CURRENT DEPENDENCE OF THE ENERGY GAP IN SUPERCONDUCTORS:
A DIRECT MEASUREMENT

Thesis by
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In Partial Fulfillment of the Requirements
For the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California
1966
(Submitted May 19, 1966)
ACKNOWLEDGMENTS

Inevitably, over several years of graduate studies, I have become indebted for advice, help, and moral support, to more people than could possibly be acknowledged in necessarily limited space. While extending my thanks to all, I must make specific mention of those to whom my obligation is particularly overwhelming.

Far more than a mere advisor, Dr. J. E. Mercereau has ever been most generously available with counsel, inspiration, and guidance throughout my graduate career. My thanks are most inadequate even to begin to cover my indebtedness to him.

To Dr. R. P. Feynman I owe deep gratitude not just for a number of stimulating and illuminating discussions, but even more for the enthusiasm that he has repeatedly inspired by his continued interest in the field of low-temperature physics.

I must also acknowledge a debt to Prof. M. Tinkham, of the University of California at Berkeley, whose most lucid course, given in 1961, at the Les Houches Summer School for Theoretical Physics of the University of Grenoble, both laid the foundation for whatever understanding I may have of modern superconductivity and also inspired the simple theoretical calculations that led directly to the present investigation.

Finally, I am grateful to the California Institute for the award of a number of fellowships: The Standard Oil Company of California fellowship, 1959-61; a summer fellowship from Woodrow Wilson
funds, which enabled me to attend, in 1961, the above mentioned
summer school; the General Atomic Fellowship, 1962-63; and a special
fellowship, 1964-65.

C. D. M.
ABSTRACT

From the tunnelling characteristics of a tin-tin oxide-lead junction, a direct measurement has been made of the energy-gap variation for a superconductor carrying a current in a compensated geometry. Throughout the region investigated — several temperatures near $T_C$ and down to a reduced temperature $t = 0.8$ — the observed current dependence agrees quite well with predictions based on the Ginzburg-Landau-Gor'kov theory. Near $T_C$ the predicted temperature dependence is also well verified, though deviations are observed at lower temperatures; even for the latter, the data are internally consistent with the temperature dependence of the experimental critical current. At the lowest temperature investigated, $t = 0.8$, a small "Josephson" tunnelling current allowed further a direct measurement of the electron drift velocity at low current densities. From this, a preliminary experimental value of the critical velocity, believed to be the first reported, can be inferred on the basis of Ginzburg-Landau theory. For tin at $t = 0.8$, we find $v_c = 87 \text{ m/sec}$. This value does not appear fully consistent with those predicted by recent theories for superconductors with short electronic mean-free-paths.
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CHAPTER I - INTRODUCTION

Few phenomena in the history of modern physics have been so successful at eluding and defying fundamental explanation for such a long period of time as have those associated with the field of low-temperature physics.

From Kamerlingh Onnes' first liquefaction of helium in 1908, and his discovery of superconductivity in 1911, nearly fifty years would elapse before in the early fifties, Feynman was to place the theory of liquid helium on a firm microscopic foundation, while in 1957, Bardeen, Cooper, and Schrieffer (BCS) would perform the same task for superconductivity. It is with this latter that we shall be concerned.

First, in 1933, came the Meissner effect, followed, in quick succession, by the now "classical" phenomenological theories of F. and H. London and of Gorter and Casimir, the one dealing with the electrodynamics while the other with the thermodynamic properties of superconductors. Then, after the war, with the advent of much superior electrical and electronic equipment, and with the maturing of physicists to whom quantum physics was no longer just an anomaly from the classical world, it was perhaps inevitable that the rate of progress should suddenly assume major proportions.

On the experimental side, the isotope effect, and the discovery of an energy-gap from specific heat and far-infrared absorption measurements, while, on the theoretical side, Pippard's brilliant deduction of non-local electrodynamics and of the existence of a coherence distance,
and Cooper's discovery of the instability of the Fermi distribution in the presence of even a weak attractive interaction, finally set the stage for the BCS theory.

But even while this last provided a firm microscopic foundation and succeeded in explaining the major properties and temperature dependences, superconductivity still had its share of surprises.

Flux quantization — predicted over fifteen years ago by F. London — type II superconductors, "gapless" superconductivity, the "Josephson effect", and the multitude of fundamental extensions of this idea — which have provided conclusive evidence of the macroscopic quantum nature of superconductivity — by Mercereau and co-workers, have made low-temperature physics, to all who have been privileged to be aware of these developments, one of the most exciting fields of modern physics.

An area of particular interest in the study of superconductivity has been that of critical phenomena — i.e., of the approach toward the transition to the normal state. Here, microscopic theory has often proved less than tractable, not because of any inherent limitations, but merely that these phenomena require the inclusion of higher orders in the perturbation treatment, thus making the problem essentially non-linear.

A singularly successful treatment of these non-linear effects has been a theory proposed in 1950 by Ginzburg and Landau. (1)

Initially set up on a phenomenological basis, it was placed in 1959 on firm microscopic ground by Gor'kov (2), who was able to show by rather sophisticated field-theoretic techniques that the same fundamental equations result if one starts from a BCS-type Hamiltonian. It is some of the consequences of this theory — to be discussed in greater detail in Chapter II — that the present work has been successful in verifying.

(a) The Present Experiment

The present experiment was suggested by some simple theoretical calculations (3,4) on the basis of the Ginzburg-Landau-Gor'kov theory. These indicated that the energy-gap of a superconductor should decrease when the metal was carrying a current, as a function of the electron drift-velocity, because the current-carrying state introduced an additional kinetic-energy term in the overall energy balance.

A first attempt at verifying these predictions by a somewhat less conventional technique (5) was thwarted after what appeared a promising beginning by the fact, unknown at the outset, that sufficiently thin films of tin show type II behavior in the region near the transition temperature. This feature turned out to give a non-linear response which quite overwhelmed the expected effect. When this was finally


(3) J. Bardeen, Rev. Mod. Phys., 34: 667 (1962)


(5) C. D. Mitescu, Rev. Mod. Phys., 36: 305 (1964)
realized, it was decided that the experiment should be attempted anew by "conventional" tunnelling techniques. (6)

For the purpose, two alternatives were available — either superconductor-to-normal-metal (method A) or superconductor-to-superconductor tunnelling (method B). (7)

Of these, the first, while technically far easier to execute — since aluminum, whose natural oxide layer provides a nearly ideal tunnelling barrier, could be used as the normal metal above 1.2°K —, and while its resultant data has, at first sight, a certain mathematical simplicity, suffers, as a matter of fact, from a major and fundamental drawback: the experimental data, consisting of the I-V characteristic — or, more precisely, the dI/dV vs. V characteristic, almost as easy to obtain experimentally and containing somewhat more precise information — is theoretically understood as a convolution of the density of states in the superconductor with the derivative of the Fermi function. The quantity of fundamental interest, however, is the density of states and the gap in it. The investigator is then put in the position of having to infer from the data, which is in effect an integration of the density of states with a "gaussian"-like function of effective width kT, small changes in the position of the sharp edges of the gap, itself of overall width of the same order of magnitude, kT. While in principle, if one deals with exact mathematical functions, the analysis can be


(7) Appendix A contains a brief explanation of the relation between tunnelling measurements and the energy-gap and density of states.
carried out, in actual practice, where the data contains some noise and uncertainty, this becomes an almost hopeless task.

