

COMITATO NAZIONALE PER L'ENERGIA NUCLEARE
Laboratori Nazionali di Frascati

LNF - 70/6
25 Febbraio 1970

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Servizio Documentazione
dei Laboratori Nazionali di Frascati del CNEN
Casella Postale 70 - Frascati (Roma)

Nota interna: n. 465
25 Febbraio 1970

N. Sacchetti: THE TUNNEL EFFECT IN SUPERCONDUCTORS. -

(Lectures given at the Intern. School of Applied Physics "Developments of Applied Superconductivity", Erice, April 1969; to be published on the Proceedings of the School)

I. - INTRODUCTION.

As it is well known from the elementary quantum mechanics⁽¹⁾, a particle of energy E has a finite probability to pass through a potential barrier whose maximum height is V_0 , even if $E < V_0$. This phenomenon is called "tunnel effect" and has no classical analogue.

The problem can be solved by means of the Schrödinger equation to get the transmission coefficient for such a process. In the simple case of the rectangular potential barrier of height V_0 and length a (see fig. 1) the transmission coefficient C is given, as a good approximation, by the following expression:

$$(1) \quad C(E) = \exp \left\{ - \left[\frac{2m}{\hbar^2} (V_0 - E) \right]^{1/2} a \right\}.$$

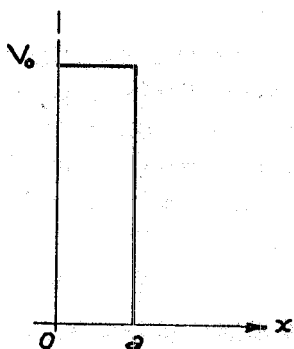


FIG. 1 - Rectangular potential barrier.

Although the expression (1) is related to a simplified situation with respect to the physical reality, some qualitative consideration can be made on its basis. The transmission coefficient C is a decreasing exponential function of a and of $(V_0 - E)^{1/2}$. This strong dependence on the characteristic parameters of a potential barrier is a typical feature of every phenomenon of this kind.

Usually the experimental detection of the tunnel effect can be reduced to measurements

of current and voltage, i. e. to the determination of the current I v. s. voltage V relation-ship. In general the tunnel effect is observed in systems which can be sketched in the following way: two regions (metals, semimetals, semiconductors, etc.) containing electrons or holes able to move separated by a potential barrier. Such a system can be realized in practice in a number of different ways: e. g. two degenerate semiconductors of p and n type respectively, separated by a region of sharp transition (tunnel diode) or two superimposed metallic films separated by same insulating layer (tunneling junction). In the following sections we will deal essentially with tunneling junction in which one or both metals can be in the superconducting state.

II. - SEMIPHENOMENOLOGICAL THEORY OF THE TUNNEL EFFECT.

In this section we will deduce the expression of the current I as a function of the applied voltage V for the system sketched in fig. 2 (tunnel junction). The theory we expose is semiphenomenological in the

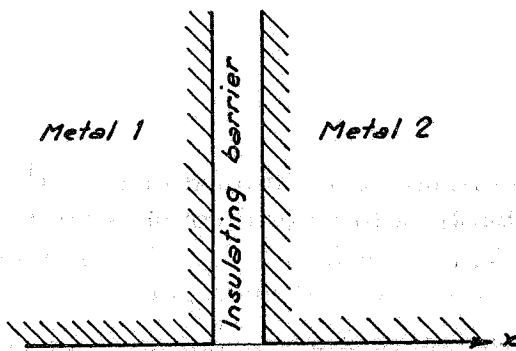


FIG. 2 - Schematic drawing of a tunnel junction.

sense that the calculation of the current is reduced to the sum of elementary single particle tunnel processes, neglecting the many body aspects of the whole phenomenon. Actually the results of the microscopic theory of the superconducting state are introduced in the semiphenomenological calculations as long as the modifications of the quasi particles excitation spectrum and the density of states are concerned. Of course the validity of such an approximation can be justified on the basis of its accor-

dance with the experimental results. On the other hand the general theory of the tunnel effect gives the same results as the semiphenomenological theory and is also able to predict some new effects (Josephson effects) by taking into account the suitable many-body properties in the calculations.

