More detailed studies on the anisotropy of the self-activated luminescence center, including the polarization of the thermoluminescence associated with the center, are now in progress.

[1]For example, D. Dutton, J. Phys. Chem. Solids 6, 101 (1958); A. Lempicki, J. Electrochem. Soc. 107, 404 (1960).

[2]D. L. Birman, J. Electrochem. Soc. 107, 409 (1960).

[3]P. P. Feofilov, J. Phys. Radium 17, 656 (1956); J. Lambe and W. D. Compton, Phys. Rev. 106, 684 (1957).

[4]R. J. Elliott, I. G. Matthews, and E. W. J. Mitchell, Phil. Mag. 3, 360 (1958).

[5]Kindly supplied by Dr. A. Addamiano, General Electric Co., Cleveland, Ohio.

[6]A. Addamiano and M. Aven, J. Appl. Phys. 31, 36 (1960).

[7]Actually about 10 % according to x-ray analysis.

[8]S. Shionoya, T. Koda, K. Era, and H. Fujiwara, J. Phys. Soc. Japan 18, Suppl. II, 299 (1963).

[9]J. S. Prener and F. E. Williams, J. Chem. Phys. 25, 361 (1956).

[10]P. H. Kasai and Y. Otomo, Phys. Rev. Letters 7, 17 (1961); J. Chem. Phys. 37, 1263 (1962).

[11]In the nomenclature used here, π or σ dipole means parallel or perpendicular, respectively, to the symmetry axis of the center. See E. U. Condon and G. H. Shortley, Theory of Atomic Spectra (University Press, Cambridge, 1935), Chap. IV; also reference 12.

[12]L. Patrick, Phys. Rev. 117, 1439 (1960).

JOSEPHSON CURRENTS IN SUPERCONDUCTING TUNNELING: THE EFFECT OF MICROWAVES AND OTHER OBSERVATIONS*

Sidney Shapiro
Arthur D. Little, Inc., Cambridge, Massachusetts
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In the course of experiments on the effect of microwave fields on superconducting tunneling, we have had occasion over the past few months to fabricate many tunneling crossings of low resistance (5-20 Ω with a crossing area of 1.5×10^{-4} cm^2). Every one of these samples has exhibited the zero-voltage currents predicted by Josephson[1] and attributed, in effect, to the tunneling of Cooper pairs. The observation of these currents has already been reported by Anderson and Rowell.[2] Our experiments have brought to light several new effects which we summarize below.

The samples were $Al/Al_2O_3/Sn$. Two five-mil-wide Al lines, evaporated onto cleaned glass substrates, were oxidized in a glow discharge generated in an atmosphere of about 0.1 Torr of dry oxygen for 15 seconds. A five-mil-wide cross-strip of Sn was then evaporated forming two samples on each substrate.

The tunneling current versus voltage characteristics were displayed on an X-Y oscilloscope. A low-impedance source was used to drive the loop containing the sample and the current-measuring resistor. The latter, and thus the circuit load line, could be varied, either in calibrated steps or continuously, from 10 Ω to 10 000 Ω. The source was either dc, ac, or both in combination. Generally 60-cps ac was used though other frequencies were employed as desired. No attempt was made to shield the earth's magnetic field. Most data were taken at about 0.9°K.

The following observations were noted in the course of experiments with a large number of tunneling crossings:

1. Using an ac display, Fig. 1 shows for a typical sample the zero-voltage current predicted by Josephson and previously observed with a dc technique by Anderson and Rowell. During each half-cycle of the sweep, current

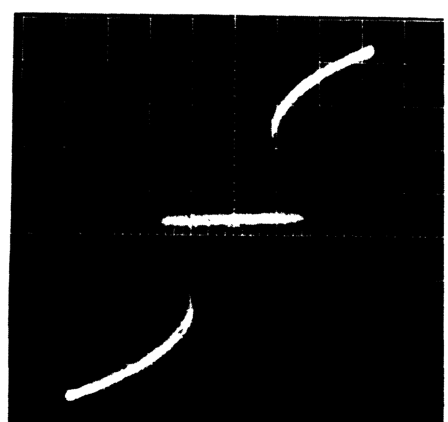

FIG. 1. I-V characteristic near origin showing zero-voltage Josephson current and negative resistance switching trace. Vertical scale 58.8 μV/cm, horizontal scale 130 nA/cm.

flows through the sample without developing any voltage across it until, at a current which depends upon temperature, crossing resistance, and circuit load line, switching to the familiar single-particle tunneling characteristic occurs along the circuit load line. The switching characteristic is stable and reproducible, and is followed both when the current is increasing and when it is decreasing. It is indicative of a negative resistance.

2. Other investigators[3] in this laboratory have observed rf oscillations associated with this region. The samples, placed in appropriately designed oscillator circuits, produced rf at the circuit resonant frequency of about 100 Mc/sec. In view of their frequency, these oscillations occur at too high dc voltages to be the ac supercurrents also predicted by Josephson.[1]

The rf oscillations appear to confirm that the Josephson current region decays toward the single-particle tunneling characteristic by means of a negative resistance, despite the fact that we have not been able to trace out any appreciable portion of the negative resistance.

