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# SUPERCONDUCTING THIN FILMS

by R. A. Kamper, L. O. Mullen, and D. B. Sullivan

Prepared by
NATIONAL BUREAU OF STANDARDS
Boulder, Colo.
for Lewis Research Center

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# SUPERCONDUCTIN & THIN FILMS

By R. A. Kamper, L. O. Mullen, and D. B. Sullivan

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Prepared under Interagency Order NASA-C-7756-B by Institute for Basic Standards NATIONAL BUREAU OF STANDARDS Boulder, Colo.

for Lewis Research Center

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#### **FOREWORD**

The research described herein, which was conducted by the Cryogenics Division, Institute for Basic Standards, National Bureau of Standards, was performed under Interagency Order NASA-C-7756-B. The Project Manager for NASA was Mr. Russell A. Lindberg, Space Power Systems Division, NASA-Lewis Research Center, with Mr. James C. Laurence, Electromagnetic Propulsion Division, NASA-Lewis Research Center, as Technical Advisor. The report was originally issued as NBS Report 9708, 1968.

#### Abstract

This work has been concentrated mainly on the properties and applications of the Josephson effect at radio frequencies. We have explored the characteristics of the emitted radiation under various conditions; constructed a simple theory of the linewidth (which has been verified); conceived new principles for an absolute millidegree thermometer and a picovoltmeter; built and tested a prototype of the picovoltmeter; and developed a reliable method for fabricating good tunnel junctions between thin films of niobium and lead.

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#### 1. INTRODUCTION

During the tenure of this contract we have concentrated most of our effort on superconductive tunneling - the passage of an electric current across a thin barrier between two weakly connected superconductors. If the barrier is very thin, current can pass without loss of energy. This phenomenon is known as the Josephson effect, after B. D. Josephson [1-3] who first predicted it theoretically, and the system of two weakly connected superconductors is called a Josephson junction. The current-vs-voltage characteristics of Josephson junctions are non-linear and extremely sensitive to external fields (see appendix). This serves to distinguish them from simple metallic shorts and also makes the Josephson effect a promising source of new and very sensitive electronic devices. The work we describe here is directed towards the realization of some of this exciting promise.

The aspect of the Josephson effect which has received most of our attention is the emission of electromagnetic radiation. If a bias voltage V is maintained across a Josephson junction, each pair of electrons which cross the junction gain an energy 2eV, where e is the electron charge. This energy is then emitted as a quantum hf of radiation at a frequency f, such that hf = 2eV. This corresponds to 483.591 MHz per  $\mu V^{[4]}$  This radiation had previously been observed in the microwave frequency range, but some preliminary arguments by P. W. Anderson had discouraged early work at lower frequencies. We became interested in the low frequency limit to the observability of Josephson radiation, and in the properties and applications of this effect in the radio frequency range below 50 MHz. During the course

of the year it became apparent, from our own work and that of J. E. Zimmerman and A. H. Silver, <sup>[7-9]</sup> at the Ford Scientific Laboratory, that Anderson's arguments contained errors. The Josephson radiation has been observed indirectly <sup>[10]</sup> at a frequency less than 1 Hz, and the prospects for applying the effect in electronic devices are very good.

Our main scientific accomplishments during the tenure of this contract have been:

- 1) Observation of Josephson radiation in the radio frequency range. In this we were preceded by a few months by the independent work of J. E. Zimmerman, J. A. Cowen and A. H. Silver<sup>[7]</sup> at the Ford Scientific Laboratory.
- 2) Construction of a successful theory of the linewidth of Josephson radiation in the radio frequency range. This theory was tested and described in a joint publication with A. H. Silver and J. E. Zimmerman. [10]
- 3) Conception of a new technique for thermometry in the millidegree range using the linewidth of the Josephson radiation. [11]
- 4) Design and construction of a prototype picovoltmeter using a pair of radiating Josephson junctions. The small voltage to be measured causes a beat between the signals from the two junctions. We have observed this beat, demonstrating that the principle is feasible.
  - 5) Development of methods for making superconductive tunnel junctions, including a simple, adjustable point contact junction and a more permanent junction between thin films of niobium and lead.

In addition, we have supplied sets of matched and graded thin films of niobium, and thin films of niobium-zirconium alloy, to our sponsor.

#### 2. RADIOFREQUENCY JOSEPHSON RADIATION

# 2.1 Point-Contact Junctions

We made nearly all our observations of Josephson radiation with adjustable point-contact junctions. In order to maintain the small bias voltage ( $< 10^{-7}$  V) required to stimulate radiofrequency radiation, we incorporated shunt resistors of the order of  $10\mu\Omega$  into the structures of the various junctions we used. A suitable voltage could then be maintained by a direct current of a few mA.