The above method was therefore rejected and the second alternative selected. While its characteristic I-V curves are mathematically more complicated, involving in the integration a product of the density-of-states of each superconductor and the difference between the Fermi functions, the sharpness of the density of states in the reference superconductor allows an accurate, direct determination of the overlap positions of the various gap edges and, consequently, direct determination of the energy-gap of the superconductor under investigation. This method had however, the major technical handicap of the difficulty of manufacturing tunnelling barriers.

After many tribulations in the technical preparation of the samples, it was finally possible to obtain good measurements of the gap changes as a function of current for various temperatures not too far from the transition. The observed dependence will be seen to show good confirmation of Ginzburg-Landau theory predictions.

It was also possible to observe on a few samples at lower temperatures a "Josephson" tunnelling current. The tunnel junction could then be used as an "electron speedometer" (8) to obtain a measurement of the electron drift velocity, which is by far the more significant microscopic parameter. Unfortunately, because of the physical

size of the junctions, this measurement could only be made at very low current densities, and as such can be used to provide directly only a lower limit to the actual critical velocities.

(b) Other Reported Data

It should be pointed out that within the last nine months, while the present work was in progress, a report (9) appeared of a measurement of the current variation of the energy gap by an interesting variation of method A, above. This consisted of measuring the change in the value of the dI/dV characteristic at zero bias voltage, obtained by electrical differentiation of the I-V curve by application of an a.c. signal. While the idea was ingenious, the experiment, as reported, suffered, in addition to the fundamental drawback of method A as described above, from several additional major defects. The first, experimental, resulted from the fact that a "differentiating" a.c. signal of amplitude approximately 10% of the full energy gap being measured was used to infer changes ranging from a few tenths to at most two percent of the gap. Secondly, and much more fundamentally serious, the changes were inferred from the assumption that the density of states in the current-carrying state retains the zero-current BCS function form \( \rho(E) = E/(E^2 - \Delta^2)^{1/2} \), with merely the value of the gap parameter changing. This assumption is flatly contradicted by the only existing theoretical calculations on the density of states which -- though

carried out only for the case of $T = 0$ — indicate (10) that not only the energy-gap but the entire shape of the density-of-states curve is substantially altered. Finally, the current dependence quoted is normalized in terms of an empirical critical current and no data is published which would allow numerical comparison of the relative change in energy-gap for given values of current density even though the communication admits that the coefficient of the dependence does not agree with theory. It must therefore be concluded that the above report can at best be considered no more than a qualitative detection of the change in energy-gap with current.

CHAPTER II - THEORY

While it is beyond the scope of this work to discuss in great detail the theoretical background of the present experiment, it will be useful to outline briefly the underlying physical ideas and to quote a number of results.

(a) Ginzburg - Landau Theory

The fundamental idea behind the theory proposed by Ginzburg and Landau (GL) is that we can associate with the superconducting electrons an effective wave function, whose absolute square, often called the order parameter, is proportional to the fraction of electrons in the ground state - microscopically, that is understood to be related to the expectation value of the occupation of ground-state pairs.

They then proposed that whenever external fields tend to cause an alteration of the order parameter within the superconductor, there will result in the energy balance an additional kinetic energy associated with the gradient of this "wave-function," which will then tend to inhibit this change over distances smaller than the coherence distance, $\xi_0$, in the superconductor. They further proposed that under those conditions where the order parameter is relatively small, the free-energy difference between the normal and superconducting states should be expressible as the first two terms of a power series in the order parameter. The net consequence of this, in a general case, is a set of coupled, non-linear, differential equations between the effective wave
function and the electromagnetic field which have the form

\[ j = -\frac{e^2}{m} |\psi|^2 \hat{A} \]  ...II.1

and

\[-\frac{\hbar^2}{2m^*} \nabla^2 \psi - \alpha \left[ 1 - \frac{e^2}{2m^*\alpha} \nabla^2 \right] \psi + \beta \psi^3 = 0 \]  ...II.2

We observe that equation II.1 has the form of the London equations but with a spatially dependent number of electrons.

In general, these equations are very difficult to solve, since deep inside a bulk superconductor all fields are shielded out and the order parameter assumes its equilibrium, temperature-independent, value, while the conditions nearer the surface depend on the actual fields.

The situation, however, becomes particularly simple in the case of superconductors with a dimension smaller than the coherence distance. Then, we have no "deep" region where the order parameter must assume its field-free value, and since it is inhibited from changing very rapidly, it will assume throughout the material the particular constant value which tends to minimize the free energy. In this situation, if a favorable geometry is selected, we can then neglect its spatial variation and treat the problem from energy considerations, as outlined below.

In the case of a bulk superconductor, we have the free-energy difference between the superconducting and normal states given by

\[ f(\omega) = -\alpha \omega + \frac{1}{2} \beta \omega^2 \]  ...II.3
where \( \omega \) is the order parameter. This will be minimized for an equilibrium value \( \omega_e = \alpha / \beta \)

If we further remember that to the equilibrium value of the free energy difference per unit volume the bulk critical field, \( H_{cb} \), is by definition related, we have

\[
f(\omega_e) = -\frac{1}{2} \mu_0 H_{cb}^2 = -\alpha \omega_e + \frac{1}{2} \beta \omega_e^2
\]

\[
\text{and } \omega_e = \frac{\alpha}{\beta} = \frac{\rho_s}{\rho} = \frac{\lambda o}{\lambda^2}
\]

where in this last we have made use of the "classical" result

\[
\lambda^2 = \frac{m}{\mu_0 n_e \pi^2}
\]

From these we can obtain the values of the coefficients \( \alpha \) and \( \beta \).

Where the superconductor is carrying a current, we assume that the same relation obtains, but we have to add to the energy balance the kinetic energy of the electrons. Here we have

\[
f(\omega) = -\alpha \omega + \frac{1}{2} \beta \omega^2 + \frac{1}{2} (n_o \omega) mv^2
\]

Minimizing the free energy as before we obtain a new value of the order parameter

\[
\omega = \omega_e (1 - \frac{v^2}{\frac{v^2}{m}})
\]
where
\[
\eta^2 = \frac{2\mu H^2}{n_0^m \omega_e} = 2\left(\frac{\sqrt{m}}{B_{cb}}\right)^2 \lambda^2
\]

...II.9

is a parameter having the dimensions of a (velocity)². If we now apply Gor'kov's result that the order parameter is proportional near \( T_c \) to the square of the energy gap, we obtain

\[
\omega = \left(\frac{\Delta}{\omega_0}\right)^2 = (1 - \frac{v^2}{v_m})
\]

...II.10

the current density then is

\[
j = nev = (n_0 \omega_e) e v (1 - \frac{v^2}{v_m})
\]

...II.11

This has a maximum value at \( v = v_m/\sqrt{3} \), which is then the critical current whenever the superconductor is driven by an external circuit.

We note that \( n_0 \omega_e \) is merely the number of electrons in the ground state at a given temperature.