We first point out that in a single tunnel process the energy of the particle tunneling through the barrier is conserved. This is a very important feature of the phenomenon and it can be understood by remembering that a tunnel transition does not require absorption or emission of energy^(x). Then, referring to fig. 2, we can perform the calculation of the tunnel current I which flows through the barrier when a voltage V

(x) - In the elementary theory of the tunnel effect the solutions of the Schrödinger equation on the left of the barrier as well as on the right correspond to the same energy value E of the particle.

is applied between the two metallic regions, on the basis of the following simple considerations. A electron which is initially in the state k in the region 1 can make a tunnel transition to the state k' in the region 2. We can treat this phenomenon like an ordinary quantum transition by introducing a matrix element $M_{kk'}$ such that $(2\pi/\hbar) |M_{kk'}|^2$ gives the probability of transition per unit time between the two states. The energy conservation is introduced by means of the multiplying factor $\delta(\mathcal{E}_k - \mathcal{E}_{k'})$ where \mathcal{E}_k is the electron energy. The electrons are distributed according to the Fermi statistics and the electron states in the two regions can be described by means of two density of states $n_1(\mathcal{E}_k)$ and $n_2(\mathcal{E}_k)$. Moreover we assume that the difference between the Fermi energies of the two regions is given by the term eV when V is the applied voltage. In these conditions the contribution to the current arising from the electrons of region 1 whose energies lie in the range between the values \mathcal{E}_k and $\mathcal{E}_k + d\mathcal{E}_k$ and tunneling into the region 2 in states in the energy range \mathcal{E}'_k , $\mathcal{E}'_k + d\mathcal{E}'_k$ can be written as follows:

$$(2) \quad dI = \frac{2\pi}{\hbar} e |M_{kk'}|^2 n_1(\mathcal{E}_k) f(\mathcal{E}_k) n_2(\mathcal{E}'_k + eV) \times \\ \times [1 - f(\mathcal{E}'_k + eV)] \delta[\mathcal{E}_k - (\mathcal{E}'_k + eV)] d\mathcal{E}_k d\mathcal{E}'_k$$

where $f(\mathcal{E}_k)$ is the function which gives the probability of the occupation of a single state of energy \mathcal{E}_k and whose expression is^(x):

$$f(\mathcal{E}) = \left[\exp\left(\frac{\mathcal{E}}{kT}\right) + 1 \right]^{-1}$$

the total current is obtained by integrating over all the values of the energy and subtracting the inverse current contribution. We obtain:

$$(3) \quad I = \frac{2\pi}{\hbar} e \int |M_{kk'}|^2 n_1(\mathcal{E}_k) n_2(\mathcal{E}_k + eV) \times \\ \times [f(\mathcal{E}_k) - f(\mathcal{E}_k + eV)] d\mathcal{E}_k .$$

Now we can introduce a simplification concerning the factor $|M_{kk'}|^2$. In general it depends on the electron states and on the potential function $V(x)$ in the barrier. However, taking into account that we will be interested essentially in low values of the applied voltages (of the order of a few millivolts), it is reasonable to assume that the potential function in the barrier is quite insensitive to the applied voltage. Moreover

(x) - We note that the electron energy is measured taking the Fermi energy as reference level.

4.

the electrons making a tunnel transition are restricted to a range kT around the Fermi energy. From all these considerations it can be inferred that $|M_{kk}|^2$ is independent on the electron energy. Qualitatively we can understand this fact by remembering the expression (1) of the transmission coefficient $C(E)$ which, if $E \ll V_0$, can be approximated by $\exp \left[- \left(\frac{2m}{\hbar^2} V_0 \right)^{1/2} a \right]$ (V_0 is of the order of 1 volt).

In this way we can see that $|M_{kk}|^2$ depends essentially on the properties of the barrier and is unaffected by the superconducting transition a metal can make. All these considerations can be justified more rigorously on the light of the general theory of the tunnel effect developed below.

We can rewrite eq. (3) in a simple form :

$$(4) \quad I = \frac{2\pi}{\hbar} e |M|^2 \int n_1(\epsilon_k) n_2(\epsilon_k + eV) [f(\epsilon_k) - f(\epsilon_k + eV)] d\epsilon_k.$$

In spite of the approximations contained in eq. (4), this expression is in a good accordance with the experimental results. We will now discuss the various cases of tunnel effect in relation to the state in which one or both metals can be.

I^o). Normal metal (1) - barrier - normal metal (2) junction (N-I-N).