3. The characteristic as shown in Fig. 1 can be traced out with dc and follows exactly the course of the ac display. On occasion, however, much more ac can be carried at zero voltage than dc; fifteen times as much or more is not uncommon. The same ac trace is obtained for all sweep frequencies employed (8 to 800 cps). Electrical transients can cause the excess ac to disappear and to reappear, but they have no effect on the rest of the characteristic. Frequently, the excess current is noisy in character, i.e., the amplitude of ac carried before switching takes place varies randomly from cycle to cycle. The excess ac appears only at temperatures well below that at which the zero-voltage current is first observed, and is quenched by lower dc magnetic fields and microwave fields than affect noticeably the stable zero-voltage current. We have no explanation for the excess ac and can only conjecture that it may be related to the ac effect predicted by Josephson.

The effect of microwave power in modifying the I-V curve, especially the zero-voltage currents, was also studied. The samples were mounted in a microwave cavity resonant, at low temperatures, at about 9300 Mc/sec and 24 850 Mc/sec. All the following observations were independent of sweep frequency and were also seen when dc was passed through the sample.

1. Figure 2 shows for a typical sample the initial effect of 9300-Mc/sec microwave power on the I-V characteristic. Without applied power, the trace (top) is similar to that of Fig. 1. With a few tens of microwatts applied, however, the zero-voltage currents become noisy and gradually vanish resulting in regions of zero slope (or almost zero slope) in which the current rises at (or almost at) fixed voltage across the sample. The voltage at which the zero-slope regions occur is equal to $\pm h\nu/2e$, where ν is the microwave frequency. Note that the origin, i.e., the point of zero voltage and zero current, is not a stable point. As more power is applied (not shown), further zero-slope regions appear at still higher voltage, and the origin alternates between being stable and unstable. The current amplitude in a given zero-slope region varies periodically with increasing power. The interval in voltage from one zero-slope region to the next is not always $h\nu/2e$; sometimes a step is missing so that the voltage interval is $h\nu/e$.

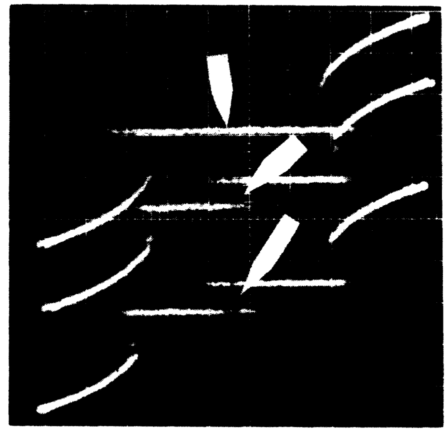

FIG. 2. Initial effect of microwave power. Pointers mark origin, which becomes noisy and vanishes as zero-slope regions at $\pm h\nu/2e$ appear. Note negative resistance at origin. Vertical scale 58.8 μV/cm, horizontal scale 13 nA/cm.

2. Figure 2 demonstrates still another startling feature of the effect of microwaves on the Josephson currents. In the bottom trace the origin has vanished as a possible state, and the system is able to remain biased at, e.g., $+h\nu/2e$, not only when positive current is flowing but even when the current is zero and, more astonishingly, even when the current is reversed and made negative. Finally, at some value of negative current, the voltage switches to $-h\nu/2e$. Thus, the zero-slope regions which occur with voltage $+h\nu/2e$ across the sample are connected by what ap-

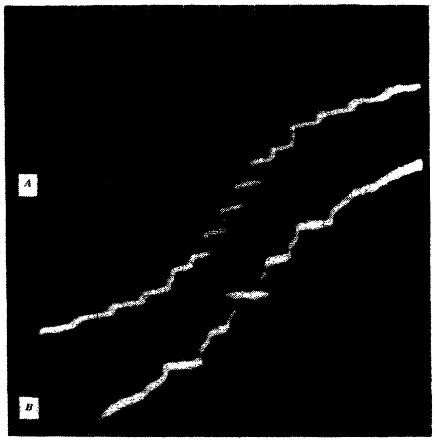

FIG. 3. Microwave power at 9300 Mc/sec (A) and 24850 Mc/sec (B) produces many zero-slope regions spaced at $h\nu/2e$ or $h\nu/e$. For A, $h\nu/e = 38.5\ \mu V$, and for B, 103 μV. For A, vertical scale is 58.8 $\mu V/cm$, horizontal scale is 67 nA/cm; for B, vertical scale is 50 $\mu V/cm$, horizontal scale is 50 $\mu A/cm$.

pears to be a negative resistance at the origin. Negative-resistance-like regions occur between virtually every pair of zero-slope regions. At power levels of about ten milliwatts, these negative-resistance-like regions gradually vanish (the sample can be biased to any voltage), and the "zero-slope" regions exhibit a finite slope. Both these high-power effects are probably due to the superimposed conventional detection processes associated with the background single-particle tunneling curve.

