for carrying out the intensity measurements.

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[1]D. C. Northrop and O. Simpson, Proc. Roy. Soc. (London) A244, 377 (1958).

[2]Sang-il Choi and Stuart A. Rice, Phys. Rev. Letters 8, 410 (1962).

[3]R. G. Kepler, Phys. Rev. 119, 1226 (1960).

[4]Richard H. Bube, Solid State Physics (Academic Press, New York, 1960), Vol. 11, p. 223, and included references.

[5]Frank Moser (private communication, 1962).

[6]A. Schmillen, Luminescence of Organic and Inorganic Materials, edited by Hartmut Kallmann and Grace Marmor Spruch (John Wiley & Sons, Inc., New York, 1962), p. 30.

[7]Sang-il Choi and Stuart A. Rice, Proceedings of the Organic Crystal Symposium, Ottawa, Canada, 1962 (unpublished).

EXCESS CURRENTS IN ELECTRON TUNNELING BETWEEN SUPERCONDUCTORS*

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In carrying out current-voltage (I-V) measurements on Al-Al, Sn-Sn, Pb-Pb, Sn-Pb, and Sn-Tl superconductor-metal oxide-superconductor tunnel junctions,[1] we have observed striking, polarity-independent deviations from the usual I-V curves associated with single particle tunneling (hereafter referred to as SPT).[2-5] These deviations are in the form of excess currents which we believe are due to additional tunneling mechanisms rather than to energy gap anisotropy or to density-of-states effects.[6] Three forms of excess currents were distinguishable at voltages $V < \Delta_a(T) + \Delta_b(T)$ [where V is the applied voltage times the electronic charge and $\Delta(T)$ is one half the energy gap of the superconductor at the operating temperature, T]: (1) an excess current characterized by a sharp temperature-independent jump at $V = \Delta(T)$ for identical superconductors (S-S), and $V = \Delta_a(T)$ and $V = \Delta_b(T)$ for two different superconductors (S_a-S_b); (2) a temperature-independent excess current which has an exponential dependence on applied voltage; and (3) an excess current which has a strong dependence on temperature as well as an approximately exponential dependence on applied voltage.

Typical I-V curves for Pb-Pb, Sn-Tl, and Al-Al tunnel junctions are shown in Fig. 1 together with the corresponding theoretical SPT curves. (Curves for Sn-Sn are similar to those for Pb-Pb, while curves for Sn-Pb are similar to those for Sn-Tl). For Pb-Pb, we note the presence of an excess current jump at $V = \Delta_{\text{Pb}}(T)$ with the extra current increasing rapidly at larger biases. The portion of the curve for $V < \Delta_{\text{Pb}}(T)$ is essentially what is expected for SPT. For

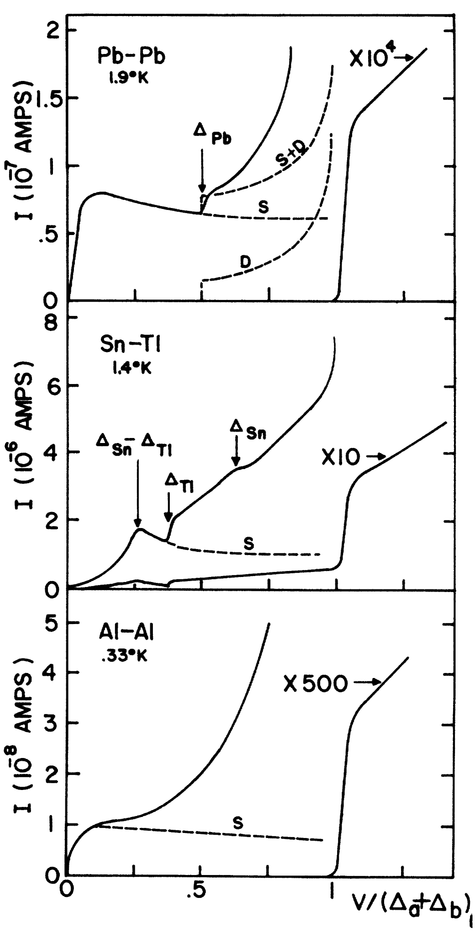

FIG. 1. Current-voltage curves for Pb-Pb, Sn-Tl, and Al-Al. The solid lines represent the experimental data and the dashed lines marked S represent theoretical SPT curves. For Pb-Pb, the theoretical DPT curve, marked D, and the sum of the SPT and DPT curves, marked $S+D$, are shown also.