Our first successful Josephson junction is shown in figure 1. The junction was at the crossing point of two lightly touching niobium wires, whose contact pressure could be adjusted by a screw mechanism worked from outside the cryostat. We chose the coaxial arrangement of the shunt resistor in order to reduce pickup of external noise. This type of junction generated coherent Josephson radiation, but was difficult to adjust because of irregularity in the mechanism. Also, it was not possible to control the area of contact. We therefore developed the improved form shown in figure 2. The two halves of the junction span a saw-cut in the brass block which functions as the shunt resistor. The contact pressure can be adjusted by squeezing the brass block with a fine screw worked from outside the cryostat. The contacts are a niobium rod and a fine Nb-Zr alloy point which is spot welded to a niobium wire spring. We chose the Nb-Zr alloy for its hardness. We formed the fine point by partly immersing a wire in

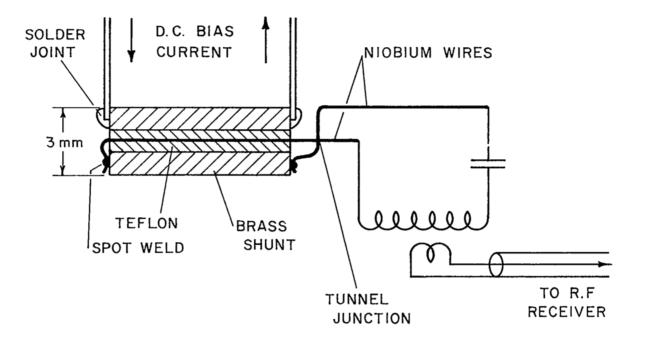
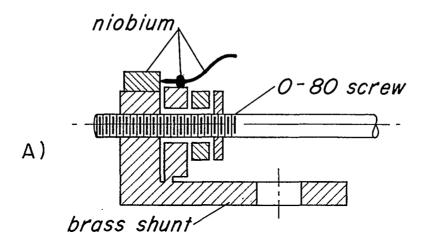


Figure 1. Details of Josephson Junction



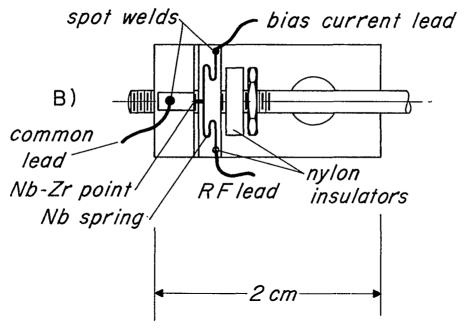


Figure 2. Improved Josephson Junction

- A) Cross section
- B) Top view

a fast chemical etch consisting of equal parts of hydrofluoric acid, sulfuric acid, nitric acid, and water. The etch attacks preferentially in the meniscus and dissolves off the immersed part of the wire, leaving a regular cone-shaped tip with a fine point. These junctions are easy to adjust and once set up they retain their characteristics for several hours without further adjustment.

# 2.2 RF Circuits

The Josephson radiation is generated by these junctions at a very low level (<10<sup>-7</sup> V) and a very low impedance. We therefore couple it out of the cryostat via a sharply tuned transformer and a coaxial line to a sensitive receiver. We used a superheterodyne communication receiver with a bandwidth variable from 200 Hz to 13 kHz for all our early observations. In connection with the picovoltmeter (to be described in section 4) we also used a simple 45 MHz amplifier and diode detector designed for use as the intermediate frequency amplifier of a microwave receiver. It had a bandwidth of about 2 MHz.

The complete circuit with which we made our first observations is shown in figure 3. It recorded the output of the junction, at a preset radio frequency, as the bias voltage was varied slowly. In order to discriminate against background noise it employed lock-in detection.

The DC bias was supplied by an integrating amplifier whose input was a small steady voltage, resulting in a bias voltage rising linearly with time so as to cover the interesting range in a period of a few minutes. A small modulation at 200 Hz was superimposed on

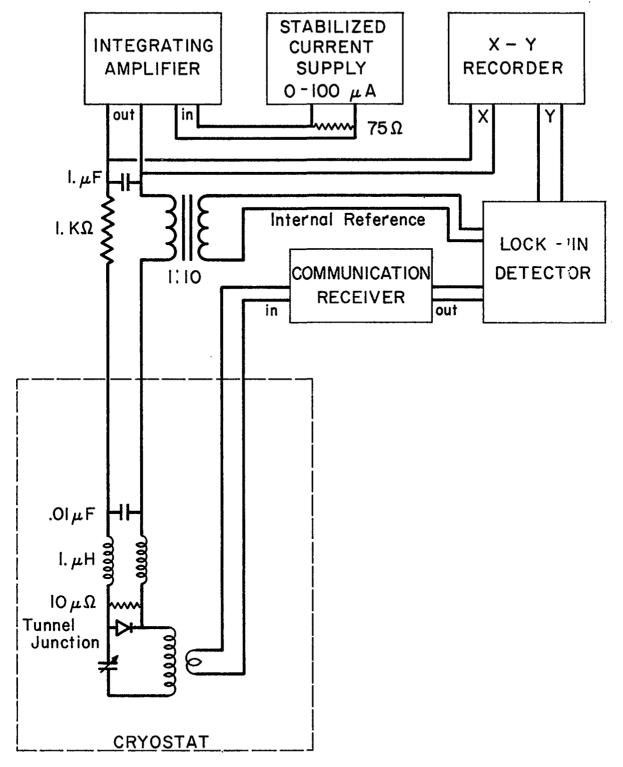


Figure 3. Block diagram of apparatus for Josephson effect.

the bias voltage, and the output of the radio receiver was passed through a lock-in detector to extract the component at the modulation frequency, which was proportional to the derivative of the RF signal as a function of bias voltage. It was displayed on an x-y recorder.

We subsequently discovered that sufficient signal was available to dispense with lock-in detection for most purposes. The simplest detection scheme we were able to use is shown in figure 4. The bias voltage was derived from the time base of an oscilloscope on which we directly displayed the output of the receiver. This arrangement was very convenient for initial adjustment of the junctions.

Another variation on the detection scheme we used was designed to provide a calibration for measuring linewidths. We modulated the amplitude of the local oscillator of our communication receiver at about 10 kHz. The resulting sidebands caused the receiver to respond to signals 10 kHz on either side of its center frequency. These extra responses gave a very convenient calibration for measuring frequency intervals (and hence linewidths) on recorder traces.