Microscopically, the interpretation of equations II.10 and II.11 is that, at higher velocities, it becomes energetically favorable for a few electrons to depair out of the ground state and thus diminish the kinetic-energy term, even though reducing the gap slightly. For a small readjustment, the decrease in kinetic energy will more than overcome the loss of condensation energy.
We should further note that, while the form of the equations is based on general physical arguments, it is conceivable that more precise microscopic treatments might alter some of the numerical coefficients involved.

(b) Josephson Tunnelling as an "Electron Speedometer"

In 1962, Josephson (11) predicted that for two superconductors which are weakly, but not too weakly, coupled through a resistive barrier, there should occur a resistanceless flow of current corresponding to tunnelling of pairs across the junction. It can be shown (12) that for two pieces $a$ and $b$ of superconductor the tunnelling current is

$$ j \sim \text{Re}[j_0 e^{i(\phi_a - \phi_b)}] \quad \text{...II.12} $$

where $\phi_a$ and $\phi_b$ are the phases of the individual quantum mechanical systems. In a general case, the phase difference between two points in a quantum system is given by

$$ \phi_{12} = \frac{1}{\hbar} \int_1^2 \mathbf{p} \cdot d\mathbf{q} $$

$$ = \frac{1}{\hbar} \int_1^2 (m \mathbf{v} + eA) \cdot d\mathbf{q} \quad \text{...II.13} $$


In a superconductor $m^* = 2m$ is the effective mass of a pair.

In the case of a junction where one superconductor is carrying a current and the other is not, and where the magnetic field due to the current does not appear at the junction by virtue of a compensated geometry - e.g., use of a current return path, or ground plane, under the current-carrying superconductor - the phase difference between any two points at the junction reduces to

$$\phi_a - \phi_b = \frac{2m v x}{\hbar}$$  \hspace{1cm} \text{...II.14}

where $x$ is a distance measured along the direction of the current. The total current passed by a junction of length $D$ along this direction is then proportional to

$$j = j_o \int_{-D/2}^{D/2} e^{i \frac{2m v x}{\hbar}} dx$$

i.e.,

$$j = j_o D \frac{\sin \left( \frac{mvD}{\hbar} \right)}{\frac{mvD}{\hbar}}$$  \hspace{1cm} \text{...II.15}

which we observe has the standard form ($\sin x/x$) of the diffraction equation. As a function of drift velocity, we will expect the resistanceless tunnelling current to have zeros as predicted by the above equation. In particular, the first minimum will occur at $x = \pi$ or

$$v_1 = \frac{\hbar}{2mD}$$  \hspace{1cm} \text{...II.16}
(c) Thickness Corrections for Finite Film Size

To take account of situations where the film thickness might not be small compared to a penetration depth, it is a simple matter to solve, for the case of a plane film of thickness $\delta$ and width $w$, carrying a current above a ground plane, the London equation

$$\mathbf{j} = -\frac{\mathbf{A}}{\mu_0 \lambda^2}$$  ...II.17

together with the appropriate Maxwell equations, to give a current distribution across the thickness of the film

$$j(y) = \frac{I}{w\lambda} \frac{\cosh \left( \frac{\delta - y}{\lambda} \right)}{\sinh \left( \frac{\delta}{\lambda} \right)}$$  ...II.18

where $y$ is measured from the edge nearest the ground plane and $I$ is the total current carried by the film.

It will be useful, for velocity and penetration depth measurements, to combine this result with equation II.16 to give the transcendental equation

$$\sinh z = \left( \frac{D}{w} \right) \frac{\delta \mu_0 I}{(h/2e) \left( \frac{1}{z} \right)}$$  ...II.19

where  
$$z = \frac{\delta}{\lambda}$$
A. SAMPLES

For the purposes of the present experiment, tin was chosen as the current-carrying - hereafter called main - superconductor, because of its convenient transition temperature, ease of evaporation, and because temperature-dependent properties of tin films are now well known to conform to the predictions of the BCS model. As the second reference - superconductor, lead was selected, because it displays a sufficiently high transition temperature that its energy-gap is already quite insensitive to temperature in the range where tin begins its transition.

The actual experimental samples consisted of the multi-layered structure illustrated in Figure III A. It will be observed that there are three metallic films separated by appropriate "insulating" layers.

The bottom layer, a relatively thick (~2000 Å) lead film, served as a "ground plane", providing the necessary image fields to ensure a uniform distribution of the current through the main superconductor - current which would otherwise peak very strongly at the edges of the film. (13)

Over this comes an insulating film described below, and then the main superconductor. While its operative region is the narrow strip (100 to 300 µ wide) at the center, the shape shown, and in particular

FIG. III A - SAMPLE STRUCTURE
(Plan View)
the large amount of tapering was found necessary in order to avoid the sample becoming normal first at the contacts, when a longitudinal current was passed.

After the formation of an oxide tunnel layer (see below) over the tin, a final lead film, about 2000 Å thick and 100 microns wide in the experimental region, provided the reference superconductor.

(a) The Metallic Films

The preparation of the metallic films was relatively trivial. They were deposited on the glass substrate by vacuum, flash-evaporation, to completion, of an accurately weighed amount of high purity metal (14) at a distance of ~25 cm from the source, with an effective deposition rate of 150 - 200 Å/sec, and at a pressure of 2 x 10^{-6} torr of residual argon. In order to minimize globulation and porosity, the substrate was cooled to liquid N₂ temperature during the deposition of the first two metallic layers. Previous experience had shown that the low-temperature deposition yielded films with much less grainy appearance and better electrical properties — e.g., higher critical currents. The shape of the samples was determined by appropriate masks, of which the very narrow regions were made of razor blade edges. By mounting the masks at a few hundred microns from the substrates, it was found possible to limit the shadow region at the edge of the films to a width of about 5 microns, in the areas of experimental interest.

(14) 99.999+% purity lead and 99.999% purity tin respectively obtained from A. D. Mackay, Inc., New York, New York.
The thickness of the films was at first inferred by weighing the amount of material evaporated over a known area and assuming the bulk density of the material. In terms of this calibration, it was found convenient, for experimental reasons, to carry out the main energy-gap experiments on tin films 710 Å thick. After the experiments had been performed, it was found possible to recalibrate the system by measuring thicknesses directly by multiple-reflection interferometry. (15) It was found that the "weighed" thicknesses of 710 Å corresponded to an actual thickness of 820 Å, i.e., that the effective density of the tin is about 0.85 of the bulk value.

(b) The Non-Metallic Layers

The formation of the non-metallic "insulating" layers presented by far the most difficult experimental problem encountered. It required over a year to perfect the necessary techniques before an acceptable degree of reproducibility was obtained.

The requirements of the non-metallic layers were exceedingly stringent. The first, between the ground sheet and the main superconductor, had to be a good electrical insulator, yet exceedingly thin, and completely pinhole free over the relatively large overlap area. The thinness requirement - less than √1000 Å - was set by the fact that, otherwise, the image effects of the ground plane would be lost at the

(15) I am grateful to Dr. C. H. Wilts of the Electrical Engineering Department for the use of a Zeiss multiple-reflection interferometer.
edge of the main superconductor, where it was particularly necessary to avoid peaking of the current density. The need for freedom from pinholes is quite obvious, to ensure that the longitudinal current is confined to the main superconductor.

