Observation of a New Superconducting State at High Quasiparticle Injection

R. C. Dynes, V. Narayanamurti, and J. P. Garno
Bell Laboratories, Murray Hill, New Jersey 07974
(Received 11 April 1977)

The behavior of a superconducting Al film under conditions of large nonequilibrium injection of quasiparticles is studied by means of a tunnel generator and detector. At a critical injection density, n_c, a second energy gap develops in the superconductor. The relevance to recent theories of nonequilibrium superconductivity is discussed.

Recently there has been much interest in nonequilibrium superconductivity.[1] Calculated quasiparticle properties, for small departures from equilibrium, are in excellent agreement with recent experiments.[2] In this Letter we describe an effect observed for quasiparticle injection at the gap edge which indicates that at some threshold quasiparticle density, a first-order transition occurs into a new, still superconducting, state. Most earlier work, at high excitation levels, has involved optical excitation.[1,3-5] Such experiments have suffered from a lack of knowledge of the quasiparticle distribution and the possible existence of thermal (heating) effects.

In the present experiment we obviate these difficulties by using tunnel junctions to inject and detect the nonequilibrium quasiparticle distribution. The geometry of the experiment (shown in the corner of Fig. 1) consists of two tunnel junctions with the film under study (the center film) common.[6] The generator is a relatively low-impedance junction to inject quasiparticles into the middle film. The detector is higher in impedance and is used to measure the quasiparticle distribution and the induced energy gap. Using the Rothwarf-Taylor equations[7] and estimates of recombination times in various materials,[8] we have chosen to study aluminum. This allows us to achieve substantial values of excess quasiparticle number n for modest currents (when compared to short recomination time materials such as Sn or Pb.

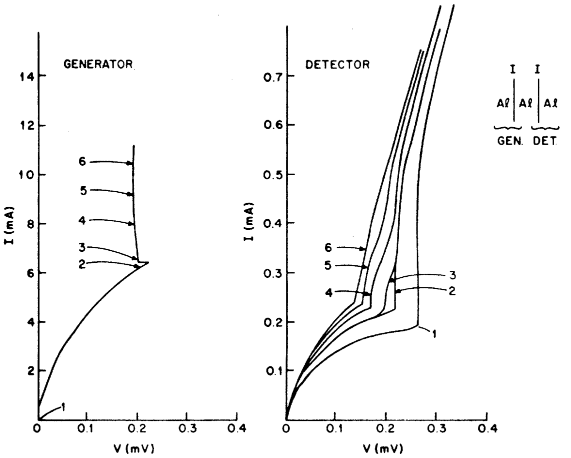

FIG. 1. Current-voltage characteristics for sample 3/11/76. The curves for the detector are taken at the various indicated bias points of the generator. A schematic of the experimental geometry is in the upper right-hand corner. The temperature is 0.94 K.

The experiments were performed in a pumped ^{4}He Dewar or a ^{3}He-^{4}He dilution refrigerator on thin films of Al (with T_c of 1.18 K) evaporated onto glass substrates. The generating junction had an area of $\approx 1\times10^{-2}$ mm^2 and the detector was $\approx 2.5\times10^{-3}$ mm^2. The thicknesses of the films were varied and ranged from ~500–5000 Å. Approximately a dozen samples have been studied to date and the phenomena discussed below have been observed repeatedly.

The I-V characteristics of the generator and detector at 0.94 K for one of the samples studied is shown in Fig. 1. A small parallel magnetic field has been applied to suppress the dc Josephson current. This structure was designed such that the middle film was the thinnest (≈ 500 Å) and so had the highest injection rate per unit volume. For no injection current (label 1), the detector I-V characteristic shows the typical behavior of a superconductor-insulator-superconductor tunnel junction at finite temperature. At a threshold bias point, somewhere along the 2Δ rise (between points 2 and 3 on the generator) there is a discontinuous break in the characteristic which shows a slight hysteresis.

At the point of the discontinuity, the detector junction changes its characteristics drastically. Below the discontinuity the I-V traces are reminiscent of those obtained by varying the temperature. Above the discontinuity a second gap edge or current rise splits off discontinuously (reminiscent of a first-order transition). Such an effect could arise from tunneling into two regions of a film with different gaps, a uniform film with an altered density of states, or some unknown voltage drops in the films. A simple check confirms that all films are still superconducting, and so in-line voltage drops are ruled out. It is also possible that because of a spatially varying tunneling probability, some regions of the film are "hotter" than others. We would not expect a seeming first-order transition from an effect of this sort and a magnetic field dependence of the dc Josephson current suggests that this is not likely. Also, if this is merely a thermal effect (local heating), it is difficult to imagine a significant thermal gradient through the thickness of the three-film sandwich and all three films should have local hot spots. By interchanging the relative thicknesses of the films comprising the generator junction, we find a generator characteristic very similar to that shown in Fig. 1, but the detector junction shows almost no gap reduction nor change in the quasiparticle current at that discontinuity. This result confirms that this transition is occurring in only the thinner film of the generator.