#### 2.3 Observed Characteristics of the Josephson Radiation

The spectrum of radiation emitted by a point contact Josephson junction depends strongly on the contact pressure. In order to investigate this dependence we displayed the signal received at a single well-defined radio frequency against the current through the bias resistor stimulating the radiation.

A very light contact pressure yielded the spectrum shown in figure 5. The signal at a bias current of 31.5 mA satisfies the relationship hf = 2eV corresponding to a quantum of radiation being emitted for every electron pair crossing the junction. The other

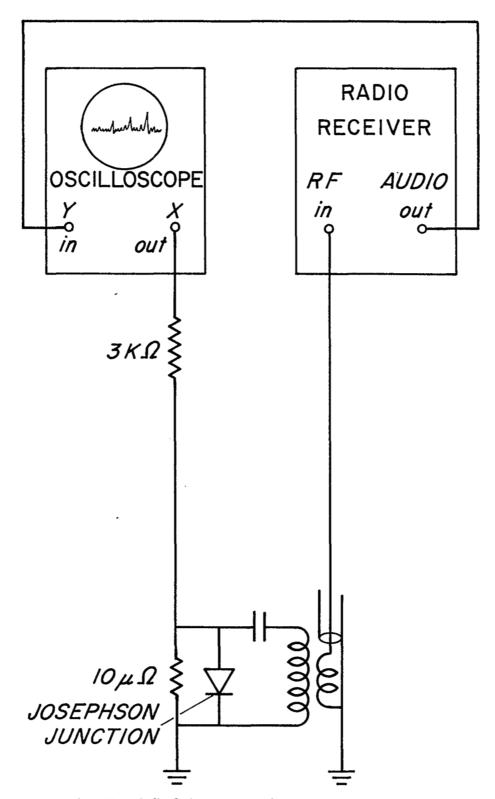


Figure 4. Simplified Apparatus for Josephson Effect

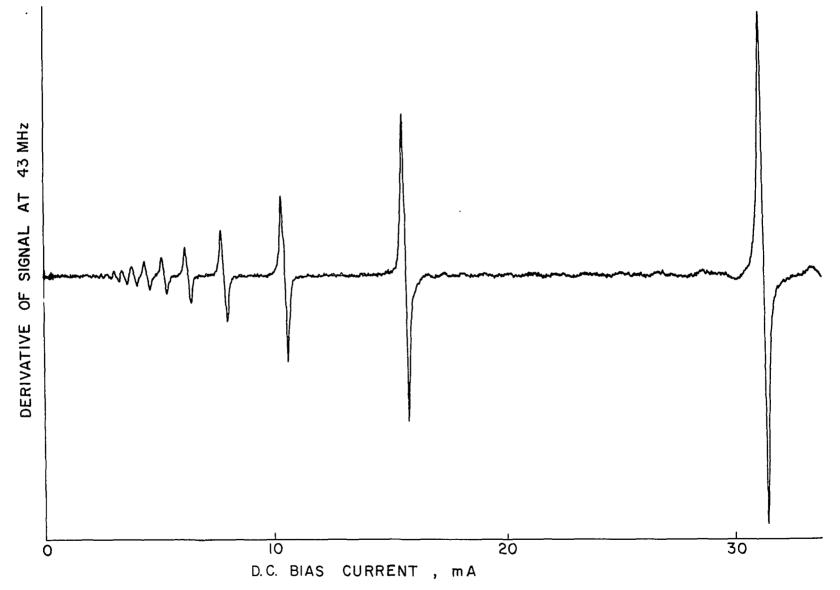


Figure 5. Recorder Trace of Josephson Radiation from Weak Contact

signals occur at bias voltages of 1/2, 1/3, 1/4 etc. of hf/2e (i.e., hf = 2neV, where n is an integer). They correspond to harmonics of the fundamental frequency, indicating that the waveform is far from sinusoidal. Quantum mechanically, they correspond to multiple electron pairs crossing the junction for each radiated quantum.

A heavier contact pressure produced the spectrum shown in figure 6. The initial spike at a bias current of about 5 mA probably corresponds to switching the junction from a mode in which it carries all the bias current with zero voltage to one in which a finite voltage appears. The regular part of the spectrum where the bias current exceeds 10 mA appears to be a strong series of very high harmonics of a fundamental frequency which would occur at an inaccessibly large bias voltage. This can be interpreted as a multiple quantum transition where several equal quanta of radiation are emitted for each electron pair crossing the junction. The frequency f is then related to the bias voltage V by hf = 2eV/N, where N is an integer. The harmonics of this signal which we observe therefore follow the relationship hf = 2neV/N.

Figure 6 corresponds to a very large quantum number N (of the order of 100). The nodes in the spectrum at about 11 mA and 13.5 mA probably indicate a change in quantum number with changing bias voltage. Intermediate behavior between figure 6 and figure 5 may be observed by easing off the contact pressure, lending some conviction to the interpretation of figure 6 which we have given.

