

III. DISCUSSION

The values of the parameters of the model in the weak coupling case as obtained by fitting the experimental curves⁷ for K_s/K_n versus T/T_c with the theoretical expression are such that \bar{p} is approximately equal to \bar{p}' and \bar{p} is also nearly unity.

The values of τ_n/τ_s versus $\epsilon/k_B T$ at different reduced temperatures $t=T/T_c$ for weak electron-phonon coupling (indium) are presented in Fig. 2. It may be observed that τ_s is comparable with τ_n and is greater than τ_n for excitation energies $\epsilon/k_B T > 2$. For small excitation energies the relaxation time of the normal-state excitation is greater than that of the quasiparticle in the superconducting state at the same temperature.⁸ In the case of strong electron-phonon interaction it may be

⁸ It is interesting to note that this behavior is similar to that obtained by Tewordt for the ratio of the lifetime of the quasiparticle in the superconducting and the normal state. (See Fig. 2 of the Ref. 2.)

observed that for $t=0.80$, τ_s is as large as 10^{14} times the relaxation time of the normal-state excitation. The usual expressions for the rate of momentum transfer from the phonons to the quasiparticles do not provide an answer to such a large value of τ_s/τ_n even at 0°K. It appears that some other interaction is needed to decrease enormously the effective matrix elements for Hg and Pb.

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Energy Gap Measurements by Tunneling Between Superconducting Films. I. Temperature Dependence

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The electron tunneling technique was used to measure the energy gap $2\Delta(t)$ as a function of temperature in aluminum and tin films. The temperature dependence of the normalized gap $\Delta(t)/\Delta(0)$ for each film agreed rather well with the BCS theory, although a small consistent deviation was found in which the measured values of the gap were slightly larger than predicted by theory. In the case of aluminum, considerable random scatter in the absolute values of $2\Delta(0)$ for the various films was found.

I. INTRODUCTION

EXPERIMENTAL measurements by Giaever¹ and Nicol *et al.*² between pairs of superconducting metals separated by a thin dielectric layer have shown that the density of (excited) states of each superconductor is reflected in the current-voltage characteristics in a dramatic way. They have shown that one can identify the energy gap of both metals more or less unambiguously. These early experiments were soon followed by additional measurements³⁻¹⁰ along with

clarification of various theoretical points.¹¹⁻¹³ Measurements of the temperature dependence of the energy gap by this technique have been reported and the results have been compared with the predictions of the Bardeen, Cooper, and Schrieffer (BCS) Theory.¹⁴ For tin, the data of Giaever and Megerle³ and of Townsend and Sutton⁷ both indicate that the experimental values of the gap are larger than theoretical at intermediate temperatures. In the case of aluminum, good qualitative agreement is achieved with theory, but large scatter in the data prevented a quantitative comparison.

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¹ I. Giaever, Phys. Rev. Letters **5**, 464 (1960).

² J. Nicol, S. Shapiro, and P. H. Smith, Phys. Rev. Letters **5**, 461 (1960).

³ I. Giaever and K. Megerle, Phys. Rev. **122**, 1101 (1961).

⁴ M. D. Sherrill and H. H. Edwards, Phys. Rev. Letters **6**, 460 (1961).

⁵ N. V. Zavaritskii, Zh. Eksperim. i Teor. Fiz. **39**, 1193 (1961) [English transl.: Soviet Phys.—JETP **12**, 831 (1961)].

⁶ D. H. Douglass, Jr., Phys. Rev. Letters **7**, 14 (1961).

⁷ P. Townsend and J. Sutton, Phys. Rev. **128**, 591 (1962).

⁸ I. Giaever, H. Hart, and K. Megerle, Phys. Rev. **126**, 941 (1962).

⁹ N. V. Zavaritskii, Zh. Eksperim. i Teor. Fiz. **41**, (1961) [English transl.: Soviet Phys.—JETP **14**, 470 (1961)].

