work was supported by the U. S. Energy Research and Development Administration through Contract No. E(11-1)-3151.

---

[1] Y. Horiguchi, R. R. Hudgins, and P. L. Silveston, Can. J. Chem. Eng. 49, 76 (1971).

[2] W. F. Giauque and H. L. Johnston, J. Am. Chem. Soc. 51, 2300 (1929).

[3] J. P. McTague and M. Nielsen, Phys. Rev. Lett. 37, 596 (1976).

[4] R. L. Elgin and D. L. Goodstein, Phys. Rev. A 9, 2657 (1974).

[5] R. A. Verhelst, R. W. Kline, A. M. de Graaf, and H. O. Hooper, Phys. Rev. B 11, 4427 (1975).

[6] The glasses of Ref. 5 possessed θ values which varied from sample to sample, but did not depend in any straightforward way on the magnetic ion concentration.

[7] See, for example, J. G. Dash, *Films on Solid Surfaces* (Academic, New York, 1975).

[8] Capillary condensation will also occur at high coverages in a microporous adsorbent such as Vycor. It should be possible to assess the effect of this on the susceptibility behavior by performing measurements on samples of porous glass which are commercially available in which the mean pore size can be as large as 3000 Å and in which capillarity effects are therefore much reduced.

Zero Dimensionality and Josephson Coupling in Granular Niobium Nitride

S. Wolf and W. H. Lowrey
Naval Research Laboratory, Washington, D. C. 20375

(Received 21 April 1977)

Ultrathin granular niobium nitride films have been found to behave like an array of zero-dimensional superconducting grains coupled through grain boundaries by a Josephson-type interaction. The temperature dependence of the current at which a voltage first appears fits the Josephson-junction–like critical-current predictions remarkably well. The films exhibit a paraconductivity which extends to 24 K, more than twice the critical temperature, T_{cG}, of the grains and varying as $(T-T_{cG})^{-2}$.

In recent years, much attention has focused on the properties of granular films.[1-9] There has been speculation that some granular superconducting films can be characterized by two regimes of superconducting behavior. The first regime reflects the properties of zero-dimensional grains of superconducting material. The second type of behavior characterizes the coupling of these grains by a Josephson-type interaction. Previous studies have suggested the validity of this model[1-7] but none have unambiguously isolated these two characteristics. This Letter reports measurements of the superconducting properties of ultrathin niobium nitride films which have for the first time illustrated these distinct regimes with a remarkable clarity. Either current or temperature can switch the films from one regime to the other. Furthermore, the zero-dimensional character of the grains was unambiguously demonstrated by a paraconductivity observed in one film to temperatures as high as 30 K or more than twice the critical temperature, T_{cG}, of the grains themselves. This is the first time that paraconductivity, clearly characteristic of zero dimensionality, was observed over so large a temperature range.

Niobium nitride films, 170–1500 Å thick, were reactively sputtered onto heated substrates.[8] Films thinner than 170 Å were produced by anodic thinning of thicker films. A standard four-lead technique was used to measure the resistance of the films as a function of temperature, current, and magnetic field. The resistive transitions of films 240–1500 Å thick were quite sharp. The change from 99% of normal resistance to "zero" (undetectable) resistance generally occurred in less than 0.5 K. The 1500-Å film has a T_c (midpoint of transition) of 15.8 K. The T_c's of the thinner films decreased exponentially with inverse thickness reaching 13 K at 240 Å. This behavior is quite similar to results previously reported on thin Nb films.[10] The thicker NbN (>240 Å) films also exhibited typical metallic conduction above the transition temperature with a resistance that increased as the temperature was raised towards room temperature. However, the superconducting properties of the films changed markedly as the film thickness was decreased below about 120 Å. Since the expected grain size for these films is 100 Å,[8] we attribute this change in behavior to the production of a

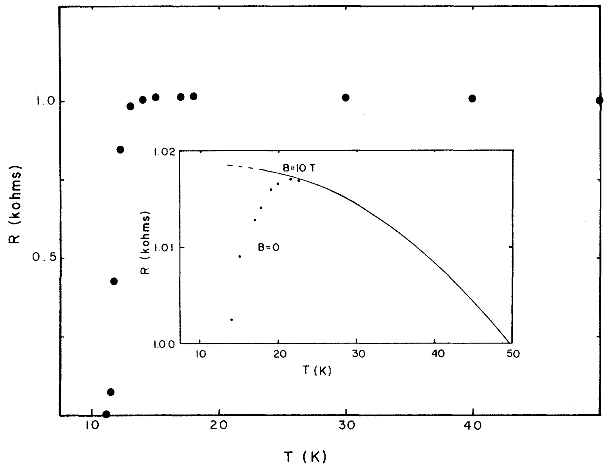

FIG. 1. The resistance vs temperature for a nominally 44-Å-thick NbN film. The inset is a blowup of the upper portion of the curve. Note that the resistance below 11 K is not zero but is less than 1 Ω.