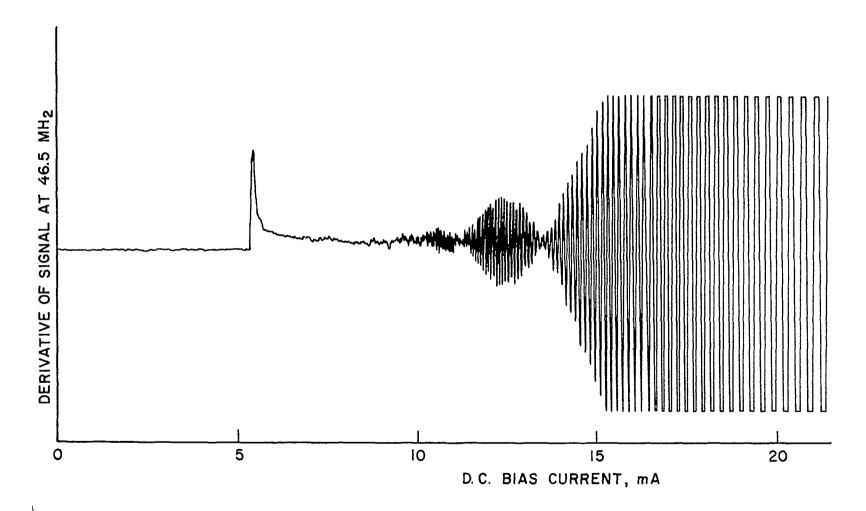


Figure 6. Recorder trace of Josephson radiation from stronger contact

A further increase in contact pressure induces a completely different mode of behavior in some junctions. Above a certain threshold bias current they radiate very sharp, regularly repeating pulses. The observed pulse duration is of the order of 10<sup>-6</sup> sec, and may be limited by the bandwidth of our receiver and oscilloscope. The repeat rate is approximately proportional to the excess bias current over the threshold. The threshold current and repeat rate both depend upon the contact pressure on the junction. Figure 7 shows the repeat rate plotted against the bias current for two settings of the same point-contact junction to different contact pressures. The amplitude of these pulses appears to be independent of the bias current driving them.

We do not understand the exact origin of these pulses. They are probably some kind of relaxation oscillation connected with the negative slope of part of the current-vs-voltage characteristics of the junctions.

## 2.4 Linewidth

In section 3 we will present a simple theoretical calculation of the contribution of thermal noise in the shunt resistor to the linewidth of the radiation. This gives the ultimate limit to the coherence of the radiation when all other sources of noise have been eliminated, a situation which has apparently been achieved by A. H. Silver and J. E. Zimmerman. [10]

We made many measurements of the linewidth of the radiation we observed and occasionally it approached this lower limit. The sharpest signal we observed had a linewidth of 1 kHz, corresponding to an uncertainty in bias voltage of  $2 \times 10^{-12}$  V. Often, however, the

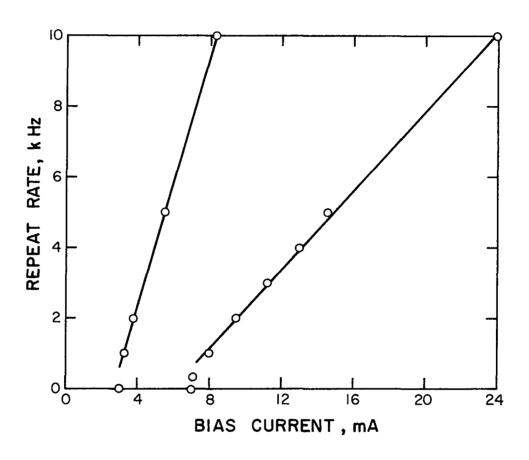


Figure 7. Pulse mode of Josephson junction

linewidth was two or three orders of magnitude greater than this. We do not understand the origin of this excessive noise which we often observe. It could be due to an excessive quasi-particle current generating shot noise in the junction, or thermal noise in the warm parts of the circuit or in metal parts inductively coupled to it, or it could be atmospheric noise picked up by this very sensitive circuit (we have no screened enclosure). Tracing and eliminating this excess noise must be an important part of our future program.

#### 3. THEORY OF THE LINEWIDTH

## 3.1 A Simple Model

As we mentioned in section 2.4, the linewidth of the Josephson radiation is caused by noise. The frequency f of the radiation is related to the bias voltage V by

$$f = 2eV/h = V/\varphi_0 \tag{1}$$

where  $\phi_0$  is the flux quantum, h/2e. Random fluctuations in V due to noise therefore cause a random frequency modulation of the radiation, spreading it out into a spectrum of finite width. Let us consider the effect of thermal noise in the bias resistor R. We start with H. Nyquist's formula for the mean square noise voltage  $\langle V_N^2 \rangle$ 

$$\langle V_{N}^{3} \rangle = 4kTRf_{C}$$
 (2)

where k is Boltzman's constant, T is the temperature and  $f_{\rm C}$  is the width of the band of noise to which the system is sensitive. This extends from zero frequency up to a cutoff which we can estimate by considering the effect of a single Fourier component of the noise spectrum at frequency  $f_{\rm m}$ .

The spectrum obtained by frequency modulating a sine wave over a range  $\delta f$  about a center frequency  $f_0$  at a modulation frequency  $f_m$  is illustrated in figure 8. It consists of an array of equally spaced sidebands at interval  $f_m$ . All the sidebands of significant amplitude occur in the range  $(\xi - \delta f)$  to  $(f_0 + \delta f)$ , so that if  $f_m > \delta f$  there are no large sidebands and a receiver would be insensitive to the modulation. This limit corresponds physically to the variation of phase due to the modulation becoming less than one cycle. It is known as the limit of low modulation index.