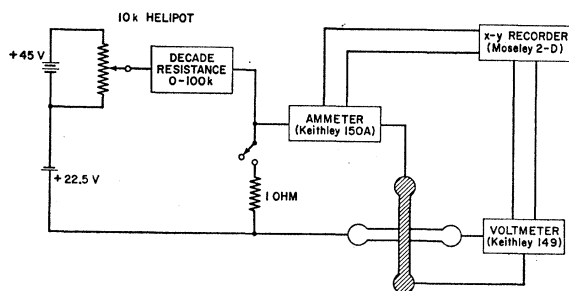
¹⁰ S. Shapiro, P. H. Smith, J. Nicol, J. Miles, and P. M. Strong, IBM J. Res. Develop. **6**, 34 (1962).

¹¹ J. Bardeen, Phys. Rev. Letters **6**, 57 (1961).

¹² M. H. Cohen, L. M. Falicov, and J. C. Phillips, Phys. Rev. Letters **8**, 316 (1962).

¹³ W. A. Harrison, Phys. Rev. **123**, 85 (1961).

¹⁴ J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

FIG. 1. Circuit used to measure I versus V .

We report in this paper rather extensive measurements on aluminum and tin in which an effort was made to measure both the temperature and the value of the gap with some accuracy.

II. EXPERIMENTAL MEASUREMENTS

The $\text{Al}/\text{Al}_2\text{O}_3/\text{Pb}$ junctions were prepared in a conventional manner. A long strip of aluminum was evaporated onto a microscope slide. After exposure to the air to form the oxide, three short lead cross strips were evaporated. (In the case of $\text{Sn}/\text{Al}_2\text{O}_3/\text{Sn}$, after depositing the first layer, a very thin layer of aluminum was evaporated and then allowed to oxidize completely.) Measurements of the film thicknesses were made at a later time by the Tolansky multiple-beam technique¹⁵ with a precision of about $\pm 20 \text{ \AA}$.

Temperatures were measured with a resistance thermometer bridge¹⁶ which had been calibrated against a paramagnetic salt. Using an automatic temperature regulator¹⁷ with the bridge, the relative temperature could be regulated and measured to $60 \times 10^{-6} \text{ K}$. The circuit (Fig. 1) shows schematically the power source, junctions, and measuring instruments used to record the current-voltage (I - V) characteristic curves.

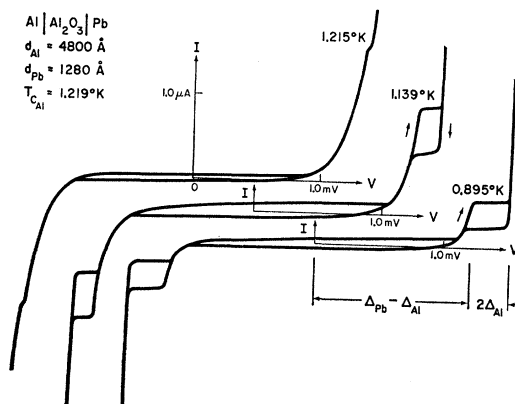
A. Aluminum

Current-voltage measurements were made on a total of eight different $\text{Al}/\text{Al}_2\text{O}_3/\text{Pb}$ junctions as a function of temperature. Typical I - V curves are shown in Fig. 2, where the energy gap (2Δ) for both Pb and Al are identified in the usual way.^{1,2} The negative resistance region is not seen because the junction was driven from a high impedance source (i.e., current generator). (The hysteresis loop around the origin is a circuit instability caused by the finite impedance of this "constant current" source.) In the early stages of this investigation, serious attention was given to the full I - V curve to ascertain the symmetry about the origin; it was found that with proper adjustment of the circuit parameters

the curves could be made completely antisymmetric. (See the next section for additional discussion of this point.) One further advantage of taking the whole curve is that thermal emf's can be ignored by taking the point of symmetry as the origin.

The temperature dependence of the Al gap is illustrated in Fig. 3, which shows in a series of curves (positive voltage portion only), how the gap increases in going from T_0 down to the lowest temperature attained, 0.872°K . These curves can be directly compared with each other since all conditions except the temperature were kept constant. (The origin of each curve has been displaced to prevent overlapping.)