Sn-Tl, there is a large current jump at $V=\Delta_{\mathrm{Tl}}(T)$ and a much smaller one (by a factor of ≈20) at $V=\Delta_{\mathrm{Sn}}(T)$.[7] Similarly for Sn-Pb, there is a large current jump at $V=\Delta_{\mathrm{Pb}}(T)$ and a much smaller one at $V=\Delta_{\mathrm{Sn}}(T)$. In some Sn-Tl and Sn-Pb junctions, no current jumps were observed. However, an extra current was apparent in these junctions near $V=\Delta_a+\Delta_b$ at temperatures of about 1.15°K. No excess current onsets were observed for any Al-Al junctions even at 0.3°K.[8] Instead, we note that there is an excess current which becomes apparent at relatively low voltages and which increases rapidly with V. On subtracting the theoretical SPT curves from the experimental curves at various temperatures, we find that this excess current is temperature independent and that it actually varies exponentially with V.

There are several mechanisms that may be responsible for the current jumps at $V=\Delta_i(T)$. One that suggests itself immediately involves tunneling from normal metal inclusions in the superconductor films. However, at the temperature of the experiments, this source of tunneling current would lead to a diffuse increase in current over a broad region near $V=\Delta_i(T)$ rather than to a sharp onset. An interesting mechanism which theoretically does give rise to sharp current jumps at $V=\Delta_i(T)$ has been proposed by Falicov.[9] It involves symmetrical Auger processes in which two electrons tunnel simultaneously. For the S_a-S_b case with S_a biased negatively relative to S_b and $\Delta_a<\Delta_b$, the Auger process at $V=\Delta_a(T)$ corresponds to two electrons tunneling from the filled band of S_a, one going to the empty band of S_b, and the other combining with a hole in the filled band of S_b [Fig. 2(a)]. At $V=\Delta_b(T)$, the process corresponds to two electrons tunneling to the empty band of S_b, one coming from the filled band of S_a, and the other from the empty band of S_a [Fig. 2(b)]. These processes would, however, be expected to exhibit an exponential temperature dependence since they depend on the density of excited particles. They cannot therefore account for the observed current jumps.

A more plausible mechanism for the excess current jumps, involving double particle tunneling via pair dissociation or recombination (hereafter referred to as DPT), was suggested by Schrieffer. This mechanism, discussed theorectically in the following Letter by Schrieffer and Wilkins,[10] yields a polarity-independent current with a discontinuous jump at $V=\Delta_i(T)$ and only a weak temperature dependence. Although the Schrieffer mechanism involves electron pairs, it can readily be incorporated into single-particle (semiconductor-type) energy diagrams by the simple expedient of adding to the diagram pairs of superfluid electrons at the Fermi level, ϵ_F. The use of such "hybrid" diagrams is illustrated in Fig. 3. Consider the S_a-S_b configuration (again with S_a negative and $\Delta_a<\Delta_b$). When $V=\Delta_a(T)$ we note that the energy of the superfluid electrons in S_b is degenerate with single-particle states in the filled band of S_a; when $V=\Delta_b(T)$ the superfluid electrons in S_a are degenerate with single-particle states in the empty band of S_b. Tunneling takes place at $V=\Delta_a(T)$ by the recom-

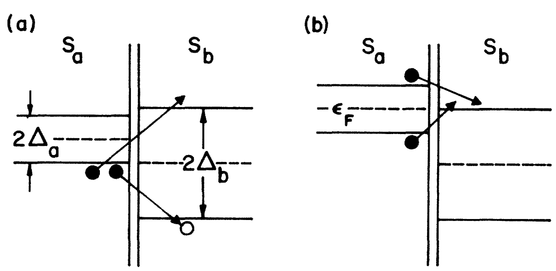

FIG. 2. Single-particle (semiconductor-type) energy diagrams for two different superconductors, S_a-S_b, showing the Falicov-Auger processes at $V=\Delta_a(T)$ and $V=\Delta_b(T)$. ϵ_F represents the Fermi energy.

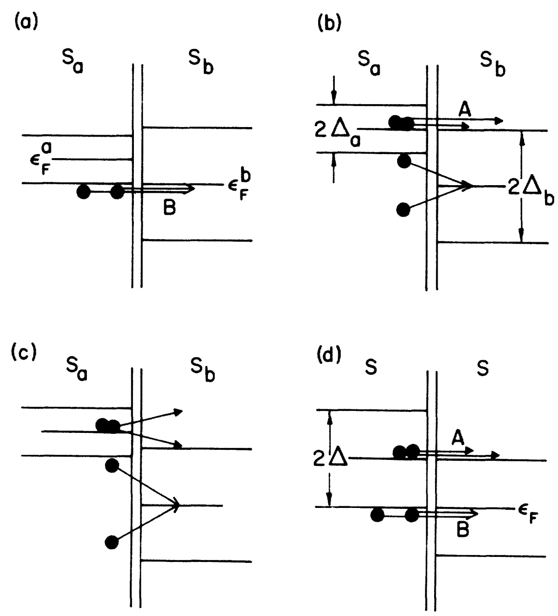

FIG. 3. "Hybrid" energy diagrams for S_a-S_b showing DPT processes at $V=\Delta_a(T)$ (a), at $V=\Delta_b(T)$ (b), and at $\Delta_b(T)<V<\Delta_a(T)+\Delta_b(T)$ (c), and for S-S showing DPT processes at $V=\Delta(T)$ (d). Pairs of superfluid electrons are shown at ϵ_F^a, ϵ_F^b, and ϵ_F for S_a, S_b, and S, respectively.