Using equation (1) we find

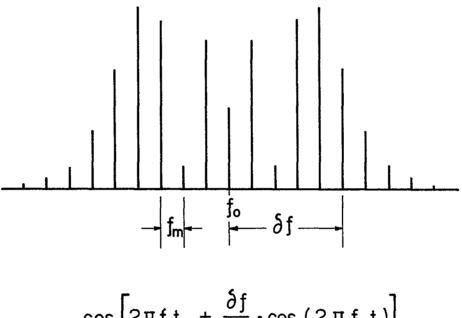
$$\delta f \approx \langle V_{\rm N}^2 \rangle^{\frac{1}{2}} / \varphi_{\rm O} . \tag{3}$$

Applying the condition that  $f_{\rm m}$  must not exceed  $\delta f$  we find that the cutoff frequency  $f_{\rm c}$  in equation (2) is of the same order of magnitude as  $\delta f$ , in equation (3). Equating  $f_{\rm c}$  and  $\delta f$ , combining equations (2) and (3), and defining the full linewidth  $\Delta f = 2\delta f$ , we find

$$\Delta f \approx 8kTR/\phi_0^2 = 2.57 \times 10^7 RT. \tag{4}$$

At our suggestion, A. H. Silver and J. E. Zimmerman at the Ford Scientific Laboratory tested equation (4) over a range of five orders of magnitude in R and a factor four in T. They verified the linear dependence on R and T and found the coefficient to be remarkably close to the prediction of this very simple model. The empirical relationship they found was

$$\Delta f = 3.8 \times 10^7 \text{ RT.} \tag{5}$$



$$\cos \left[ 2\pi f_0 t + \frac{\delta f}{f_m} \cdot \cos \left( 2\pi f_m t \right) \right]$$

Figure 8. Spectrum of Frequency-modulated sine wave

Incidentally, it was a failure to take proper account of the cutoff frequency  $f_{\rm C}$  that led P. W. Anderson to make his pessimistic
predictions about the observability and usefulness of the Josephson
effect at radio frequencies. [6]

# 3.2 Millidegree Noise Thermometry

Equation (4) indicates that the linewidth of the Josephson radiation due to thermal noise is proportional to the absolute temperature of the bias resistor. A more sophisticated calculation would determine the coefficient more accurately in terms of fundamental constants, and the value of the resistance R can always be measured by relating the radiated frequency to the bias current. Measuring this linewidth is therefore a possible method for absolute thermometry.

With some development, it is reasonable to assume that a bias resistor R of  $100\Omega$  would give a usable signal. The limitations on R are imposed by the source impedance (the voltage amplitude of the signal cannot exceed the bias voltage so the available signal power is inversely proportional to the source impedance) and the current drawn by the junction. Taking R to be  $100\mu\Omega$ , then, equation (5) would predict a linewidth of a few Hz at a temperature of 0.001K. This would therefore give a usable range for this technique of thermometry from 0.001K to 10K, a range in which absolute temperature measurements would be exceedingly welcome.

We suggest two methods for measuring linewidths. One is to construct a very narrow band reciever with a crystal-controlled local oscillator and a very low intermediate frequency which is filtered through high-Q circuits (either quartz crystal or superconductor),

It would then be possible to observe the frequency spectrum of the Josephson radiation directly. The other method is to use two Josephson junctions, with independent bias supplies, set to oscillate at frequencies which differ by an interval somewhat greater than the linewidth. If they radiate into a common receiver it would be possible to detect a beat between the two signals which carries the combined fluctuations. The scatter in successive measurements of this beat frequency by a frequency counter would then be a measure of the linewidth.

It is necessary to have a bias current supply which contributes negligible noise to the system. Electronically stabilized current supplies are usually too noisy for this purpose. K. F. Knott [12] has shown that the noise level in ordinary dry cell batteries is low enough to be acceptable for this purpose. Hopefully mercury cells would be even better, and there should be no serious problem in making a simple current supply with a mercury cell and a chain of fixed and variable resistors which would be adequate for these linewidth measurements.

The development of this technique for low temperature thermometry is one of the future goals of our program.

#### 4. A PICOVOLTMETER

We have designed and tested a prototype instrument for measuring very small voltage. In its final form, we hope it will be a direct-reading, differential, digital voltmeter with a sensitivity which may approach  $10^{-15}$  V and whose calibration is already known to a few parts per million. We have presently reached a sensitivity of  $10^{-10}$  V.

The idea is to have two Josephson junctions connected in parallel in a superconducting loop broken only by a very small resistor. Both junctions are biased (at about  $10^{-7}$  V) to oscillate at about 45 MHz, but their frequencies differ by an amount proportional to the voltage developed across the small resistor. Their signals will therefore beat and if they are coupled into a common receiver the beat note can be extracted and used to drive a frequency counter. The reading of the frequency counter would then be related to the small voltage difference by the usual 483.591 Hz per pV.