After substantial effort, it was found possible to use for the purpose a silicone polymer (16), formed by electron bombardment of the lead "ground" film while exposed to a stream of diffusion-pump-oil vapor (Dow Corning DC-704, silicone oil). (17) The electron bombardment polymerizes the silicone oil to form an exceedingly high resistivity insulating layer (>10^{13} ohm-cm, even for films as thin as 100 - 200 Å).

As the polymerizing action is a function of the current density of the bombarding electron beam, the process tends to give particularly uniform films - as thin spots automatically draw more current. It was eventually possible to produce with reasonable consistency insulating layers several hundred angstroms thick with a resistance of at least several megohms at 1.5 volts.

It was an even more difficult task to attain a satisfactory measure of reproducibility in the production of the second "insulating" layer, that which provided the tunnel barrier between the tin and the reference superconductor. In this case, it was necessary to form an

(16) L. Holland and L. Laurenson, Vacuum, 14: 325 (1964)

(17) I am grateful to Dr. Horace Mann of the STL division of TRW Systems, Redondo Beach, for a detailed personal description of the technique.
oxide layer on the tin which would give a reasonable resistance (30 - 300 ohms) over the junction area (0.01 cm x 0.01 - 0.03 cm, for various films). There again, the "traditional" method, heating the tin film to 50° - 100° C for about an hour in an oxygen atmosphere, left a great deal to be desired in the way of reproducibility and control of conditions.

It was found possible to modify (see Appendix B) a gaseous anodizing technique (18) which had been reported useful for other metals. The method consists, briefly, of forming an oxide layer on the tin by anodizing with respect to an oxygen plasma formed by an auxiliary, low-pressure (50 - 100 µ) discharge in the vacuum system. After suitable empirical adjustment of the various parameters, it is possible to establish conditions such that the current drawn by the film decays with time as expected with normal anodization, and to exercise a modicum of control over the resultant junction resistance, by the length of time for which the anodization is carried out.

For the experimental samples used, junction resistances, typically 200 - 300 ohms, were obtained with anodizing times of about 5 minutes.

B. APPARATUS

The cryogenic environment consisted of a standard experimental station - dewars, manometer, pumping and pressure control systems, etc -

capable of maintaining pressures from atmospheric down to 0.1 torr (corresponding to temperatures of 4.2 to 1.0° K.) with a short-term stability, at not too low pressures, of better than 0.1 torr. In addition, a Helmholtz-coil arrangement around the system allowed the ambient magnetic field in the experimental region to be nulled to a few milligauss.

A block diagram of the electrical system is shown in Figure III B, with a detailed list of the major components in Table IIIa. Basically, the electrical system is seen to consist of five major blocks, three "sources" and two sensing systems.

Of the former, one, a current source, supplies the longitudinal current for the main superconductor; while it is operated in a constant-current mode, it has a voltage-limiting feature set sufficiently low that the film is not burned out when it is driven normal. The second source provides an adjustable d.c. voltage for application to the tunnel junction, together with a continuously changing d.c.component of adjustable time-constant, for sweeping the I-V characteristic. Finally, the third source introduces a very low amplitude 1 Kc signal which, superimposed on the d.c. bias across the tunnelling junction yields a current proportional to dI/dV.

The first sensing block is composed of a transformer-input, low-noise,a.c. amplifier which detects a signal proportional to the a.c. current in the junction circuit, and feeds it into a phase-sensitive detector (synchronous demodulator); the latter, in turn, drives the Y-input of the X-Y recorder. The second sensing unit consists of a
FIG. III B - BLOCK DIAGRAM FOR ELECTRICAL CIRCUITS
TABLE IIIa - ELECTRONIC COMPONENTS (Legend for Figure IIIB)

<table>
<thead>
<tr>
<th>A</th>
<th>Variable D.C. junction bias</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>Continuous sweep junction voltage (capacitor charging)</td>
</tr>
<tr>
<td>C</td>
<td>Current Supply (H-Labs, Model 855C, constant-current, constant-voltage regulator)</td>
</tr>
<tr>
<td>D</td>
<td>Audio oscillator (Hewlett-Packard 200CD)</td>
</tr>
<tr>
<td>E</td>
<td>Attenuator and shielded transformer</td>
</tr>
<tr>
<td>F</td>
<td>Low impedance source for junction (5Ω)</td>
</tr>
<tr>
<td>G</td>
<td>Sample (in dewar)</td>
</tr>
<tr>
<td>H</td>
<td>Differential A.C. amplifier (Keithley, Model 103)</td>
</tr>
<tr>
<td>I</td>
<td>Shielded transformer (Triad, G-4)</td>
</tr>
<tr>
<td>J</td>
<td>Potentiometric comparator (0-3mV, 100µV steps)</td>
</tr>
<tr>
<td>K</td>
<td>Phase-sensitive detector (Electronics, Missiles and Communications, Model RJB)</td>
</tr>
<tr>
<td>L</td>
<td>X-Y recorder (Moseley, Model 2D2)</td>
</tr>
<tr>
<td>M</td>
<td>Bias circuit for x-axis zero-suppression</td>
</tr>
<tr>
<td>N</td>
<td>D.C. differential, floating-input floating-output amplifier (Sanborn, Model 860-4300)</td>
</tr>
</tbody>
</table>
high-gain, low-noise (1µVp-p) floating-input, floating-output d.c. differential amplifier which amplifies the voltage across the tunnelling junction and drives the X-circuit of the X-Y recorder. An adjustable, bias voltage allows substantial zero-suppression of the recorder scale, while a potentiometric divider, with 100µV steps, can be alternately connected to the d.c. amplifier input, thus allowing direct calibration of the recorder trace.

A schematic diagram of the basic junction circuits is shown in Figure III C. It will be observed that both the d.c. and a.c. voltages are applied to the tunnelling junction by feeding them from what are effectively current sources into a low (5 ohm) resistance, which then acts as a low impedance source for the tunnel junction; in series with the latter, another low (10 ohm) resistance is inserted across which the a.c. output signal is sensed. As both the above resistances were low in comparison with those of the tunnel layers in the films used (typically 200 - 300 ohms), the junction is effectively driven by a good approximation to a voltage source, and the a.c. output is closely proportional to dI/dV.
Fig. III C - Schematic Diagram for Junction Circuitry
CHAPTER IV - EXPERIMENTAL PROCEDURE

(a) Critical Currents

Preliminary investigations were first carried out on the critical currents of a large number of samples, both for film thicknesses in the range of 500 - 1000 Å and widths of the experimental area of 100 to 300 microns.

It was found that either of two criteria could be used for the determination of a "critical current". One was the first appearance of a voltage across the experimental region; as the minimum detectable voltage was a fraction of a microvolt, this corresponded to the appearance of a resistance typically $10^{-5}$ to $10^{-4}$ ohms, for a region (0.25 cm x 0.03 cm) whose normal resistance at 4.2° K might be in the range 10 - 100 ohms. The second criterion was the complete thermal avalanche of the experimental region. It was encouraging to discover that the "avalanche" current determined in this way was always approximately 30 - 40% higher than the "minimal" critical current above, a relationship that was found quite constant and independent of temperature for a given sample. This temperature independence is particularly important in that, when it is also remembered that the actual current values vary over several orders of magnitude, particularly in the region near $T_c$, this implies that, from the initial appearance of resistance, and until thermal instability is actually reached, there is a purely local transition in one portion of the film, and not an overall heating - which would tend to show a power dependence.
It was found that all critical-current measurements displayed, in the region near the transition temperature, the variation \((T_c - T)^{3/2}\) predicted by all the theories. In addition, critical-current densities from the various samples usually were found to agree within better than 10%. The agreement between samples of varying widths indicates that edge effects are relatively negligible for our films.