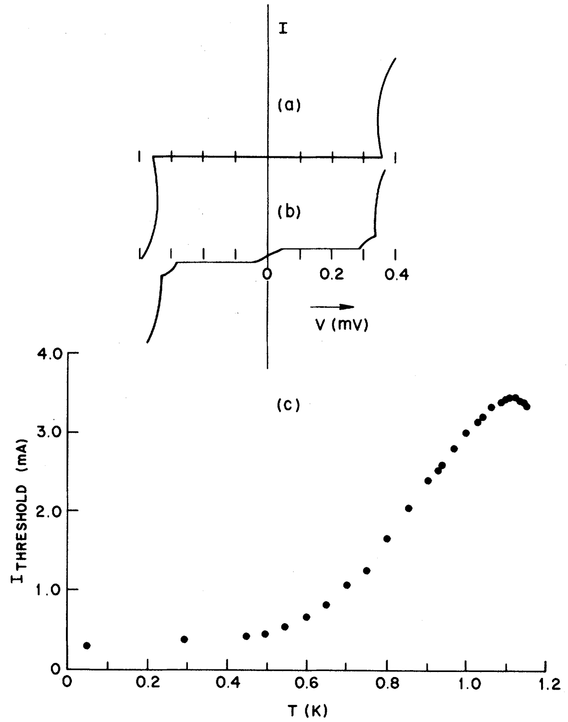

FIG. 2. Characteristics of sample 3/10/76. (a) With no injection at 0.36 K, and (b) with injection just above threshold. The temperature dependence of the threshold current is shown in (c).

We believe that this transition is an intrinsic result signaling a new state in the superconducting Al under injection. It has been seen in several different configurations, and conditions, but thus far only in Al. We have not yet seen such results in Pb or Sn and believe this is because of their relatively faster recombination and thermalization rates.[8]

We can also rule out critical-current effects in the films by studying the temperature dependence of this phenomenon. In Fig. 2(c) we show the threshold current (defined as the current in the generator at which the transition occurs) as a function of temperature down to 50 mK. A critical current would, of course, continue to increase with decreasing temperature. Here we observe first a small increase and then a decrease by over an order of magnitude with decreasing temperature. The final saturation value of $I_{\rm thresh}$ depends to some extent on the history and quality of the tunnel junction. (Junctions of higher quality and no trapped flux have lower threshold currents at low temperatures.) Also shown in Figs. 2(a) and 2(b) are the I-V characteristics for the detector junction at 0.36 K for zero injection and for injection just above the threshold. The effect is most spectacular at these lower temperatures. One can clearly see in Fig. 2(b) the second current rise splitting off from the usual energy gap. In addition, there is also current flow about zero bias and we associate this with the current rise that one sees in a tunnel junction with two dissimilar superconductors. If a material demonstrates two energy gaps Δ_1 and Δ_2, a tunnel junction with a second superconductor of energy gap Δ_1 would show structure at $\Delta_1-\Delta_2$, $\Delta_1+\Delta_2$, and $2\Delta_1$. In all samples studied to date, the difference $\Delta_1-\Delta_2$ at 0.92 K is ~40–50 μV while at lower temperatures, it increases to 70–80 μV. For lower injection level junctions we would expect possibly this difference to decrease until ultimately the phenomenon is not observed.