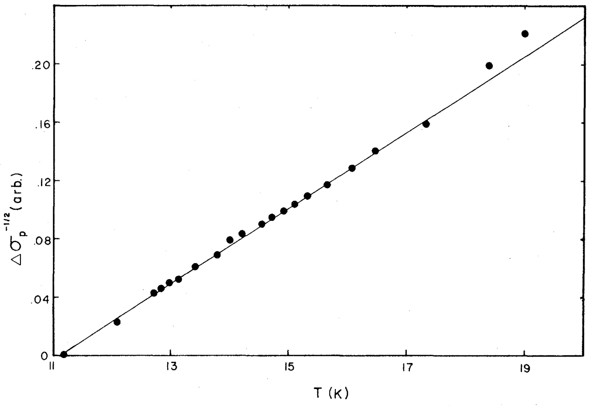

FIG. 2. The inverse square root of the excess conductivity, $\Delta\sigma_p^{-1/2}$, vs temperature for the 44-Å-thick NbN film. The solid curve is a straight line drawn through the points.

sample consisting of a single layer of grains.

A 170-Å as-sputtered film and others thinned by anodization to 100 Å or less had a resistance that increased very slightly as the temperature was lowered from room temperature (characteristic of some hopping conduction or semiconducting behavior which has been observed previously on granular NbN) until the onset of the superconducting transition. Temperature-induced superconducting-to-normal transitions of these ultrathin films (<100 Å) were characterized by a temperature at which only a very small fraction of the normal-state resistance (<0.1%) was recovered, $T_{c\mathrm{J}}$, followed by an interval where the resistance stayed relatively constant. This was in turn followed by a range of temperature over which the resistance rapidly increased (T_{cG}) and then gradually approached the normal-state value. The temperature difference between the onsets of these two regions, $T_{c\mathrm{J}}$ and T_{cG}, increased with decreasing film thickness, becoming several degrees for films less than 100 Å thick.

Figure 1 is a plot of the resistive transition of a 44-Å-thick film. The resistance of this film at room temperature was 996 Ω. Notice the slight (~ 2%) but obvious increase in resistance of the sample as the temperature is lowered (see inset in Fig. 2). Such an increase in resistance is characteristic of granular materials where the conduction between grains is governed by a nonmetallic conduction mechanism.[8] The resistance below 10 K is not quite zero but is less than 0.1 Ω. This resistance *does not vanish* until the temperature is reduced below $T_{c\mathrm{J}}$, which for this film was 6.5 K for 1 μA of measuring current.

The inset in Fig. 1 is a blowup of the upper end of this transition. The solid line, indicating the normal-state resistance, is a lower limit on R_n for temperatures below 24 K since it was obtained by measuring the resistance from 18 to 24 K in a magnetic field of 10 T and extrapolating for temperatures below 18 K. Since zero-temperature critical magnetic fields for such films can be as high as 30 T,[11] it is possible that fluctuation effects have not been completely suppressed. The transition of the grains to the superconducting state begins at about 24 K and is essentially complete at 11 K. We believe that the average grain size in these films is comparable to the zero-temperature coherence length,[11] and consequently the grains should behave as zero-dimensional superconductors. Kirtley, Imry, and Hansma[7] have extended the Aslamasov-Larkin-type fluctuation-induced conductivity theory to the zero-dimensional limit and have derived the following result for the excess conductivity per grain, $\Delta\sigma_p$:

$$\Delta\sigma_p = \frac{\pi e^2 \xi_0^{\,2}}{4\Omega\hbar}\left(\frac{T_{cG}}{T-T_{cG}}\right)^2, \tag{1}$$

where Ω is the volume of the particles and e is the electron charge. At temperatures well above T_c where $\Delta\sigma_p$ is much smaller than σ_N, the normal-state conductance, the effects of the interparticle resistance can be ignored and the result for a single grain can be simply extended to an array of grains and Eq. (1) becomes $\Delta\sigma_{\mathrm{tot}} = S\Delta\sigma_p$ where S is a geometrical constant and $\Delta\sigma_{\mathrm{tot}}$ is the difference between the normal-state conductivity and the measured zero-field conductivity.[7]

Thus Eq. (1) indicates that the excess conductivity observed for temperatures well above T_c should be proportional to $(T - T_{cG})^{-2}$. If the sample were truly zero dimensional, a plot of the inverse square root of the excess conductivity versus temperature should be linear. Figure 2 is such a plot for the data illustrated in Fig. 1 where use has been made of the 10-T resistance data for the normal state. Notice the remarkable linearity from 12 to 19 K. The data above 19 K are very sensitive to the normal-state value and would lie above the line drawn through the lower-temperature points. This is consistent with the fact that we have probably not completely suppressed the fluctuation effects with the application of a 10-T field.