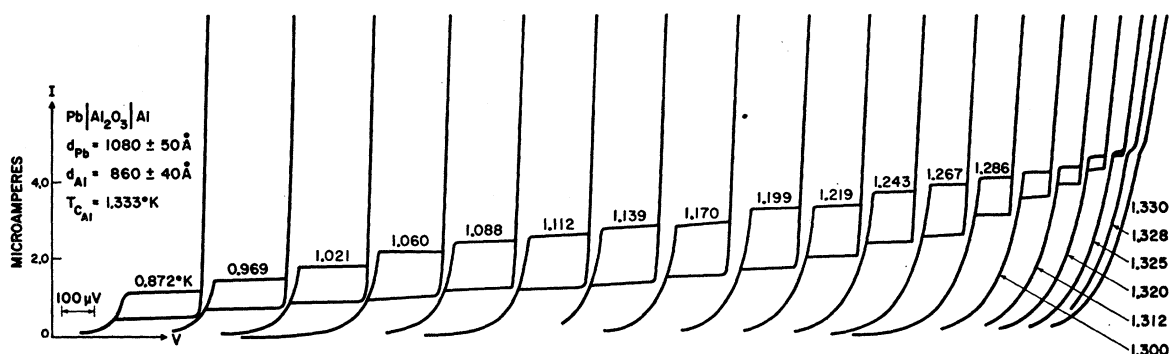
The experimental I - V curves are similar to, but not coincident with, current theoretical calculations. At $eV = \Delta_{\text{Pb}} - \Delta_{\text{Al}}$, a logarithmic singularity in I is predicted,¹⁰ whereas, experimentally a rounded maximum is observed, and at $\Delta_{\text{Pb}} + \Delta_{\text{Al}}$ the predicted discontinuity in V is observed as a sharp rise of finite curvature and finite slope. The cause of this rounding of singularities is not certain, but it presumably is caused by finite lifetime effects or a distribution of energy gaps in the individual crystallites owing to anisotropy or variations in strain. It was noted that the amount of rounding was not noticeably different for different temperatures and different film thicknesses. Because the data is evidently more precise than the above discrepancies with the theory, the operational definition of the aluminum energy gap illustrated in Fig. 4 was adopted. Line (a) is tangent to the curve at its first point of inflection (starting from the origin); line (b) is parallel to line (a) and tangent to the curve on the other side of the minimum in dynamic resistance; the aluminum energy gap $2\Delta_{\text{Al}}$ is defined as the horizontal distance between these lines. This criterion has the following characteristics: It is completely objective, reproducible, and unaffected by recorder gain for all values of the gap; it agrees well with any "reasonable" criterion for large, sharp gaps, for which there is little ambiguity. For small gaps where the negative resistance region is

FIG. 2. Full I - V curves for an $\text{Al}/\text{Al}_2\text{O}_3/\text{Pb}$ junction (from x - y recorder tracing).

¹⁵ S. Tolansky, *Multiple Beam Interferometry* (Oxford University Press, New York, 1948).

¹⁶ C. Blake, C. E. Chase, and E. Maxwell, *Rev. Sci. Instr.* **29**, 715 (1958).

¹⁷ C. Blake and C. E. Chase, *Rev. Sci. Instr.* **34**, 984 (1963).

FIG. 3. Partial I-V curves for Pb/Al₂O₃/Al junction showing temperature dependence of the Al gap (from x-y recorder tracing).

no longer present, but the influence of the gap is clearly seen on the I-V curve (e.g., near T_c or in a magnetic field near H_c), this criterion gives a self-consistent interpolation scheme with the correct limiting value for no gap.

Using this criterion, the energy gap of aluminum was obtained with eight different junctions corresponding to aluminum thicknesses ranging from 420 to 9850 Å. The temperature dependence of 2Δ for three representative junctions is shown in Fig. 5; the same data is then replotted in Fig. 6 against $B(t)$, the function predicted by BCS in the weak coupling limit.¹⁸

From the data, one can see that the points follow along smooth curves with very little scatter. In Fig. 6, the best smooth curve going through the origin has been extrapolated to $B(t)=1$ (i.e., $t=0$). An exact fit to the BCS function allowing for an adjustable $2\Delta(0)$ would appear as a straight line on this plot; the experimental points lie higher in the middle of the range by