Our prototype instrument is shown schematically in figure 9. The detailed layout we have used for the pair of Josephson junctions is shown in figure 10. They are built on a common split brass block, parts of which serve as the  $10^{-5}\Omega$  (nominal) bias resistors shown in figure 9. The connections between the junctions are all made with niobium wire, except for the  $10^{-8}\Omega$  (nominal) resistor, which consists of a piece of copper foil tinned with superconducting lead-tin solder on opposite faces. The niobium leads are in intimate contact with the solder and form a superconducting connection strong enough to carry the current of a few mA which passes. The RF transformer

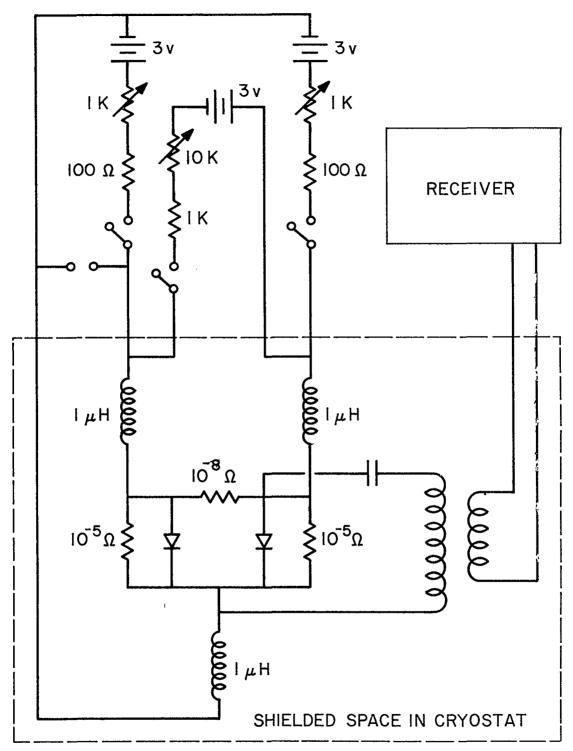


Figure 9. Schematic Diagram of Picovoltmeter

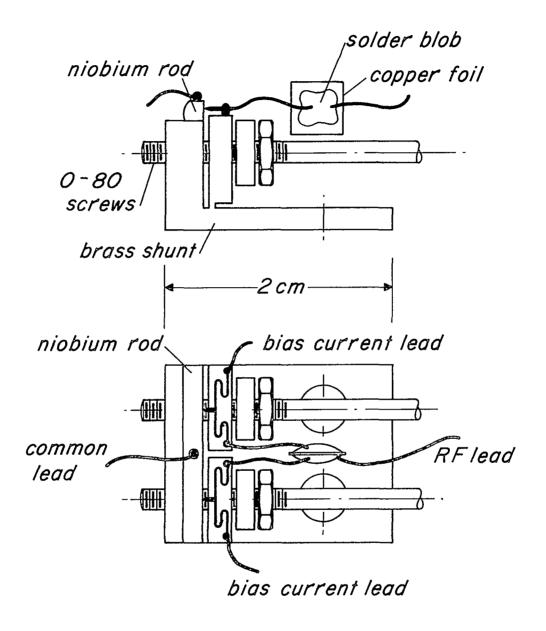


Figure 10. Layout of double Josephson Junction for Picovoltmeter

and receiver are both tuned to 45 MHz, and in operation the common bias voltage across the two junctions is adjusted so that they radiate at this frequency. In order to detect the complete spectrum of radiation emitted by the junctions, we used our broad-band receiver, with a bandwidth of about 2 MHz.

In some preliminary runs, we replaced the  $10^{-8}\Omega$  (nominal) resistor by a larger one ( $\sim 10^{-6}\Omega$ ) so as to have a large range of frequency offset (i.e. beat frequency) available. We found that we could indeed observe the individual signals from the two junctions as well as the beat between them. We observed beat frequencies down to about 50 kHz, corresponding to about  $10^{-10}$  volts. The system was too noisy in its present state to go any lower.

We then inserted the  $10^{-8}\Omega$  (nominal) resistor. Our expectation was that this very low resistance connection between the two junctions would tend to maintain a constant voltage difference despite the fluctuation of the common voltage due to noise, so that the beat frequency would remain relatively steady even though the carrier fluctuates over a wide band. We did indeed observe a very strong, clean signal which could operate our frequency counter directly and appeared to be stable to 100 Hz. At first we took this to be the beat note we were seeking, but we were disturbed to find that it did not respond as we expected to adjustment of the balance of the bias current supplied to the system. Our present interpretation is that this strong signal originates from the pulse mode of operation of the junctions rather than a beat between their true Josephson signals. The best voltage measurement we can claim, therefore, is the 10<sup>-10</sup> volts obtained during the preliminary run. This work is in an early stage and we hope for a dramatic improvement in sensitivity after further development.

#### 5. THIN FILM TUNNEL JUNCTIONS

With the development of instruments based on the Josephson effect into their final form it will become desirable to replace the adjustable point contact junctions by more permanent structures. To this end we have investigated several different methods for making tunnel junctions between thin films of niobium and lead, as these appear to survive aging better than most other combinations of thin films. It is necessary to separate the two metal films with a thin insulating layer, and it is usual to use the oxide of one of the metals for this purpose. One complication we must face is that the lowest oxide of niobium is itself a superconductor so it is necessary to use either a higher oxide of niobium or one of the oxides of lead. There is also the restriction that in order to form a superconducting film of niobium it is necessary to heat the substrate to 400C during or after deposition, and this temperature would destroy any thin oxide layer. It is therefore necessary to deposit the niobium film first and the lead afterwards. In the following paragraphs we comment on the various methods we have tried for forming oxide barriers, ending with a method which appears to be distinctly superior to all the others.