3. Similar effects occur at 24 000 Mc/sec. Figure 3 shows the numerous steps at 9300 Mc/sec (A) and at 24 850 Mc/sec (B) which are present at intermediate microwave power levels.

Josephson[1] has already discussed briefly the effect rf should have on the pair-tunneling supercurrent. He predicted the occurrence of zero-slope regions separated by $h\nu/2e$ in the I-V characteristic in the presence of the rf field. This prediction was based on the frequency modulation by the rf of the ac supercurrents previously referred to. Our experiments have confirmed this prediction and represent indirect proof of the reality of Josephson's ac supercurrent. In addition, they have brought to light several startling accompaniments of the Josephson effect, namely, the instability of the origin; the dc negative resistance at the origin; the noise associated with the onset of instability; and the periodic change at a given voltage level, e.g., at zero voltage, between stable and unstable as the microwave power changes.

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ANOMALOUS SHIFTS IN THE FLUORESCENCE OF MnF_2 AND $KMnF_3$

W. W. Holloway, Jr., M. Kestigian, R. Newman, and E. W. Prohofsky
Sperry Rand Research Center, Sudbury, Massachusetts
(Received 31 May 1963)

In this Letter measurements are reported of large temperature-dependent changes in the fluorescence of MnF_2 and $KMnF_3$. These changes take the form of relatively abrupt alterations in the wavelength and intensity of the fluorescence. The effects appear to be related to exchange interactions. To our knowledge, they have not been observed or reported previously.[1] We have observed similar effects in $KMnCl_3$,[2] but these effects were absent in the luminescence of $K(Mn_{0.01}$-$Zn_{0.99})F_3$ [3] and $MnCl_2$.[4]

The fluoride crystals used in these experiments were grown by the horizontal Bridgman technique and the temperature gradient method in an HF atmosphere. The observations were performed using a Perkin-Elmer Model 12-C spectrometer. The crystals were mounted on a copper post in a metal Dewar provided with windows for optical access. Separate thermocouples monitored the temperature of both the post and the sample attached to the post.

The procedure for taking measurements began with the cooling of the sample by placing liquid helium in the coolant reservoir of the Dewar. Af-

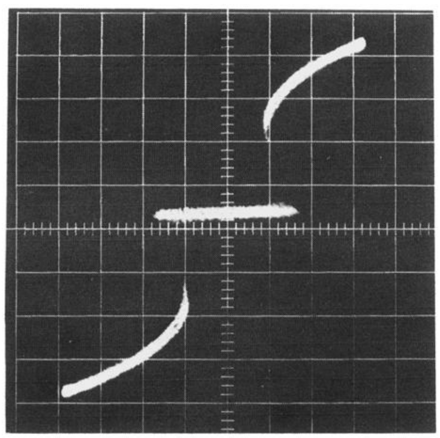

FIG. 1. *I*-*V* characteristic near origin showing zero-voltage Josephson current and negative resistance switching trace. Vertical scale 58.8 μV/cm, horizontal scale 130 nA/cm.

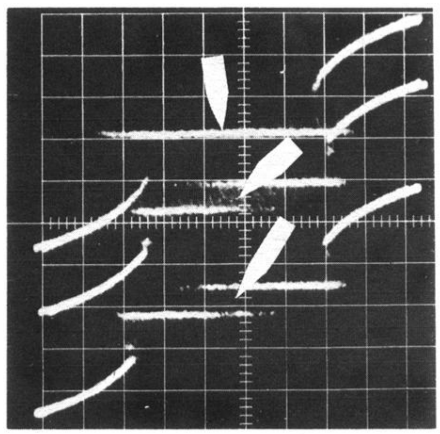

FIG. 2. Initial effect of microwave power. Pointers mark origin, which becomes noisy and vanishes as zero-slope regions at $\pm h\nu/2e$ appear. Note negative resistance at origin. Vertical scale 58.8 μV/cm, horizontal scale 13 nA/cm.

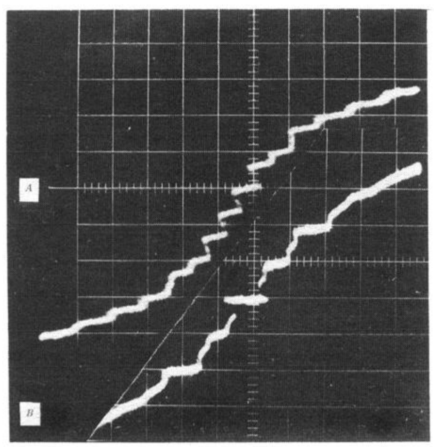

FIG. 3. Microwave power at 9300 Mc/sec (*A*) and 24850 Mc/sec (*B*) produces many zero-slope regions spaced at $h\nu/2e$ or $h\nu/e$. For *A*, $h\nu/e = 38.5$ μV, and for *B*, 103 μV. For *A*, vertical scale is 58.8 μV/cm, horizontal scale is 67 nA/cm; for *B*, vertical scale is 50 μV/cm, horizontal scale is 50 μA/cm.