It was further found that there was only very slight difference in the critical currents between using the lead ground sheet as a true ground plane or as an actual return path for the current. Though, as a matter of fact, the critical currents observed were occasionally a few percent higher with the lead as a ground plane.

(b) Main Energy-Gap Data

The actual experimental procedure consisted of determining directly the change in the energy-gap of the "main" superconductor, with and without a longitudinal current, from the position of the voltage intercepts of the \(dI/dV\) vs. \(V\) curve. Since on this determination the results of the entire experiment depended, it was particularly important that these intercepts be established with considerable accuracy. It was thus essential to eliminate any instrumental bias in the location of the zero baseline - such as might result from a zero offset in the phase-sensitive detector or the X-Y recorder. This result was achieved by reversing the polarity of the applied a.c. signal, hence reversing the sign of the output of the phase-detector, and determining the position of the intercept from the intersection of the two
traces. It was found that the zero line thus determined agreed quite well among a number of successive measurements. The procedure is well illustrated by Figure IV A, a reproduction of an actual experimental trace, showing a complete dI/dV vs. V characteristic for both positive and negative junction voltages, and for both polarities of the superimposed a.c. Attention is particularly drawn to the high degree of symmetry displayed by the figure. It might be noted that, in this illustration, the zero crossings do not all appear at the same level. This is an accidental feature due to the fact that a somewhat higher sweep speed was used in this case in order to display the complete characteristics. In the region where the dI/dV curve is changing quite rapidly, this particular sweep rate proved a bit high for the time-constant of the phase detector. In the actual experimental determination, each recorder scale was expanded by a factor of fifty from that of Figure IV A, while the sweep rate was reduced by several hundred — since only the regions in the vicinity of the intercepts needed to be recorded; it was then found that the zero intersections did agree quite well. In order to insure against time-lag effects, each trace was swept with both increasing and decreasing voltage, so that when the a.c. polarity was reversed as well, each intercept was the resultant of four intersecting traces. It was therefore possible to establish the position of the zero intersections most often within a fraction of a microvolt, and always within one to two microvolts, the ultimate limitation being the noise in the recorder input signals; the latter is the entire source of the uncertainty displayed in the
FIG. IVA - ENERGY GAP FROM dI/dV TUNNELLING DATA  
(Experimental Curve)
main data. As it was necessary to use an external bias circuit in order to obtain sufficient zero-suppression on the X-axis recorder, the problem of calibration was solved by switching the input of the d.c. differential amplifier, before and after each intercept determination, to the potentiometric voltage divider, set to the nearest multiple of 100 microvolts. In a series of measurements, an intercept was located first for zero current in the main superconductor, and then for a particular pair of equal and opposite values of the longitudinal current, the whole procedure being repeated for the other intercept. As each group of three intersections was established with reference to the same potentiometer setting, the difference between them, and hence gap differences, could be directly determined with maximum accuracy. Measurements of the change in the energy-gap with longitudinal current, for a number of values of current, were carried out at a given temperature.

The largest currents for which it was possible to make gap-change measurements were usually about 10% lower than the experimentally determined critical "avalanche" currents. The reason for this is that a complete set of intersections for a single value of current turned out to require on the average 45 - 60 minutes; at currents nearer the avalanche value, occasional electrical transients would occur with sufficient frequency to trigger an avalanche to the normal state before measurements could be completed.

It should perhaps be noted that, for currents very near the "critical" value, there often occurred, in the position of the inter-
section, a bias of 5 - 10 microvolts which changed sign with the sign of the longitudinal current. The total gap changes obtained from the positive- and negative-current intercepts were still found to agree within observational accuracy, thus leading to the conclusion that the bias was due to an incipient resistance in some portion of the film which happened to be in series with the tunnel-layer voltage measurement.

In order to check for internal consistency, experiments were carried out on a number of different samples at the same value of reduced temperature, and for two of the samples at various temperatures (19). The latter two were of different widths in order to verify consistency in the current densities. It was found that the best data was obtainable in the region close to $T_c$. Below a reduced temperature $t = (T/T_c) \approx 0.8$ it was discovered that the higher voltage intersection became very ill-defined. (Reference to Figure IV A will indicate that this particular intersection is already considerably less sharp. As the temperature is lowered, it tends to flatten out appreciably because of the thermal depopulation of the states above the gap in the superconductor.)

(19) It should be pointed out that experimental data from a given sample was usually taken over a period of several days and, on occasion, weeks. While the sample was not continuously maintained at helium temperatures for more than one day at a time, it was never allowed to warm up above liquid-nitrogen temperature. Under this condition, it was found that a sample could be maintained indefinitely with no significant changes in any of its properties. Cycling a sample to room temperature, however, was always found to have deleterious effects.
(c) Velocity Data from "Josephson" Measurements

It was a pleasant surprise to discover that at the lower temperatures, \( t = 0.8 \) and below, some of the samples (in particular the last two) displayed, with zero tunnelling voltage, a very small but quite measurable, resistanceless current in the tunnelling characteristic, even though the junction resistances were, at 200 - 300 ohms, appreciably higher than those for which Josephson effect has been reported in the literature. This was identified as a Josephson current, since it was observed to oscillate as a function of longitudinal current, in the now familiar diffraction pattern. The central peak and two lateral peaks on each side were usually observed, their maxima and minima agreeing remarkably well with the predictions of the "diffraction equation", II.15. This agreement is illustrated in Figure IV B. It was thus possible to obtain at the lowest temperature, \((t = 0.8)\), at which a gap was measured, a direct drift-velocity measurement (20).

---

(20) Strictly speaking, this is only a direct measurement of the "kinetic momentum" \( mv \), and in combination with the corresponding value of current density, of the effective penetration depth. The velocity can only be obtained from an independent knowledge of the mass \( m \).
Fig. IVB - Extrema of "Josephson" Current
(Velocity Data)
CHAPTER V - RESULTS

(a) Preliminary Data

Since it was not uncommon for the various tin films tested to have slightly different (20 - 30 millidegrees) transition temperatures, it is necessary for purposes of comparison between samples to express the temperature at which a measurement was made as a reduced temperature \( t = T/T_c \). For this purpose it was essential to make an accurate determination of the transition temperature. Because it was found that near \( T_c \) both the critical current [see Chapter IV (a)] and the energy-gap at zero current had the theoretically predicted temperature dependence -

\[ j_c \propto (T_c - T)^{3/2} \quad \text{and} \quad \Delta \propto (T_c - T)^{3/2} \]

- it was possible to make plots of \( j^{2/3} \) and \( \Delta^2 \) against temperature and, by extrapolating the resulting straight lines to zero, obtain a value for the transition temperature \( T_c \). It was very gratifying to note that the two values of \( T_c \) determined from the respective extrapolations usually agreed within one or two millidegrees.

It was also found that if the zero-current energy-gap values obtained at various temperatures were plotted against the reduced BCS gap function \( (\Delta_T/\Delta_o) \) for the particular value of reduced temperature \( t \), a reasonably good linear relationship appeared (see Figure V A), confirming that the tin follows quite well BCS theory.