The first method was to expose the freshly deposited niobium film to oxygen. We tried dry oxygen at pressures varying  $10^{-6}$  torr to atmospheric, and water-saturated oxygen at atmospheric pressure. We also tried varying the film temperature during oxidation in a range from ambient up to 130C, and the time of exposure in a range from 5 minutes up to 18 hours. Results were disappointing. We obtained a few junctions which showed interesting tunneling behavior, but most of the junctions prepared this way contained metallic shorts due to pinholes in the oxide layer. These shorts sometimes became super-

conducting at 4K and usually destroyed the tunneling phenomenon. The situation was slightly improved by giving the niobium films a preliminary exposure to oxygen at a low pressure (between  $10^{-6}$  torr and 1 torr) in the presence of a source of ionization, followed by oxidation at atmospheric pressure. In this way we were able to build up junctions with resistances over 10000 at room temperature, indicating substantial oxide barriers, but these junctions did not show satisfactory tunneling characteristics. We also tried exposing the oxidized films to boiling water to seal the pores, as is commonly done to anodized aluminum. This produced junctions with high resistance but unsatisfactory tunneling characteristics. In summary, this technique is capable of producing usable junctions but the yield is very low.

The second method was to evaporate niobium onto the surface of the film slowly in an atmosphere of oxygen at a pressure of about  $10^{-6}$  torr. We tried this several times with no success at all. The resulting oxide layers always had enough pinholes to destroy the tunneling phenomenon completely.

The third method was to immerse the films in dilute nitric acid at ambient temperature. Every batch we have made by this method so far contained at least one good tunneling junction. We varied the strength of the acid in the range from 1/4% to 20%, and the exposure time in the range from one minute to 2 hours. In general a weaker acid solution requires a longer time, as one might expect. Our best batch so far was immersed for 2 hours in 1/4% nitric acid. All the resulting junctions had resistances of some tens of ohms at room temperature, and 5 out of 8 showed good and usable tunneling characteristics.

The fourth method was anodizing. We used weak solutions of nitric acid, chromic acid, hydrogen peroxide and also nominally "demineralized" water, which still contained sufficient impurity for a usable conductivity. We tried stabilizing the voltage at 1.5 volts and stabilizing the current at lower levels than would pass at 1.5 volts, and we ran for periods up to 5 minutes. A large number of attempts failed to yield any satisfactory junctions. They all contained shorts, probably due to pinholes in the oxide layer.

The fifth method was oxidation in a glow discharge in oxygen gas at  $4 \times 10^{-3}$  torr pressure. Exposure for  $\frac{1}{2}$  hour at ambient temperature produced junctions whose resistances were in the range from  $200 \times 2000$ . They appeared to be free of shorts and some of the junctions of lower resistance displayed feeble tunnel characteristics at 4K. Clearly these oxide barriers were too thick and the possibility remains of producing usable tunnel junctions by this method after adjustment of the exposure time.

Finally, our best method. After depositing the niobium film on a substrate at 400C, we cooled it down with liquid nitrogen to near 80K and exposed it to a glow discharge in pure oxygen, at a pressure of 0.05 torr, for about 20 minutes. We then pumped out the oxygen and warmed the film up to a temperature between -10C and 0C. We then immediately cooled the substrate down to 80K again with liquid nitrogen and deposited the lead film. The result was a 60% yield of junctions, with resistances near  $1\Omega$  at ambient temperature, which showed the best tunneling characteristics we have yet seen at 4K. They appeared to be almost entirely free of metallic shorts.

The conditions must be controlled rather well to produce these results. The temperature to which the substrate is warmed after exposure to the glow discharge has a profound influence on the thickness of the barrier. If this temperature is too high, no barrier forms at all. If it is too low, then a good oxide barrier forms but the resistance of the junction increases slowly with time until it becomes unusable. We have checked that the presence of the glow discharge is indeed essential to the process.

Our interpretation of these results is that the glow discharge forms ozone, which condenses on the cold niobium film (indeed, a frost is visible at this stage) and evaporates, leaving a thin uniform adsorbed layer, when we warm it up (the frost disperses at about -40C). The ozone probably attacks the lead film, when it is deposited, forming a layer of lead oxide. In support of this interpretation we observed on one occasion, when we ran the discharge for a longer time than usual and failed to warm the substrate afterwards, that the lead film was completely oxidized.

This appears to be an excellent method for making tunnel junctions. In the future we intend to continue to investigate the influence of variations in conditions and to test these junctions in Josephson effect devices.

#### 6. CONCLUSIONS

At this point the Josephson effect appears to be extremely promising for application to low noise electronics in the radio frequency range. It can be observed with simple equipment and the linewidth, which limits resolution, is small and calculable. As a contribution towards the realization of this promise we have done some of the initial development of a millidegree thermometer and a picovoltmeter, and made some contribution to the art of fabricating junctions.

#### APPENDIX

# Electromagnetic Properties of Josephson Junctions

For background information, we include here a brief sketch of the electrical properties of Josephson junctions which had been observed before the work described in this report.

The relationship between current and voltage, that would be observed with a DC source supplying current through a low-pass filter, is shown for a point-contact junction in figure 11a and for a thin film junction in figure 11b. Both types of junction pass current at zero voltage, but they differ in their response to a finite voltage.

The shape of the response curve for a point-contact varies strongly with contact pressure and condition of the contacts and may include an unstable region of negative differential resistance.

The main features of the response curve for a thin film junction are more reproducible. In particular, the voltage at which the sharp rise in current occurs is related to the energy gaps of the superconductors forming the junction. The quantity  $I_{\rm C}$  (see figure 11b) is very sensitive to a magnetic field applied in the plane of a thin film junction, and responds as shown in figure 12. The spacing of the nodes of this curve depends upon the geometry of the junction and is typically of the order of 10 microtesla.

If a thin film junction is connected to a resonant circuit, a peak appears in its DC current vs. voltage characteristic as shown in figure 13a. The voltage V at which the peak occurs is related to the resonant frequency f by 2eV = hf, where e is the electron charge and h is Planck's constant. In the presence of electromagnetic radiation the

DC characteristics of both point contact and thin film junctions assume the step structure shown in figure 13b. The steps occur at equal intervals V of voltage given by 2 eV = hf, where f is the frequency of the incident radiation.