Another advantage of this three-film geometry is that the quasiparticle distribution can also be probed. In Fig. 3 we show an expanced I-V trace for a detector junction at 0.1 K with a generator current just below threshold ($I_{\rm gen}=0.15$ mA). Superimposed on this curve we show the best fit (by fitting the current rise at 2Δ) that we can achieve by adjusting the temperature with no injected current. It is clear from this curve that the distribution of quasiparticles is not thermal (as it cannot be to stimulate a first-order transition), but

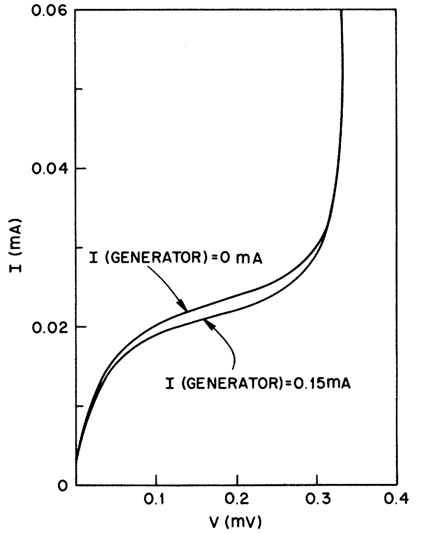

FIG. 3. Characteristics of the detector of sample 3/10/76. The lower curve is taken at $T = 0.1$ K with the generator biased just below threshold. The upper curve is the equilibrium characteristic at 0.64 K (giving a best fit to the current rise at the gap edge).

is not as simple as originally supposed by the model of Owen and Scalapino, which would show a peak at low biases.[9] A more detailed analysis is necessary for comparison with the solutions of Chang and Scalapino.[10] From this curve, however, one qualitatively concludes that the quasiparticle distribution has a larger density nearer the gap edge than a thermal distribution bearing some similarity to the Owen-Scalapino model. We emphasize that the transition occurs for injection at the gap edge. For $eV < 2\Delta$ to first order there is no increase in quasiparticle density[11] and the changes in Fig. 1 for biases 1 and 2 are presumably due to heating. At low temperatures where there are no thermal excitations, the current is all at $eV = 2\Delta$ and hence I_{th} is substantially lower. The peak in I_{th} near T_c in Fig. 2(c) is simply the current at which $eV = 2\Delta$ is reached as a function of temperature.

We can estimate the critical quasiparticle density n_c necessary to stimulate this transition. In the limit where the injected density of quasiparticles dominates the thermal density, the recombination time τ_R varies as $1/n$ and so results[7] in $n = (\tau_0 I)^{1/2}$, where τ_0 is a constant with units of time. We have estimated the critical density n_c from measurements of the threshold current at low temperatures, assuming the intrinsic recombination time and a film thickness of 1000 Å, and this yields $n_c \sim 2\times10^{17}/\mathrm{cm}^3$. We caution, however, that this number is sensitive to the quality of the junction, the existence of trapped flux, and the assumption of the intrinsic recombination time. It is well known in thin films that the effective τ_R can vary by up to an order of magnitude because of phonon-trapping effects. Also, trapped flux, edge effects, imperfections, etc., could all conspire to affect τ_R at these low temperatures. Nevertheless, we believe the value of n_c to be in the range 10^{17}–$10^{18}/\mathrm{cm}^3$.

We now turn to possible physical mechanisms for the above data. A situation which has been pointed out several times in the past[1,3] is the similarity of the Rothwarf-Taylor rate equations to those for exciton condensation into droplets in, for example, Ge under high excitation conditions.[1] It is tempting to associate the new gap we observe with a new state of condensed quasiparticles, the binding energy being $\Delta_1 - \Delta_2$. Without a proper estimate of the exchange and correlation effects (responsible for the condensation in Ge) one cannot comment further.

Another possibility is that outlined by Chang and Scalapino[13] to describe earlier results[3,4] where the predicted first-order transition was not observed. Using the Owen-Scalapino μ^* model[9] they calculated the free-energy difference between a uniform excess distribution of quasiparticles and that with large spatial variations. They showed that in general, when $d\mu^*/dn$ becomes negative, the material will break up into spatially varying regions. Within the Owen-Scalapino model, the phase diagram for such an instability was calculated and it was shown that at low temperatures, this instability line approached zero at $T = 0$. In fact, our estimates of n_c are in line with this model. $2\times10^{17}/\mathrm{cm}^3$ is $0.01\times[4N(0)\Delta]$ [$N(0)$ is the density of states at the Fermi surface] which is in reasonable agreement with this model. It would be interesting to redo that calculation with the results of the kinetic equations for the quasiparticle density.[10] At the time it was assumed that the breakup was into normal and superconducting regions but it is not at all obvious that the unstable region will not stabilize at a new gap value. Only a detailed theory with expanded knowledge of the quasiparticle distribution would answer that question. At any rate, a new "intermediate state" with two different gap values is a possibility[14] and could quantitatively describe the tunneling data.