In this case eq. (4) can be easily integrated with the hypothesis of low applied voltage and temperature such that $kT \ll \epsilon_F$. For a normal metal the density of states $n_1(\epsilon_k)$ and $n_2(\epsilon_k)$ are nearly independent on the electron energy at least in the range kT around the Fermi energy. We then obtain from (4) :

$$(5) \quad I_{NN} = \frac{2\pi}{\hbar} e |M|^2 n_1(0) n_2(0) eV = AV.$$

Eq. (5) has been verified experimentally⁽²⁾ in Al - Al₂O₃ - Al junctions although there is some discrepancy with respect to the calculated values of A.

II^o). Superconducting metal (1) - barrier - normal metal (2) junction (S-I-N).

It is well known that when a metal goes into the superconducting state the electron distribution in the momentum space undergoes a deep modification. An energy gap sets up in the excitation spectrum and the density of state changes in a substantial way. Eq. (4) can be discussed if a suitable model for the density of states as a function of the energy is introduced. The simplest description of the superconducting state is given by the B. C. S. theory⁽³⁾ where the expression for $n_1(\epsilon)$ is :

$$(6) \quad (n_1)^S = n_1(0) \frac{|\epsilon|}{(\epsilon^2 - \Delta^2)^{1/2}} = n_1(0) n_1^S(\epsilon) \quad |\epsilon| > \Delta$$

$$(n_1)^S = 0 \quad |\epsilon| < \Delta$$

and Δ is the energy gap, independent on the electron energy. It is convenient at this point to distinguish two cases:

a) Temperature $T = 0^{\circ}\text{K}$. - Owing to the analytic form of the Fermi function at $T = 0^{\circ}\text{K}$ eq. (4) can be rewritten as follows:

$$(7) \quad I_{SN} = A \int_{-\infty}^{\infty} n_1^S(\epsilon) d\epsilon = A \int_{-eV}^0 n_1^S(\epsilon) d\epsilon$$

where the integration limits occurring in the last member of eq. (7) can be easily understood by observing the plots of fig. 3a. By differentiating eq. (7) with respect to V we calculate the differential conductance (at $T = 0^{\circ}\text{K}$):

$$(8) \quad \frac{dI_{SN}}{dV} = A n_1^S(eV).$$

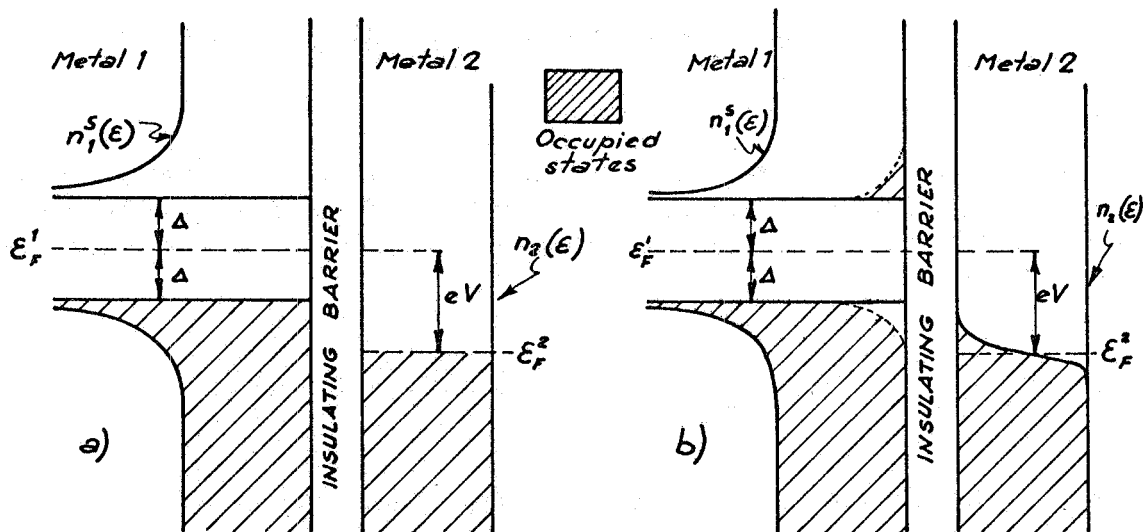


FIG. 3 - Schematic representation of the density of states of a S-I-N junction. a) $T = 0^{\circ}\text{K}$; b) $T \neq 0^{\circ}\text{K}$.