bination of two electrons from S_a into an electron pair in S_b, leaving two holes behind in the filled band of S_a [process B, Fig. 3(a)], and at $V=\Delta_b(T)$ by the dissociation of an electron pair from S_a into two electrons in the empty band of S_b [process A, Fig. 3(b)]. For $V>\Delta_a(T)$ [and $V>\Delta_b(T)$] energy conservation requires only that the sum of the energy of the two single electrons be equal to the energy of the superfluid pair and the two electrons need not have equal energies [Fig. 3(c) and (b)]. The entire analysis carries over in an obvious way to the S-S case where now both processes A and B can occur when $V=\Delta(T)$ [Fig. 3(d)]. An excess current involving similar DPT processes may also be expected for metal-superconductor junctions. For this case, the excess current would again be relatively temperature independent, but would begin at $V=0$.

Since DPT involves the simultaneous tunneling of two electrons, the matrix element for the process will depend on $|T_{ab}|^2$, the square of the matrix element involved in SPT processes. Accordingly, the contribution to the current from DPT processes will be small compared to that of SPT processes. However, the magnitude of the SPT current decreases exponentially with temperature since it depends on the density of excited particles, whereas the DPT current is relatively temperature independent. It should therefore be possible, by lowering the temperature, to decrease the SPT current to a point where the DPT current would be observable, provided that there is no other temperature-independent excess current present. Since $|T_{ab}|^2$ depends exponentially on the thickness of the barrier layer, the smaller the thickness, the higher the temperature at which the DPT current will become apparent.[11] For the S_a-S_b configuration, the ratio of the two current jumps at $V=\Delta_a(T)$ and $V=\Delta_b(T)$ is independent of the barrier thickness and should therefore yield information about the other factors which determine the magnitude of the DPT current. It is interesting to note that for Sn-Tl and for Sn-Pb, the larger of the two DPT current jumps corresponds to the DPT process in which the electron pairs are associated with Sn and the single particles are associated with Pb or Tl, a result which is not predicted by the theory in its present form.[10]

The theoretical I-V curves for the DPT process and for the sum of the SPT and DPT processes are shown in Fig. 1 for Pb-Pb. We see that the experimental curve rises much more rapidly beyond $V=\Delta_{\text{Pb}}$ than does the theoretical, indicating the presence of additional excess currents. This is also true for the other junctions which exhibit current jumps. By taking the difference between the experimental curves and the appropriate theoretical SPT plus DPT curves for the various tunnel junctions, we find that except for Pb-Pb, the additional excess current has an appreciable voltage dependence but is independent of temperature. In several of the junctions this additional excess current appears to be of the Al-Al type. For Pb-Pb, we find that the additional excess current decreases rapidly with temperature and increases approximately exponentially with voltage.

We believe that the strongly temperature- and voltage-dependent part of the excess current for Pb-Pb is associated with a thermally assisted SPT process in which either phonons, photons, or electrons having sufficient energy excite an electron from the filled band of S_a into the empty band of S_b. This process is the thermal counterpart of the photon-assisted SPT process proposed by Dayem and Martin[12] to explain their microwave experiments. At a given temperature, the probability of thermally assisted SPT should increase rapidly with voltage as the energy separation between the two bands involved decreases and, at a given volgage, should decrease rapidly with temperature as the number of energetic phonons, photons, or electrons decreases. We are as yet uncertain about the mechanism responsible for the temperature-independent excess current observed for Al-Al.[13]

We are indebted to L. Falicov, J. R. Schrieffer, and J. W. Wilkins for an extensive exchange of ideas. We wish to acknowledge valuable discussions with M. Cohen, D. N. Langenberg, A. Rothwarf, and P. J. Stiles. We thank R. Burnley, R. Frank, W. Fountain, and V. O'Donnell for their assistance in carrying out some of the experiments. The measurements below 1°K were done in collaboration with D. N. Baldock. We also wish to express our appreciation to Dr. D. K. Stevens of the U. S. Atomic Energy Commission for his interest and encouragement in supporting this work.

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[1]For samples involving Sn, the barrier layer was Sn

oxide; for Al-Al junctions, the barrier layer was Al oxide; for the Pb-Pb junctions, the barrier layer was Al oxide formed by completely oxidizing a very thin evaporated Al film.