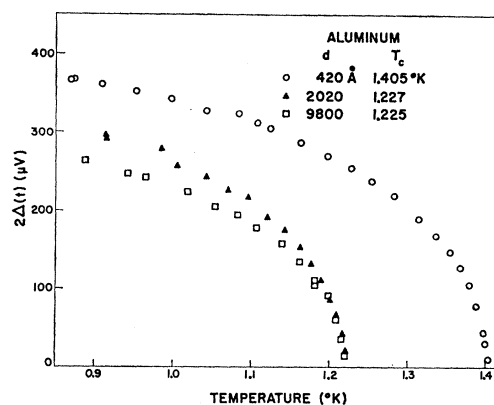
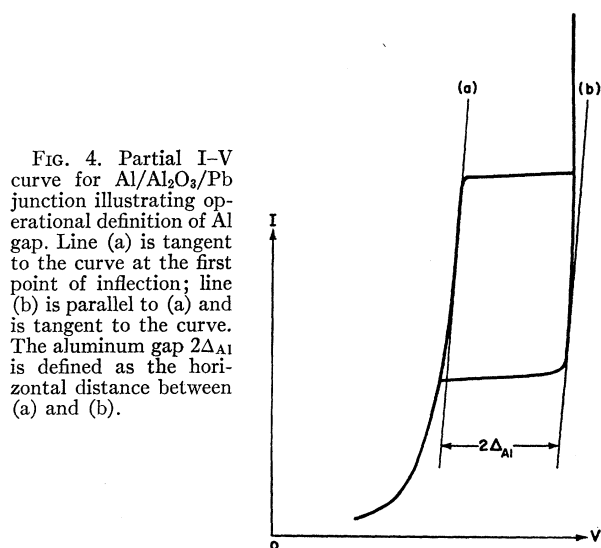
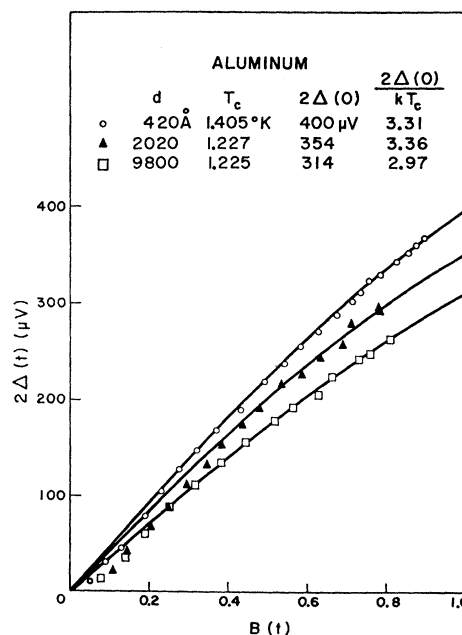
FIG. 5. Energy gap $2\Delta(t)$ of Al versus T for 3 different thicknesses.

FIG. 4. Partial I-V curve for Al/Al₂O₃/Pb junction illustrating operational definition of Al gap. Line (a) is tangent to the curve at the first point of inflection; line (b) is parallel to (a) and is tangent to the curve. The aluminum gap $2\Delta_{\text{Al}}$ is defined as the horizontal distance between (a) and (b).

¹⁸ The theoretical normalized gap function $B(t) = \Delta(t)/\Delta(0)$ in the weak-coupling limit has been tabulated by B. Muhlschlegel, Z. Physik 155, 313 (1959).

FIG. 6. Energy gap $2\Delta(t)$ of Al versus theoretical value $B(t)$ for three different thicknesses.

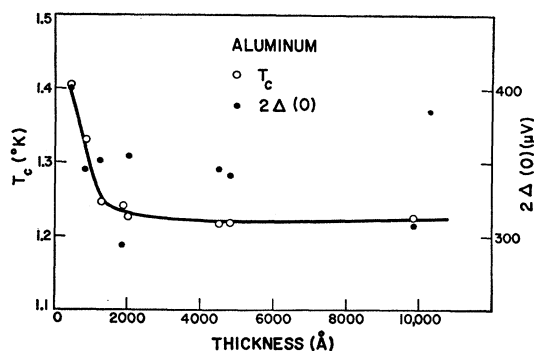
FIG. 7. Energy gap $2\Delta(0)$ of Al and T_c versus thickness.

TABLE I. Characteristics of the aluminum films.