(b) Changes in the Energy-Gap

Figures V B and V C illustrate the dependence of the relative
FIG. VA - BCS DEPENDENCE OF TIN ENERGY GAP
change in energy-gap on current density \( j \) - more precisely on \( j^2 \) - for a number of samples at various temperatures.

A brief explanation might be useful at this point as to the manner of displaying the data. Remembering the results of the Ginzburg-Landau-Gor'kov theory, we recall the following equations:

\[
j = (n_o \omega) e v (1 - \frac{v^2}{v_m^2}) \quad \text{...II.11}
\]

\[
\omega = \frac{\Delta v^2}{\Delta o} = (1 - \frac{v^2}{v_m^2}) \quad \text{...II.10}
\]

Realizing that the direct experimentally-measured quantity is the relative change in the gap,

\[
\epsilon = 1 - \frac{\Delta v}{\Delta o} \quad \text{...V.1}
\]

we can combine the equations to yield

\[
j^2 = n^2 e^2 v_m^2 (1 - \frac{\Delta v^2}{\Delta o^2}) \frac{\Delta v}{\Delta o} \frac{\Delta v}{\Delta v}^4 \quad \text{...V.2}
\]

or

\[
j^2 = 2n^2 e^2 v_m^2 \epsilon (1 - \frac{\epsilon}{2})(1 - \epsilon)^4
\]

\[= 2n^2 e^2 v_m^2 X \quad \text{...V.3}
\]

where

\[
X = \epsilon (1 - \frac{\epsilon}{2})(1 - \epsilon)^4 \quad \text{...V.4}
\]
It would therefore be expected that if the predictions of the Ginzburg-Landau theory are valid for our data, $\varepsilon$ should be a linear function of $j^2$ at low values but deviating at the higher currents, while the parameter $X$ should be a linear function for all values of $j^2$. Furthermore, since the critical current is predicted to occur for the value $v = v_m/\sqrt{3}$, this corresponds to a particular value of $\varepsilon$ and $X$ - respectively $(1 - \sqrt{2}/3)$ and $(2/27 = 0.074)$ - for all temperatures at which the above relations are valid. If we plot then $X$ vs. $j^2$, the slope, or rather its reciprocal, should have the temperature dependence of the square of the critical current.

The graphs of Figure V B display the relationship between $\varepsilon$ or $X$ and $j^2$, for several temperatures and two different samples. For the sake of clarity, error bars have been left off the symbols representing the values of $\varepsilon$, but they are of the same order as in the corresponding values of $X$. It will be noted that in all cases, the $\varepsilon$'s deviate from a linear relationship at the higher current values, but that the plot of the parameter $X$ is always linear in accordance with predictions. Further, if the value of the critical current is inferred from extrapolation to $X = 0.074$, it is found that it corresponds to a value usually 20 - 30% higher than the "avalanche" current experimentally observed. In view of the particularly elongated and narrow geometry of the experimental region, it is not at all unreasonable to expect that at some point away from the junction there might be a small constriction or imperfection in the sample, causing it to go critical there.
FIG. VB - GAP VARIATION WITH CURRENT DENSITY
As a check on the reproducibility and consistency of the measurements, the X data from a number of films at the same reduced temperature are displayed on Figure V C. In some cases, the errors tend to be larger than for Figure V B, since the present figure contains some earlier data.

As a further check on the predictions of the theory, Figure V D has been prepared to examine the temperature dependence of the experimental results. There we see the parameter X plotted against a temperature-corrected function $j^2/K(t)$ - where $K(t) = (T - T_c)^3$ represents the well known temperature dependence of $j^2$ near the transition temperature. It is observed that the data for temperatures near $T_c$ fall on a universal curve as predicted. It might be worth emphasizing that for the points displayed $K(t)$ varies over nearly an order of magnitude, so that the plot represents a reasonably sensitive test. Two dashed lines have been drawn to indicate the average position of the data from the lower temperature measurements - $t = 0.89$ and 0.81. It is observed that these do not fall on the universal curve. This is not unreasonable, as the critical current is known at lower temperatures to deviate from the $(T_c - T)^{3/2}$ dependence to a more linear relationship. The observed deviations are consistent with this dependence.

It is unfortunately impossible to insert accurately the temperature dependence of the critical currents into the temperature parameter $K(t)$ for the lower temperature data. The only comprehensive treatment of critical currents at all temperatures on the basis of microscopic theory, that of Rogers (21), contains unfortunately an
FIG. VC - REPRODUCIBILITY IN GAP VARIATION
\[ \frac{j^2}{K(t)} \text{(Amp-Cm}^{-2}\text{)}^2 \times 10^{-14} \]

**Figure VD - Gap Variation ("Universal" Curve)**

<table>
<thead>
<tr>
<th>Film</th>
<th>( w \text{(cm)} )</th>
<th>( t )</th>
<th>( K(t) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O - D</td>
<td>0.02</td>
<td>0.9793</td>
<td>( 5.4 \times 10^{-5} )</td>
</tr>
<tr>
<td>( \Delta ) - C</td>
<td>0.03</td>
<td>0.9776</td>
<td>( 6.9 \times 10^{-5} )</td>
</tr>
<tr>
<td>+ - C</td>
<td>0.03</td>
<td>0.9631</td>
<td>( 3.1 \times 10^{-4} )</td>
</tr>
</tbody>
</table>
error due to the neglect of a certain second-order term, which is of particular significance in the region of interest (22). One internal test is, however, possible. It is to obtain a relationship between the critical currents predicted by the theory from the energy-gap data and the experimental avalanche current. Since very near $T_0$ both of these are known to obey the theoretically predicted temperature dependence, it is possible to establish a linear relation between them. At the lower temperatures then, this relationship should still hold if the theory is applicable, with the temperature dependence being implicitly taken care of. Figure V E(a) shows the fitting of the linear relation very near $T_0$, while Figure V E(b) represents the larger-scale extrapolation from the previous figure, together with the two experimental points corresponding to the lower temperature data. The agreement is quite gratifying, even perhaps a shade better than might be expected.

(c) Velocity Data

As the small Josephson currents observed for the last two samples at $t = 0.8$ and $t = 0.28$, were found to have minima and maxima at values of longitudinal current in the theoretically predicted ratios, an average value of the current for the first minimum $I_1$, was used together with the equation

\[ (21) \text{K. T. Rogers, Thesis, University of Illinois (1960).} \]

(22) While the proper calculation is too lengthy to be included as part of the present work, it is hoped that it will be carried out in the near future.
FIG. VE - SELF-CONSISTENCE OF CRITICAL CURRENTS
\[ \sinh z = \left( \frac{D}{W} \right) \frac{\delta \mu I_1}{(h/2e)} \left( \frac{1}{z} \right) \] \hspace{2cm} \text{...II.19}

and \[ v_1 = \frac{h}{2mD} \] \hspace{2cm} \text{...II.16}

to obtain values of \( v_1 \) and the parameter \( z = \delta/\lambda \), and hence of the penetration depth at those particular temperatures. Using then the temperature dependence predicted by BCS theory (23), a value for \( \lambda_0 \), could be calculated. The results are displayed in Table V a. It is observed that the values are reasonably consistent at \( \lambda_0 \approx 750 \text{ Å} \). This is high in comparison with the value (~560 Å) for bulk tin, but not inconsistent with the short mean-free-path expected for our films (24).