This is a very important result because it shows that the differential conductance is directly proportional to the density of states of the superconducting metal, whatever the model for n_1^S . With the B. C. S. theory we obtain:

6.

$$\begin{aligned}
 I_{SN} &= 0 & 0 \leq eV \leq \Delta \\
 (9) \quad I_{SN} &= A(V^2 - \Delta^2)^{1/2} & eV \geq \Delta \\
 I_{SN}(-V) &= -I_{SN}(V).
 \end{aligned}$$

In fig. 4 we have reported the qualitative behaviour of a $I(V)$ characteristics of this kind. We point out that for sufficiently high values of V the I_{SN} curve coincides with the I_{NN} straight line.

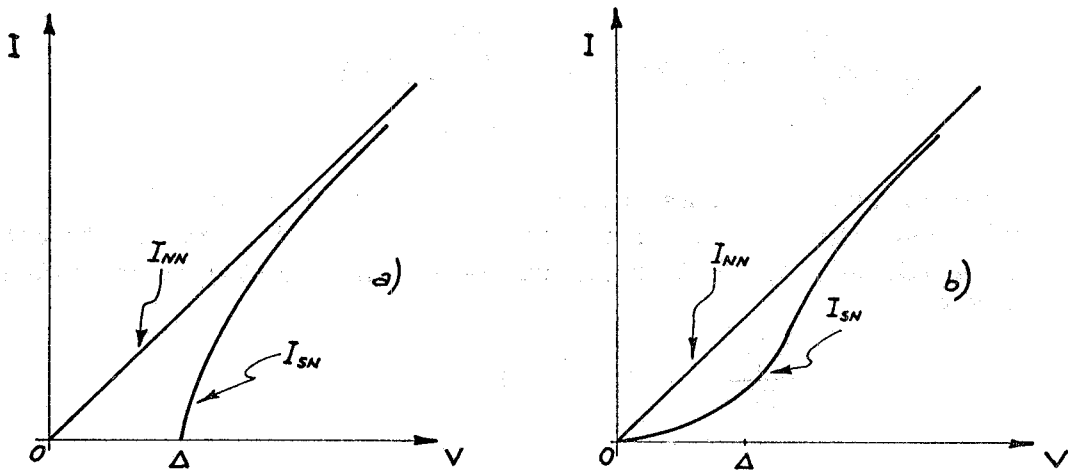


FIG. 4 - Tunneling curves for a S-I-N junction: a) $T = 0^{\circ}\text{K}$; $T \neq 0^{\circ}\text{K}$.

b) Temperature $T \neq 0^{\circ}\text{K}$. - In this case eq. (4) no longer reduces to a simple form even in the simple model of the B. C. S. theory. However in the limit $V < \Delta$ the integral can be expressed in the following series form⁽⁴⁾:

$$(10) \quad I_{SN} = 2A\Delta \sum_{n=1}^{\infty} (-1)^{n+1} K_1\left(\frac{n\Delta}{kT}\right) \sinh\left(\frac{nV}{kT}\right)$$

where K_1 is the first order of the modified Bessel function of the second kind. In fig. 4b it is shown the qualitative behaviour of the $I_{SN}(V)$. Although the curve of fig. 4b is relative to a temperature such that $kT/\Delta \sim 0.15$, we point the thermal smearing at $V \sim \Delta$. We give also some useful limit expression for I_{SN} :

$$\begin{aligned}
 \lim_{V \rightarrow 0} \frac{I_{SN}}{I_{NN}} &= 2 \sum_{m=1}^{\infty} (-1)^{m+1} \frac{m\Delta}{kT} K_1\left(\frac{m\Delta}{kT}\right) \times \\
 &\times \left(\frac{2\pi\Delta}{kT}\right)^{1/2} \exp\left(-\frac{\Delta}{kT}\right) \quad (\text{valid for } \Delta \gg kT).
 \end{aligned}$$

A measurement of the energy gap could be obtained from a curve like that reported in fig. 4b. However such a measurement would not be very accurate because of the thermal smearing. We can avoid this difficulty by considering the differential conductance, which, after eq. (10), can be expressed as follows:

$$(11) \quad \frac{dI_{SN}}{dV} = 2A \frac{\Delta}{kT} \sum_{m=1}^{\infty} (-1)^{m+1} m K_1 \left(\frac{m\Delta}{kT} \right) \cosh \left(\frac{mV}{kT} \right).$$