[2]I. Giaever and K. Megerle, Phys. Rev. 122, 1101 (1962).

[3]S. Shapiro, P. H. Smith, J. Nicol, J. L. Miles, and P. F. Strong, IBM J. Res. Develop. 6, 34 (1962).

[4]B. N. Taylor, E. Burstein, and D. N. Langenberg, Bull. Am. Phys. Soc. 7, 190 (1961).

[5]The validity of the simple semiconductor model of a superconductor and the I-V curves derived from such a model have been discussed by J. Bardeen, Phys. Rev. Letters 6, 57 (1961); 9, 147 (1962); M. H. Cohen, L. M. Falicov, and J. C. Phillips, Phys. Rev. Letters 8, 316 (1962).

[6]P. Townsend and J. Sutton, Phys. Rev. 128, 591 (1962).

[7]We find that the extrapolated value for $2\Delta_{\mathrm{Tl}}(0)$ (not to our knowledge previously reported) is $(0.73 \pm 0.01) \times 10^{-3}$ eV with $2\Delta_{\mathrm{Tl}}(0)/kT_c$ equal to 3.57 ± 0.05. The transition temperature T_c for the Tl films is 2.36°K, and the observed dependence of $\Delta(T)/\Delta(0)$ on T/T_c is in good agreement with the BCS theory. Our Δ values for the other superconductors agree with those already reported in the literature.

[8]The fact that a current onset is not observed for the Al-Al junctions does not imply that it is absent but only that it is smaller than a few percent of the observed current at $V=\Delta_{\mathrm{Al}}(T)$. This places an upper limit on an excess current jump in Al-Al of the order of the excess current jump observed in Pb-Pb.

[9]L. M. Falicov (private communication).

[10]J. R. Schrieffer and J. W. Wilkins, following Letter [Phys. Rev. Letters 10, 17 (1963)].

[11]For very thin barriers, three- and four-particle tunneling processes would also be possible. This may account for the additional structure which is observed at $V=2\Delta_{\mathrm{Sn}}(T)/3$ and $V=2\Delta_{\mathrm{Sn}}(T)/4$ in the I-V curves of some Sn-Sn junctions.

[12]A. H. Dayem and J. R. Martin, Phys. Rev. Letters 8, 246 (1962).

[13]I. Giaever, H. R. Hart, Jr., and K. Megerle [Phys. Rev. 126, 941 (1962)] have reported an Ohmic temperature-independent "leakage current" present in Al-Pb tunnel junctions.

TWO-PARTICLE TUNNELING PROCESSES BETWEEN SUPERCONDUCTORS*

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The conventional single quasi-particle model of tunneling between two superconductors at zero temperature predicts an onset of tunneling current at an applied voltage (times the electronic charge) $V=\Delta_a(T)+\Delta_b(T)$. Here $\Delta_a(T)$ and $\Delta_b(T)$ are one half the energy gap for superconductors S_a and S_b at temperature T. In the preceding Letter[1] Taylor and Burstein present experimental evidence for temperature- and polarity-independent excess currents having onsets at $V=\Delta_a(T)$ and $V=\Delta_b(T)$. In this Letter we shall discuss processes which seem a likely explanation for those excess currents. Calculations of these processes have shown that (1) their onset occurs discontinuously at one half the energy gap; (2) barrier thicknesses required to explain the observed currents are quite reasonable.

We propose that these excess currents are due to two-electron processes involving superfluid electrons. A typical process which begins at $V=\Delta_a(T)$ is one in which two electrons of the superfluid in S_a tunnel through the oxide and become two quasi-particles in S_b. In this process the number of superfluid pairs in S_a decreases by one without excitation of quasi-particles. There are similar processes which begin at $V=\Delta_b(T)$.

These double-particle tunneling processes are essentially temperature independent at low temperatures, in agreement with experiment. Also, the excess tunneling conductance is correctly predicted to be an even function of V, i.e., polarity independent.

In Fig. 1 the quasi-particle energy is plotted versus wave number. The quasi-particle energy E_k measured relative to the Fermi level ϵ_F is given by

$$E_k=(\epsilon_k^2+\Delta_k^2)^{1/2} \tag{1}$$

for each superconductor, where ϵ_k is the single-particle energy in the normal state, measured relative to ϵ_F. The conventional single-particle tunneling process present at zero temperature is illustrated in Fig. 1 by a single electron being extracted from the superfluid in S_a, leaving a quasi-particle in state k_1. The electron tunnels through the oxide to become a quasi-particle in state k_2 in S_b. Energy conservation requires

$$V=E_{k_1}^{a}+E_{k_2}^{b} \geq \Delta_a+\Delta_b. \tag{2}$$