of several grains. The phase transition terminates at this point, since a further lowering of the temperature simply changes the critical current of the weak links.

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