In the limit $V \rightarrow 0$:

$$(12) \quad \left(\frac{dI_{SN}}{dV} \right)_{V=0} = 2A \frac{\Delta}{kT} \sum_{m=1}^{\infty} m K_1 \left(\frac{m\Delta}{kT} \right).$$

On the other hand A is the conductance when both metals are in the normal state. Then by considering the ratio:

$$(13) \quad \zeta = \left(\frac{dI_{SN}}{dV} \right)_{V=0} / A = 2 \frac{\Delta}{kT} \sum_{m=1}^{\infty} (-1)^{m+1} m K_1 \left(\frac{m\Delta}{kT} \right)$$

we can obtain Δ/kT from a measurement of ζ ($V=0$) and by resolving numerically the eq. (13)⁽⁵⁾. As an example we have reported in fig. 5

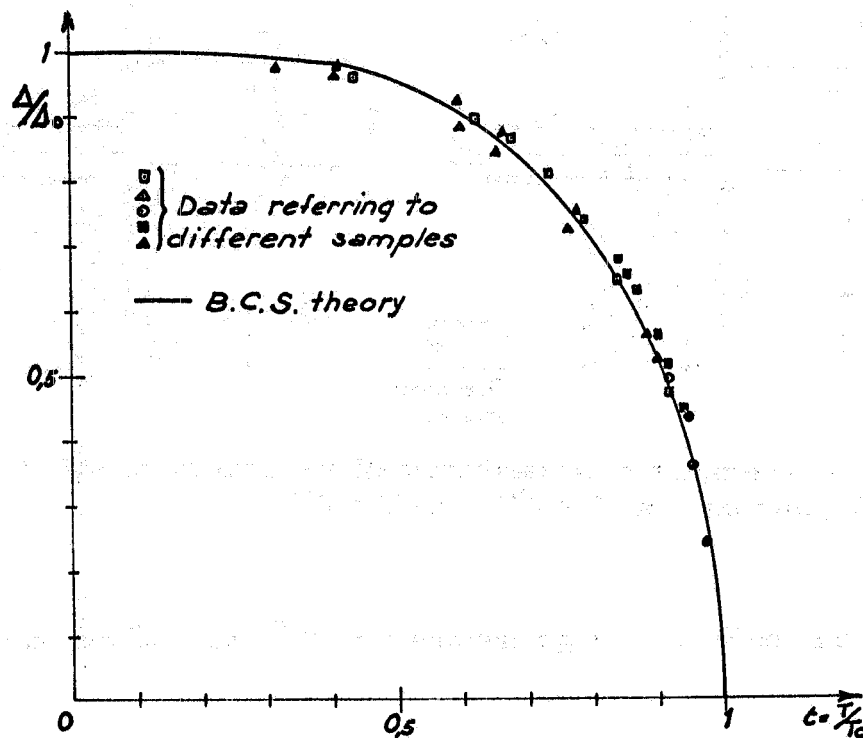


FIG. 5 - Experimental curve of the energy gap Δ of tin as a function of temperature (after ref. (6)).

the experimental behaviour of $(\Delta)_{\text{sn}}$ as a function of the reduced temperature $t = T/T_C$ for a number of different Al-Al₂O₃-Sn junctions where $(\Delta)_{\text{sn}}$ has been deduced by the above mentioned methods⁽⁶⁾. In the same figure it is also shown the theoretical behaviour as predicted by the B. C. S. theory.

III^o). Superconducting metal (1) - barrier - superconducting metal (2) - junction (S₁-I-S₂).

Also in this case it is necessary to distinguish between $T = 0^\circ\text{K}$ and $T \neq 0^\circ\text{K}$. Moreover we can have two different superconductors ($S_1 \neq S_2$) or the same superconductor ($S_1 = S_2 = S$) on the two sides of a junction.

a) $T = 0^\circ\text{K}$, $S_1 \neq S_2$. - Eq. (4) now becomes :

$$(14) \quad I_{S_1 S_2} = A \int_{-\infty}^{\infty} n_1^S(\mathcal{E}) n_2^S(\mathcal{E}) d\mathcal{E} = A \int_{-V+2}^{\Delta_1} n_1^S(\mathcal{E}) n_2^S(\mathcal{E}) d\mathcal{E}$$

(see fig. 6 for the limits of integration in eq. (14)).