The fluctuation region extends to at least twice the T_{cG} obtained by extrapolating the linear portion of the curve to the temperature axis. This transition width is exactly what is predicted for a zero-dimensional superconductor.[8] The fact that the conductivity is enhanced up to at least 24 K, which is 7 K higher than the highest reported critical temperature of niobium nitride, indicates that our data are not the result of sample inhomogeneity. Preliminary results on a nominal 30-Å-thick specimen anodized from a different starting sample showed paraconductivity above 30 K. [Similar results have recently been reported on $(SN)_x$ where the fluctuation conductivity was observed to ~700 mK, about twice the normal T_c of this material.[12]] Preliminary measurements have also been made with regard to the magnetic field dependence of the resistive transitions in fields up to 10 T. These measurements show a linear dependence of the inverse root of the excess conductivity with temperature as do the zero-field data. However, the slope increases with increasing field and the extrapolated T_{cG} drops linearly with field, decreasing to 10 K at 10 T. This linear decrease of T_{cG} with field is consistent with the BCS expression for the critical field. The increase in slope is consistent with replacing $(T - T_c)/T_c$ by $[T - T_c(H)]/T_c(H)$ in Eq. (1). This replacement should reflect the first-order effects of field on Eq. (1).

The critical-current data on this sample are also very interesting. At any temperature below 6.5 K (T_{cJ}) the current-voltage characteristic has two *distinct* regions separated by at least *three orders of magnitude* in current. For example, at 4.2 K as the current through the sample is increased the voltage becomes finite at a current of 69 μA which corresponds to a critical current density of 50 A/cm^2. The resistance at these current levels is less than 1 Ω, which is three orders of magnitude less than the normal-state resistance of the film. As the current is increased the resistance increases slightly in a discontinuous fashion (stepwise) but remains of the order of an ohm until a current of 240 mA is obtained. At this value of current density, 2×10^5 A/cm^2, the sample goes completely normal. Unfortunately the upper critical current cannot be fitted by any model since internal sample heating is a problem. At 240 mA and 1 Ω of resistance the sample is dissipating a substantial amount of power (>100 mW) which is effectively heating the grains above the background temperature. In fact the value of current at which the bulk of the resistance is recovered is a function of the rate at which the current is increased. On the other hand the lower transition is easily interpreted. In Fig. 3 the normalized critical current is displayed versus $(1 - T/T_{cJ})$ on a log-log plot. Temperature is indicated on the upper axis. The solid and dashed lines are theoretical predictions based on two different characteristic critical currents. The upper (solid) curve is the critical current of a Josephson junction (J-J) and the lower curve is the mean-field critical current for a

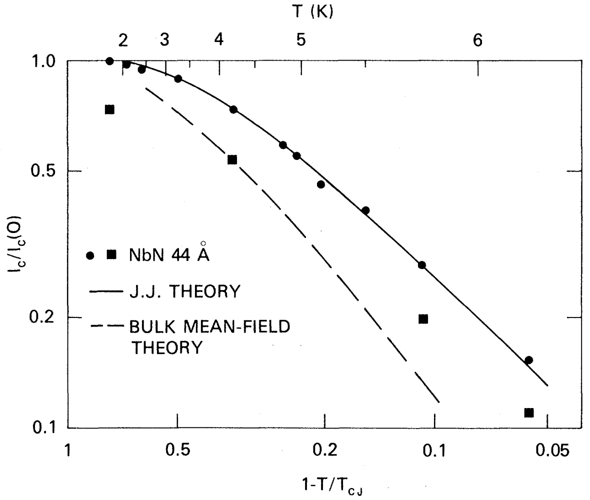

FIG. 3. Normalized critical current $I_c/I_c(0)$ is plotted as a function of $(1 - T/T_{cJ})$ on a log-log graph. The Josephson junction (J-J) theoretical variation is given by the solid curve, and the mean-field result by the dashed curve. The circles are the data normalized at 4.2 K to the J-J curve and the squares are four of the data points normalized, also at 4.2 K, to the mean-field curve.

wire.[6] The filled circles are the data normalized to the J-J model at 4.2 K, while the filled squares show four of the same points normalized to the mean-field expression at 4.2 K. The fit with the Josephson-like critical current is nearly perfect whereas the data cannot be satisfactorily fitted by the mean-field prediction.[13] This variation of critical current with temperature has been observed for small-particle arrays[6] and over a very limited temperature range for microbridges.[14] Data reported for extremely granular aluminum films[3] seem to be approaching the Josephson curve as it lies above the mean-field critical current but neither theory adequately represents the data.