It is now possible to perform one final test of the theory. Using the value of \( I_1 \), and its corresponding \( v_1 \) from either film (both are consistent to about 1% in this respect), we can use the graph of Figure V B(d) to obtain the value of \( \chi \) and hence of \( \epsilon \), for the current \( I_1 \), and thence calculate \( v_m \) from the relation

\[ \left( \frac{\Delta V}{\Delta \phi} \right)^2 = (1 - \epsilon)^2 = \left( 1 - \frac{v^2}{v_m^2} \right) \] \hspace{2cm} \text{...II.10}

We here obtain, for \( I_1 \) of film C, \( \epsilon = 2.94 \times 10^{-4} \) and \( v_m = 150 \text{ m/sec} \), and infer the critical velocity \( v_c = v_m/\sqrt{3} = 87 \text{ m/sec} \) at \( t = 0.8 \). But

(23) B. Mühlschlegel, Z. Physik, 155: 313 (1959)

(24) A correction factor \( l/\xi_0 \) is suggested by microscopic theory to the effective number of superelectrons contributing to the electrodynamic shielding.
<table>
<thead>
<tr>
<th>Film</th>
<th>δ (Å)</th>
<th>w (μ)</th>
<th>D (μ)</th>
<th>$v_1$ (m/sec)</th>
<th>$t = \frac{T}{T_c}$</th>
<th>$I_1$ (mA)</th>
<th>$z$</th>
<th>$\lambda$ (Å)</th>
<th>$\frac{\lambda_o}{\lambda_t}$ (BCS)</th>
<th>$\lambda_o$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>820</td>
<td>306</td>
<td>100</td>
<td>3.64</td>
<td>0.805</td>
<td>29.4</td>
<td>0.66</td>
<td>1240</td>
<td>0.610</td>
<td>755</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.290</td>
<td>68.2</td>
<td>0.98</td>
<td>835</td>
<td>0.994</td>
<td>830</td>
</tr>
<tr>
<td>D</td>
<td>820</td>
<td>188</td>
<td>115</td>
<td>3.16</td>
<td>0.795</td>
<td>15.7</td>
<td>0.67</td>
<td>1220</td>
<td>0.625</td>
<td>760</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.290</td>
<td>45.6</td>
<td>1.07</td>
<td>766</td>
<td>0.994</td>
<td>760</td>
</tr>
</tbody>
</table>
an interpretation of the theory also expresses $v_m$ directly in terms of the bulk critical field and penetration depth $\lambda$,

$$v_m = \sqrt{2} \frac{e}{m} B_{cb}(t) \lambda \quad \ldots \text{II.9}$$

If we use our experimentally determined $\lambda = 1240 \, \text{Å}$, the bulk field $B_{cb}(t)$ which can be obtained from the known zero-temperature critical field of bulk tin — 300 gauss — and the BCS temperature dependence (25), we obtain a value $v_m = 268 \, \text{m/sec}$ (26).

For the sake of completeness, we should indicate that the

(25) B. Mühlenschlegel, loc. cit. (23)

(26) It should be emphasized that the use of the experimental $\lambda$ in this equation introduces into the theory an implicit assumption: that where the effective number of carriers has been reduced by mean-free-path effects, the effective $v_m$ and hence the critical velocity are thereby increased above those for the bulk material. All the theoretical treatments [J. Bardeen, loc. cit. (3), P. Fulde, loc. cit. (10), and K. Maki, Prog. Theor. Phys. (Japan), 29: 333 (1963)] contain this assumption, which effectively implies that the "rigidity" of the superconducting state remains unaffected, while the non-linearity effect decreases because there are fewer electrons contributing. This assumption is found to lead to a reasonable dependence for the critical current, but it has not been directly verified.

A further assumption is introduced by the use of the critical field of bulk tin in the above equations. Again a universally made one, it is usually justified on the ground that the energy gap and transition temperature are little affected by mean-free-path effects. We might consider, however, that microscopic theory equates the energy difference between the normal and superconducting states at $t = 0$ with $\frac{1}{2}N(0)\Delta_0^2$ and with $\frac{1}{2}\mu_0 H_{cb}^2$ — where $N(0)$ is the density of states at the Fermi level, proportional to the number of electrons per unit volume; the constancy of the energy gap then implies a constancy of $H_{cb}^2/N(0)$ and not of $H_{cb}$. A corresponding adjustment of $B_{cb}$ brings the value of $v_m$ into much better agreement with the experimental value.
experimental "avalanche" current at \( t = 0.8 \) corresponds to a value of \( X = 0.0475 \), hence of \( \epsilon = 0.064 \) and to a velocity \( v = 53 \text{ m/sec} \). In comparing this with the critical velocity calculated from the gap data \( (v_c = 87 \text{ m/sec}) \), it should be remembered that in this region a small difference in the observed critical current will lead to a large change in the critical velocity.

It should also be stated that the highest avalanche currents observed at the lowest temperature attained, \( t = 0.29 \), were about 900 mA for the 300 micron wide film. According to equation II.18, this would correspond to a current density of \( 3 \times 10^6 \text{ amp/cm}^2 \) at the upper surface and \( 4.8 \times 10^6 \text{ amp/cm}^2 \) at the lower surface, assuming a penetration depth of 750 Å. The various theoretical expressions for the temperature dependence of the critical current would multiply these values by factors of about 1.2 to 1.4 to give the zero-temperature current.
The immediate and obvious conclusion is that this experiment can indeed be considered the further, quite striking, confirmation of the internal consistence of the Ginzburg-Landau ideas, as well as of the fundamental correctness of Gor'kov's relation between the order parameter and the energy gap of a superconductor, even at temperatures as low as $t = 0.8$, where the order parameter can no longer be considered small.

But even while the functional form of the equations can be considered well established, it would seem that there is still some uncertainty as to the energies that should be considered in the theoretical treatment - or, more precisely, the coefficients which should appear with them. We are forced to conclude that, in this respect, our understanding still leaves something to be desired.

Perhaps the most fascinating results of this investigation are the further experiments that immediately suggest themselves and which now appear reasonably feasible.

While the velocity data is insufficient to be considered as more than a first, indicative, measurement, the apparent discrepancy between the "gap" critical velocities and those predicted from energy considerations indicate the need for further experimental investigation, particularly of samples with different mean free paths, as well as for a possible reconsideration of the theoretical ideas about critical velocities.
Since the drift velocity is the significant microscopic parameter in all theoretical considerations, it seems somewhat disturbing that its critical values should be exceedingly sensitive to mean-free-path effects, particularly in the sense that larger and larger values become permissible, even while most of the fundamental microscopic properties are relatively insensitive.

Finally, it appears feasible though at the price of substantial further analytic effort, to extend the $dI/dV$ measurements to the entire range of the tunnelling characteristic, rather than just its zero crossings, and to obtain from this some approximation to the actual density of states in a current-carrying superconductor. Only when we have obtained and compared the entire shape of the density of states with theoretical predictions (27) will we be justified in feeling that this aspect of superconductivity is fully understood.