Thickness (Å)	T_c (°K)	$2\Delta(0)$ (μV)	$2\Delta(0)/kT_c$
420±20	1.405	400	3.31
860±40	1.330	345	3.01
1280±20	1.246	351	3.27
1880±60	1.241	294	2.75
2020±20	1.227	354	3.36
4520±40	1.217	346	3.30
4800±50	1.219	342	3.26
9850±50	1.225	314	2.97

about 5% above such a line. Near $T_c(B(t) \rightarrow 0)$, the measured values lie below the smooth curve which has been drawn through the origin. This probably means that different crystallites have slightly different transition temperatures, an effect which would distort the curve near T_c but have little effect at low temperatures. Table I gives the measured T_c and extrapolated $2\Delta(0)$ for each of the eight films and Table II gives the measured $2\Delta(0)$ for the lead films. The transition temperature and $2\Delta(0)$ for Al have been plotted in Fig. 7 as a function of thickness. It is seen that T_c follows a smooth curve which rises steeply for small d , a result that is in good agreement with measurements of

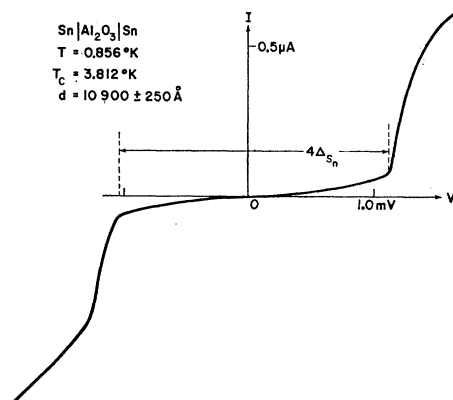
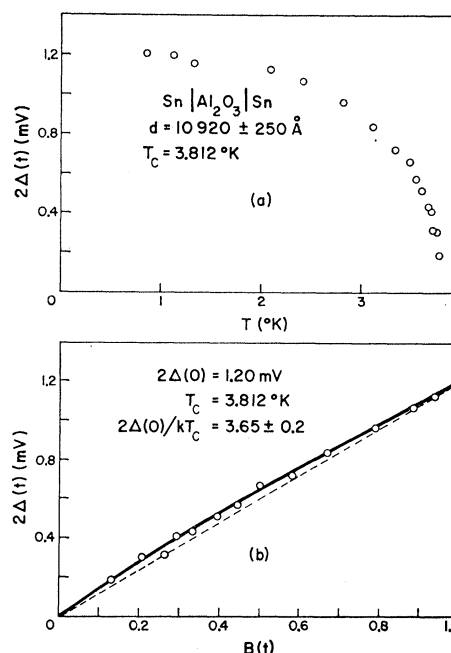
FIG. 8. Current-voltage curve for a Sn/Al₂O₃/Sn junction illustrating the energy gap $2\Delta_{Sn}$ (from x-y recorder tracing).

TABLE II. Characteristics of the lead films.

d	$2\Delta(0)$ (mV)
1080±50	2.42
1100	2.60
1280±60	2.60
1700	2.53
1800	2.60
2130	2.62
2300±150	2.68
	2.59 = Average

Khukhareva.¹⁹ The phenomenon of the rise of T_c for small d is quite well known^{20,21} and is due to differential contraction of the substrate and the film. On the other hand, the values of $2\Delta(0)$, although showing the same

FIG. 9. Energy gap $2\Delta(t)$ of Sn versus (a) temperature and (b) BCS theoretical function.

trend as T_c expected from the law of corresponding states, show much scatter; no explanation is offered for this. Thus, for these aluminum films, although $2\Delta/kT_c$ can be measured to 3 significant figures, the agreement between films is not better than 2 significant figures.

B. Tin

A junction of Sn/Al₂O₃/Sn was prepared with a Sn thickness of $10\,920 \pm 250$ Å. The tin energy gap $2\Delta_{Sn}$ was determined from the I-V curves as indicated in

¹⁹ I. S. Khukhareva, Zh. Eksperim. i Teor. Fiz. **43**, 1173 (1962) [English transl.: Soviet Phys.—JETP **16**, 828 (1963)].

²⁰ J. M. Lock, Proc. Roy. Soc. (London) **208**, 391 (1951).

²¹ A. M. Toxen, Phys. Rev. **127**, 382 (1962).