It is therefore evident that our ultrathin NbN films are in fact a two-dimensional array of zero-dimensional superconducting grains which can couple by a Josephson interaction. Since these effects have not been clearly observed in films of granular Al-AL_2O_3, some comments will be made on distinctions between the NbN and Al systems. For one, the oxides of Nb produced at the grain boundaries of NbN by anodization are not all insulating. In fact, NbO, which is the oxide produced in direct contact with the NbN grains,[15] is a good metallic superconductor ($T_c = 1.4$ K).[16] Thus in addition to Josephson tunneling through an insulating barrier there might be proximity effects as well which would tend to decrease the Josephson T_{cJ}, giving rise to the "two-T_c" behavior seen in this system. The low-resistivity oxides would also account for the very low resistance observed when the temperature and current were increased beyond the onset of the transition. This low interparticle resistance might be responsible for the clarity with which we can separate the two regimes since heating in the low-critical-current regime would be much less severe than in a granular system with a high interparticle resistance. In addition, the grain size of very granular Al films is about 25 Å which is much smaller than the grain size in the NbN films and more than two orders of magnitude smaller than ξ_0. In fact the theory of Deutscher and coworkers[3] predicts that films such as ours should indeed exhibit two distinct transitions. However, a strict quantitative comparison with their theory could not be made since they treat explicitly only the zero- to three-dimensional case whereas our samples should go from zero-dimensional to two-dimensional. Thus it can be concluded that in the ultrathin NbN films the characteristics of the regions separating the grains as well as the grains themselves are such as to allow these independent mechanisms to be observed separately.

The authors are indebted to M. Nisenoff for stimulating our interest in NbN, to G. Deutscher for his assistance in helping us to understand granular materials, and to Joe Feldman for a critical reading of the manuscript. One of us (W.H.L.) acknowledges receipt of a National Research Council Resident Research Associateship.

---

[1] J. W. Ekin, Phys. Rev. 12, 2676 (1975).

[2] D. Abraham, S. Alterovitz, and R. Rosenbaum, IEEE Trans. Mag. 13, 866 (1977).

[3] G. Deutscher, Rev. Phys. Appl. 8, 127 (1973); G. Deutscher, Y. Imry, and L. Gunther, Phys. Rev. B 10, 4598 (1974).

[4] G. Deutscher, H. Fenichel, M. Gershenson, E. Grunbaum, and Z. Ovadyahu, J. Low Temp. Phys. 10, 231 (1973).

[5] W. L. McLean, T. Worthington, and M. Gershenson, Bull. Am. Phys. Soc. 22, 404 (1977).

[6] Paul K. Hansma and John R. Kirtley, J. Appl. Phys. 45, 4016 (1974).

[7] J. Kirtley, Y. Imry, and P. K. Hansma, J. Low Temp. Phys. 17, 247 (1974).

[8] Harris C. Jones, Appl. Phys. Lett. 27, 471 (1975); H. Jones, O. Fisher, and G. Biondi, Coll. Int. CNRS 242, 107 (1975).

[9] M. Strongin, J. M. Dickey, and J. E. Crow, Solid State Commun. 8, 1647 (1970).

[10] S. Wolf, J. Kennedy, and M. Nisenoff, J. Vac. Sci. Technol. 13, 145 (1976).

[11] Tsutomu Yamashita, Shogo Kitahara, Yutaka Onodera, Yukihiro Goto, and Tadao Aso, J. Appl. Phys. 43, 4749 (1972).

[12] R. I. Civiak, C. Elbaum, L. F. Nichols, H. I. Kao, and M. M. Labes, Phys. Rev. B 14, 5413 (1976).

[13] Preliminary results to be published indicated that these films do show Josephson effects below T_{cJ}. These ultrathin films operate as SQUIDs when coupled to rf SQUID electronics.

[14] Yeong-du Song and Gene I. Rochlin, Phys. Rev. Lett. 29, 416 (1972).

[15] K. E. Gray, Appl. Phys. Lett. 27, 462 (1975).

[16] J. K. Hulm, C. K. Jones, R. A. Hein, and J. W. Gibson, J. Low Temp. Phys. 7, 291 (1972).