The response to alternating voltage and current is quite complex. Thin film junctions can propagate electromagnetic waves, with a slow phase velocity compared with free space. In the presence of a transverse magnetic field they can also sustain standing waves. The impedance presented by either a point contact or a thin film junction of small area appears like a leakage resistance connected in parallel with the capacitance C of the junction and an effective inductance L given by

$$L = (\hbar/2e)(I_0^2 - I^2)^{-\frac{1}{2}}$$

where I is the instantaneous current and  $I_0$  is related to the maximum current which may be sustained at zero voltage. This results in a passive resonance at a frequency  $1/2\pi\sqrt{LC}$  which depends upon the average current through the junction. Another consequence of this non-linear impedance is self-oscillation, with a saw-tooth waveform, at a frequency  $2\,eV/h$ , where V is the average voltage.

### REFERENCES

- 1. B. D. Josephson: Physics Letters 1, 251 (1962).
- 2. B. D. Josephson: Rev. Mod. Phys. 36, 216 (1964).
- 3. B. D. Josephson: Advances in Physics 14, 419 (1965).
- 4. W. H. Parker, B. N. Taylor and D. N. Langenberg: Phys. Rev. Letters 18, 287 (1967).
- 5. D. N. Langenberg, D. J. Scalapino, B. N. Taylor and R. E. Eck: Phys. Rev. Letters 15, 294 (1965).
- 6. P. W. Anderson: Proceedings of the Ravello Spring School, (1963), p.113.
- 7. J. E. Zimmerman, J. A. Cowen and A. H. Silver: Appl. Phys. Letters 9, 353 (1966).
- 8. A. H. Silver and J. E. Zimmerman: Appl. Phys. Letters 10, 142 (1967).
- 9. J. E. Zimmerman and A. H. Silver: Phys. Rev. Letters 19, 14 (1967).
- 10. A. H. Silver, J. E. Zimmerman and R. A. Kamper: Appl. Phys. Letters 11, 209 (1967).
- 11. R. A. Kamper: Symposium on the Physics of Superconducting Devices, Charlottesville, ONR Report, p. M-1 (1967).
- 12. K. F. Knott: Electronics Letters 1, 132 (1965).

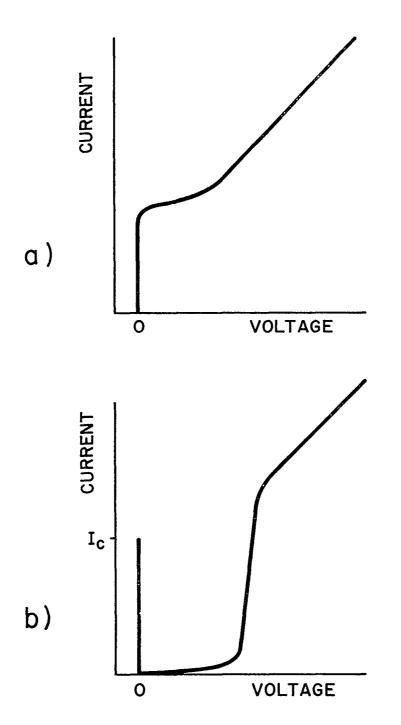


Figure 11. Typical current vs. voltage characteristics of a) point contact and
b) thin film Josephson junctions.

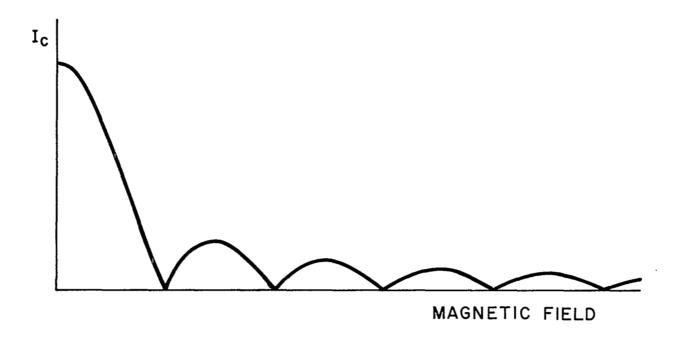
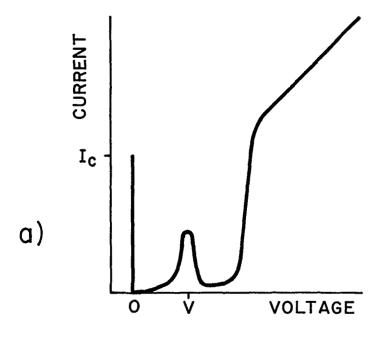


Figure 12.  $I_c$  (see fig. 11b) plotted against tangential magnetic field for a typical thin film Josephson junction.



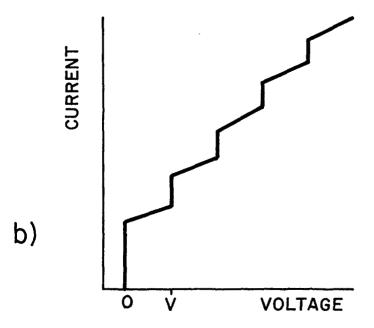


Figure 13. Typical current vs. voltage characteristics of Josephson junctions coupled to a) a resonant circuit tuned to frequency f; b) electromagnetic radiation at frequency f, where hf = 2 eV.