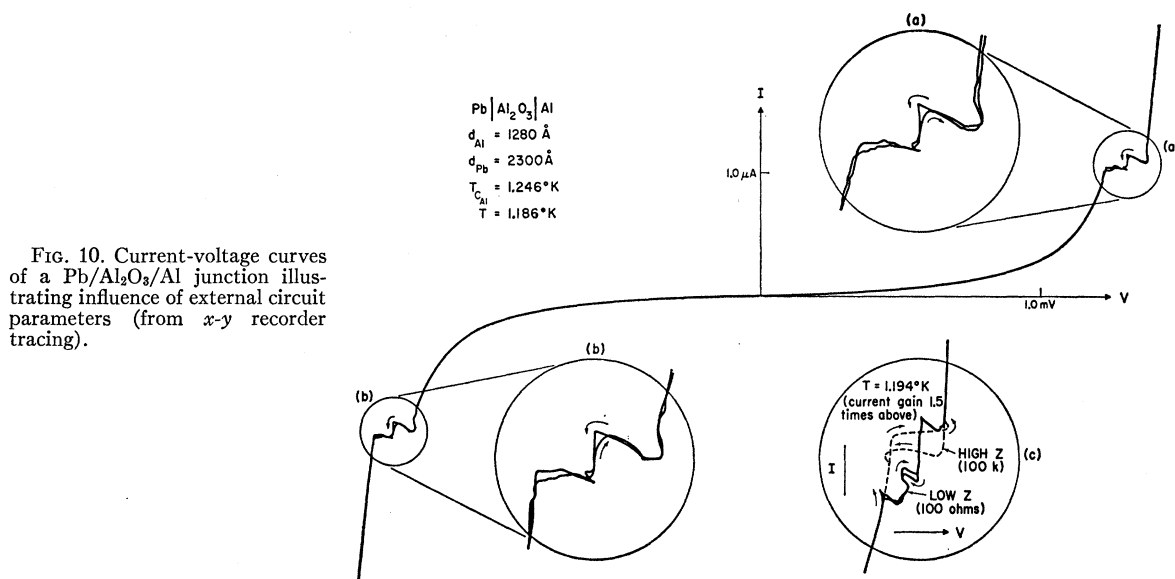


FIG. 10. Current-voltage curves of a Pb/Al₂O₃/Al junction illustrating influence of external circuit parameters (from *x-y* recorder tracing).

Fig. 8. Values of 2Δ determined in this way plotted versus temperature are shown in Fig. 9(a); and, in Fig. 9(b), they are plotted against the theoretical function, $B(t)$. The experimental values appear to lie above the theoretical curve and thus agree with the observations of Townsend and Sutton.⁷ Also, an analysis of surface impedance data on Sn by Waldram²² implies an upward deviation from the BCS theory. The present measurement gives $2\Delta(0)/kT_c = 3.65 \pm 0.2$, where the error is the estimated systematic error of determining $2\Delta(0)$ from the curves.

III. DISCUSSION

By and large, measurements of the gap showed rather good agreement with the temperature dependence of the BCS theory with the experimental values being slightly larger than theory. For Al, considerable scatter in the value of $2\Delta(0)$ among specimens was observed. A control experiment in which most of the original evaporated junction edges were removed with a diamond scribe showed no effect on the I-V characteristic indicating that the observed scatter probably was not due to edge effects.

Attempts to resolve any possible structure in the negative resistance region revealed some interesting effects. In Fig. 10 is shown a full I-V curve with apparent structure in the gap which was observed on

one occasion. Except for the negative resistance region, the curve is antisymmetric about the origin. The negative resistance regions for both $+V$ and $-V$ [regions (a) and (b)] have been enlarged to illustrate the detail. Note that they are not antisymmetric with each other as expected. It is seen that the regions are identical and can be superimposed by a translational displacement only. It was found that the details of the negative resistance region were sensitive to external circuit parameters (i.e., ground points, lengths of cable, capacitance across the junction, etc.). A change of these parameters could change the features of the negative resistance region and even its symmetry. Figure 10(c) shows the effect of a change in source impedance on this same junction (at a slightly different temperature). However, it was always possible with careful attention to grounding points and impedances to make the two regions completely antisymmetric with no sign of any structure in the negative region. These observations have been reported in some detail to show that caution should be used in interpreting phenomena in the negative resistance region.

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²² J. R. Waldram, International Conference on the Science of Superconductivity, 1963 (to be published).