In summary, for quasiparticle injection at the gap edge in Al in a three-film tunnel-junction sandwich, we have observed a phase transition occurring in a single film of that sandwich. Tunneling measurements have shown a second energy gap splitting off in a discontinuous fashion at this threshold and from temperature and thickness dependences we can eliminate critical-current and heating effects. At the moment we do not have a totally satisfactory theoretical explanation.

We would like to thank R. B. Kummer and M. A. Chin for advice and/or assistance with the low-temperature experiments.

---

[1] See D. N. Langenberg, in *Proceedings of the Fourteenth Conference on Low Temperature Physics, Otaniemi, Finland, 1975,* edited by M. Krusius and M. Vuorio (North-Holland, Amsterdam, 1975).

[2] P. Hu, R. C. Dynes, V. Narayanamurti, H. Smith, and W. F. Brinkman, Phys. Rev. Lett. 38, 361 (1977).

[3] P. Hu, R. C. Dynes, and V. Narayanamurti, Phys. Rev. B 10, 2786 (1974).

[4] G. A. Sai-Halasz, C. C. Chi, A. Denenstein, and D. N. Langenberg, Phys. Rev. Lett. 33, 315 (1974).

[5] J. Yeh and D. N. Langenberg (to be published) have used a single Sn tunnel junction to study the reduction of the gap at high current injection. However, from this single measurements it is not possible to sort out the dependence of Δ on n independently and to rule out thermal effects unambiguously.

[6] B. I. Miller and A. H. Dayem, Phys. Rev. Lett. 18, 1000 (1967).

[7] A. Rothwarf and B. M. Taylor, Phys. Rev. Lett. 19, 27 (1967).

[8] S. B. Kaplan, C. C. Chi, D. N. Langenberg, J. J. Chang, S. Jafarey, and D. J. Scalapino, Phys. Rev. B 14, 4854 (1976).

[9] C. S. Owen and D. J. Scalapino, Phys. Rev. Lett. 28, 1559 (1972).

[10] J. J. Chang and D. J. Scalapino, Phys. Rev. Lett. 37, 522 (1976), and NATO Advanced Study Institute on Small Scale Superconducting Devices, Lago di Garda, Italy, 1976 (to be published).

[11] We thank K. E. Gray for pointing this out.

[12] For a review of electron-hole droplets see J. C. Hensel, G. A. Thomas, and T. G. Phillips, to be published, or T. M. Rice, to be published.

[13] J. J. Chang and D. J. Scalapino, Phys. Rev. B 10, 4047 (1974).

[14] Recently L. N. Smith (to be published) has shown that for a large class of nonthermal quasiparticle distributions, qualitatively similar to that observed in Fig. 3, the superconductor is subject to spatial instability into two states with different gaps. Our data bear some similarity to this model.

Electronic Transport in Amorphous H_xWO_3

Richard S. Crandall and Brian W. Faughnan
RCA Laboratories, Princeton, New Jersey 08540

(Received 21 April 1977)

We report measurements of the electrical conductivity, σ, of thin amorphous films of hydrogen tungsten bronze, H_xWO_3, as a function of temperature and hydrogen/tungsten ratio, x. For $x \lesssim 0.3$ the temperature dependence of σ can be explained by the variable-range hopping model. At $x = 0.32$ an insulator-to-metal transition occurs with a minimum metallic conductance of about $5.1\times 10^{-5}\ \Omega^{-1}$.

Considerable effort has been devoted to a study of the electron transport properties of single-crystal alkali-metal tungsten bronzes.[1-5] These are nonstoichiometric compounds of the general formula M_xWO_3, where M is the alkali metal and x the stoichiometric parameter which can vary between 0 and 1. For large x, M_xWO_3 is metallic. However, the nature of the conductivity at low x is still unclear. It is thought that a metal-insulator transition occurs below $x = 0.2$. Lightsey[1] interpreted his measurements of the x dependence of the conductivity in Na_xWO_3 in terms of a percolation threshold at $x = 0.17$. However, it was recently pointed out[4] that the existing data on Na_xWO_3 are not sufficiently refined to test models of the insulator-metal transition. Webman, Jortner, and Cohen[5] attempt to explain the transport in the bronzes in terms of a model where the metal ions cluster to form regions of MWO_3 surrounded by insulating WO_3. However, this idea has been recently criticized[4,6,7] and we shall show that it is not consistent with the results presented in this paper.

We are not aware of any quantitative transport studies on the amorphous tungsten bronzes. However, because of the ease with which x can be varied over a wide range, they are particularly well suited for a quantitative study of the metal-insulator transition. Recently there has been wide interest in these materials as the basis for