(27) P. Fulde, loc. cit. (10)
APPENDIX A - TUNNELLING CHARACTERISTICS

The tunnelling current across a thin barrier between two metals in contact is governed by the quantum-mechanical transition probability

\[ w_{12} = \frac{2\pi}{\hbar} |M_{12}|^2 g(\varepsilon) \]  \hspace{1cm} ...

where \( M \) is the matrix element for the transition and \( g(\varepsilon) \) is the available density of states. Since we are dealing with Fermi particles, \( g(\varepsilon) \) is the product of the density of states \( \rho_2(\varepsilon) \) in the metal and the probability \( (1 - f_2) \) that the state is unoccupied - here

\[ f = \frac{\exp(\beta\varepsilon) + 1}{\exp(\beta\varepsilon) - 1} \]  \hspace{1cm} is the Fermi distribution function. The current in one direction across the barrier is thus the product of \( w_{12} \) and \( \rho_1 f_1 \), the number of states occupied in metal 1. The net current across the junction is then the difference between the currents in the two directions

\[ I_{12} = c' \int |M_{12}|^2 \rho_1 \rho_2 (f_1 - f_2) \, d\varepsilon \]  \hspace{1cm} ...

In the case of two metals with an applied potential \( V \) between them, it is useful to measure the energy in terms of the deviation \( E = \varepsilon - \varepsilon_F \) from the Fermi level, so that we then have

\[ I(V) = \int_{-\infty}^{\infty} dE \rho_1(E) \rho_2(E-V) [f(E-V) - f(E)] \]  \hspace{1cm} ...

where we have further assumed $|M_{12}|^2$ a constant because the difference term in the integral contributes significantly, at low temperatures, only over a small range of energies; this fact further allows us to extend the limits to infinity. It is a trivial exercise to show that the term $[f(E-V) - f(E)]$ is a "peak" (square if $V$ is large enough) symmetric about $V/2$, and to show that $I(V)$ is antisymmetric in $V$ if $\rho_1$ and $\rho_2$ are symmetric functions.

It is now useful to look at the consequences of A.3 for normal metal and superconducting systems. In these cases we have for a normal metal

$$\rho(E) = 1 \quad \text{for all } E \quad \text{...A.4a}$$

while for a superconductor, according to BCS theory,

$$\rho(E) = 0 \quad |E| < \Delta$$
$$\rho(E) = \frac{|E|}{\sqrt{E^2 - \Delta^2}} \quad |E| > \Delta \quad \text{...A.4b}$$

where $\Delta$ is the "half gap" in the superconducting density of states.

For a normal-normal system, we find the integration is easy to carry out analytically to give

$$I_{NN} = C(kT)V \quad \text{...A.5}$$

i.e., we have Ohm's law if the temperature is constant.

With tunnelling between a normal metal and a superconductor the picture is slightly more complicated, but a good qualitative insight may be obtained with the aid of Figure A A(a), a schematic
FIG. AA - SCHEMATIC DENSITY OF STATES AT A JUNCTION
energy representation of the density of states in the two metals - here the cross-hatching represents occupied states. Changing the voltage corresponds to sliding the two diagrams relative to each other along the energy scale. The tunnelling current, is the product of the two densities of states and the difference function \([f(E-V) - f(E)]\) which, we remember, is a symmetric function centered about \(V/2\) and with area \((kT)\). When a voltage is changed from zero, the current increases, but quite obviously at a less rapid rate than the normal-normal junction, as the gap takes out a piece of the central portion of the difference function. When the voltage \(V\) approaches \(\Delta\), we have a steep rise since more and more of the peak is suddenly contributing. Eventually, we approach the same linear relation when the voltage has become large compared to \(\Delta\), since the areas under the densities of states are equal, and the "peak" is now far from each Fermi surface. An alternate way of visualizing the situation is the consideration of the derivative curve

\[
\frac{dI}{dV} = C \int_{-\infty}^{\infty} \rho_2(E-V) [ -f'(E) ] \, dE \quad \ldots A.6
\]

This is a straightforward convolution which, because of the peaked nature of \([-f'(E)\]) about \(E = 0\), will have the general shape of \(\rho_2\) "smeared out" because of the finite thermal width of \([-f'(E)]\). Such a curve is illustrated in Figure AB(a) which reproduces an actual experimental trace taken while the tin was still above its transition temperature.

Finally we come to the interesting case of two superconductors.
FIG. AB - TUNNELLING $dI/dV$ FOR VARIOUS JUNCTIONS
(Experimental Curves)

(a) Superconductor to Normal-Metal (Sn above $T_c$)

(b) Superconductor (Pb) to Superconductor (Sn)

(c) Incipient Sn Transition
For the I-V characteristic we can again refer to the energy diagram, Figure AA(b). As we increase the voltage from zero, at finite temperatures, the current rises again slowly, because of the gradually increasing density of states that excited particles "see". But, suddenly, at $V = (\Delta_1 - \Delta_2)$, where the gap edges meet, they see a decreasing density of states, and the current drops. We thus obtain a negative resistance region which persists until the next two gap edges meet at $V = (\Delta_1 + \Delta_2)$, when we have a tremendous rise in the tunnelling current, again asymptotically approaching the "ohmic" curve. Because of the infinites at the edges of the densities of states, we will have a sharp discontinuity in the slope at the critical points. Even if only one of the densities of states had the infinite peak, we would still get a discontinuity providing the other one at least comes to zero with a vertical slope at the gap. When we electrically differentiate I(V) we do not, of course, get the infinite discontinuities, but the derivative curve goes through zero at $V = (\Delta_1 - \Delta_2)$ and $(\Delta_1 + \Delta_2)$. We can then obtain the full smaller gap, $2\Delta_2$, by direct measurement of the crossover points.

Figure AB(b) indicates an experimental dI/dV trace for the two superconductor systems.

Figure AB(c) was taken 8 millidegrees above the transition temperature of the tin to show the approach to the transition. It is shown just for interest, as it might represent a region of "gapless" superconductivity, but further evidence in this is lacking.
APPENDIX B - PREPARATION OF OXIDE BARRIER ON TIN

As the preparation of thin film surfaces is so strongly dependent on the exact experimental conditions that an extensive amount of empirical adjustment is always required in any set up, it is not considered worthwhile to give a detailed description of experimental procedure. One fact that does deserve mention, however, is a modification which was found essential to the anodizing technique in order to achieve an oxide barrier on tin.

In the "conventional" anodizing method, an oxygen glow discharge is set up in dry oxygen, at 50 to 100 µ pressure, between a negative electrode and the mask covering all but the region of the sample which it is desired to anodize. A current-limiting resistor and a small battery are then connected so as to keep the sample 1 - 2 volts positive with respect to the mask, and the anodizing current is monitored as a function of time. With proper oxide formation, this current decays exponentially as a function of time.

In our experimental set up, it was not found possible to achieve a continuous oxide layer over the junction area in this fashion. A measure of success and reproducibility was obtained, however, by placing a screen at the same potential as the mask at a distance 1 - 2 cm - i.e., at least several mean-free-paths - in front of it. It was then found that a reasonably satisfactory anodization could be achieved. It is inferred from this that the oxide layer on tin is sufficiently fragile that highly energetic ions can damage it, and only when the
oxidizing ions are sufficiently slowed can a controllable oxide layer be formed.