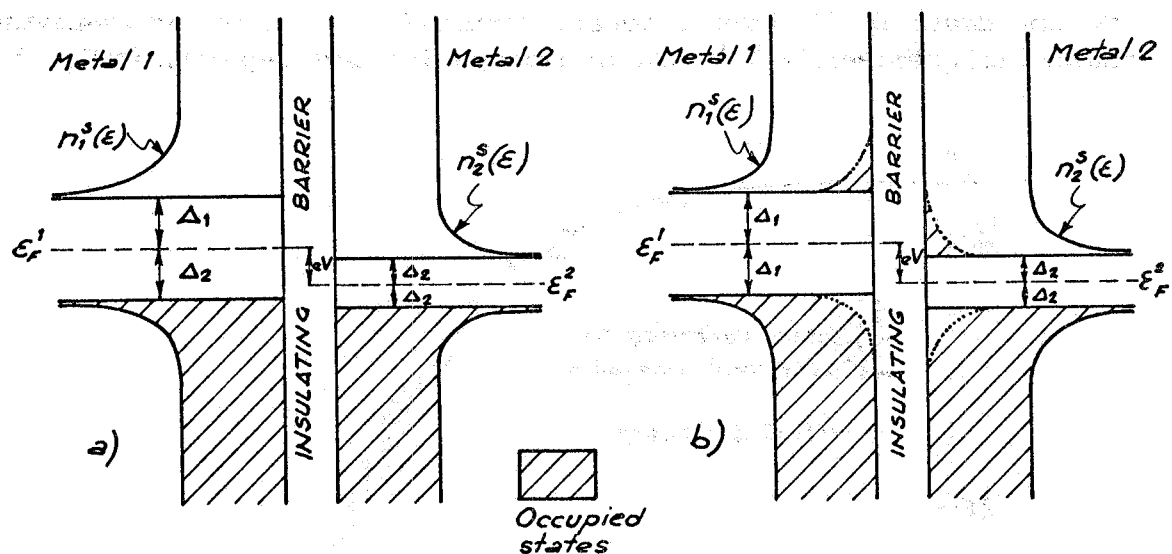


FIG. 6 - Schematic representation of the density of states of a S₁-I-S₂ junction: a) $T = 0^\circ\text{K}$; b) $T \neq 0^\circ\text{K}$.

By introducing the B. C. S. expressions for n_1^S and n_2^S we obtain from eq. (14):

$$(15) \quad I_{S_1 S_2} = 0 \quad \text{for } V < 0 \quad \text{and} \quad 0 \leq V \leq \Delta_1 + \Delta_2$$

$$(15) \quad I_{S_1 S_2} = -2A \Delta_1 \Delta_2 \left[V^2 - (\Delta_2 - \Delta_1)^2 \right]^{-1/2} K(\alpha) + \\ + A \left[V^2 - (\Delta_2 - \Delta_1)^2 \right]^{1/2} E(\alpha) \quad V > \Delta_1 + \Delta_2$$

$$I_{S_1 S_2}(-V) = -I_{S_1 S_2}(V)$$

where $\alpha = \left[V^2 - (\Delta_1 + \Delta_2)^2 \right]^{1/2} \left[V^2 - (\Delta_2 - \Delta_1)^2 \right]^{-1/2}$ and K and E are elliptic integrals of first and second kind respectively. The expression (15) contains a discontinuous jump in the current, occurring at $V = \Delta_1 + \Delta_2$ the value of this jump being $\delta I = (\pi/2)A(\Delta_1 \Delta_2)^{1/2}$. Such a discontinuity is a direct consequence of the singularity of the density of states in the superconducting state. Of course in the limit $\Delta_2 \rightarrow 0$ eq. (15) reduces to eq. (9).

b) $T = 0^\circ K$, $S_1 = S_2 = S$. - In this case we can rewrite (15) by putting $\Delta_1 = \Delta_2 = \Delta$. This gives:

$$(16) \quad I_{SS} = 0 \quad 0 \leq V \leq 2\Delta \\ I_{SS} = -2\Delta^2 V^{-1} K(\alpha) + AVE(\alpha) \quad V > 2\Delta$$

$$I_{SS}(-V) = -I_{SS}(V)$$

with $\alpha = \left[V^2 - A\Delta^2 \right]^{1/2} V^{-1}$. The value of the discontinuous jump in the current is $\delta I = (\pi/2)A\Delta$.

c) $T \neq 0^\circ K$, $S_1 \neq S_2$. - The integrals appearing in the expression of the current cannot be evaluated analytically. Numerical calculations show the following properties of the $I_{S_1 S_2}(V)$ characteristics:

1) for $V \sim |\Delta_2 - \Delta_1|$ there is a discontinuity of logarithmic type such as:

$$I_{S_1 S_2} \sim \log \left| V - |\Delta_2 - \Delta_1| \right|$$

2) for $V = \Delta_2 + \Delta_1$ there is, on the contrary, a finite discontinuity $I_{S_1 S_2}$ given by the expression:

$$\delta I_{S_1 S_2} = \frac{\pi}{4} A (\Delta_1 \Delta_2)^{1/2} \frac{\sinh\left(\frac{(\Delta_1 + \Delta_2)}{kT}\right)}{\cosh\left(\frac{\Delta_1}{kT}\right) \cosh\left(\frac{\Delta_2}{kT}\right)}$$

Between these two values of the applied voltage the $I_{S_1S_2}(V)$ curve exhibits a negative resistance region. In fig. 7 we have reported the theo

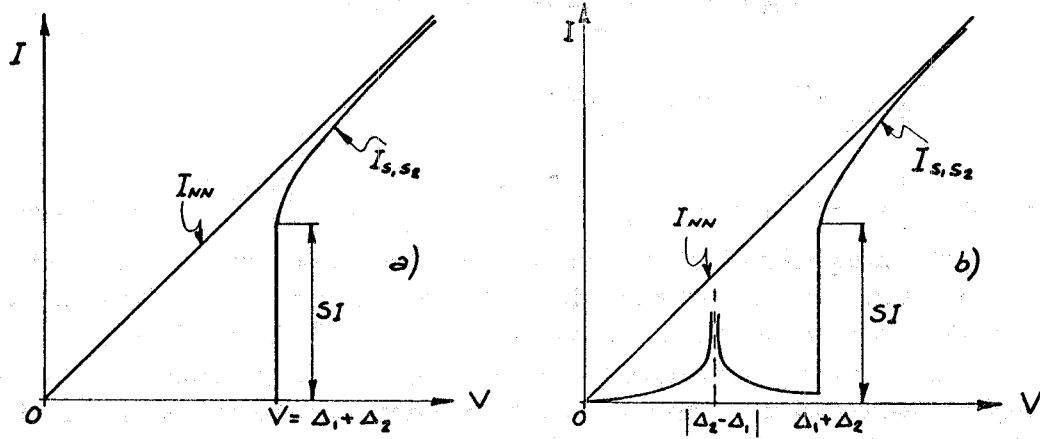


FIG. 7 - Theoretical tunneling characteristics for a S_1 -I- S_2 junction: a) $T = 0^{\circ}\text{K}$; b) $T \neq 0^{\circ}\text{K}$.

retical behaviour obtained from the above considerations. Experimentally what we observe is the occurrence of a minimum in the tunneling current separated by a negative resistance region and it is assumed that the maximum and the minimum correspond to the values $|\Delta_2 - \Delta_1|$ and $\Delta_2 + \Delta_1$ respectively. As an example in fig. 8 we have reported a series of experimental graphs of the characteristics of Al- Al_2O_3 -Sn junction at various temperatures exhibiting the different features discussed above⁽⁶⁾.

d) $T \neq 0^{\circ}\text{K}$, $S_1 = S_2 = S$. - We can evaluate numerically I_{SS} , if $V \leq 2\Delta$ and, if the condition $kT < 0.3\Delta$ is satisfied, a negative resistance region appears in the tunnel characteristics. When $\Delta \gg kT$ and $V < 2\Delta$ I_{SS} is well approximated by the following expression:

$$(17) \quad I_{SS} \sim 2A \exp\left(-\frac{\Delta}{kT}\right) \left(\frac{2\Delta}{V+2\Delta}\right)^{1/2} (V+\Delta) \operatorname{senh}\left(\frac{V}{2kT}\right) K_0\left(\frac{V}{2kT}\right)$$

where K_0 is the zero order of the modified Bessel function of the second kind.

As we have already pointed out from the $I(V)$ curves in the S-I-N case it is possible to deduce the value of Δ for a superconductor; of course such a measurement can be obtained once we know the position of the maximum and the minimum in a $I(V)$ graph relative to the S_1 -I- S_2 case.

Moreover, remembering eq. (8), it is evident that a measurement of dI_{SN}/dV as a function of V gives directly a quantity which is directly proportional to the density of states in the superconductor. On the other hand to obtain significant information it is necessary to work

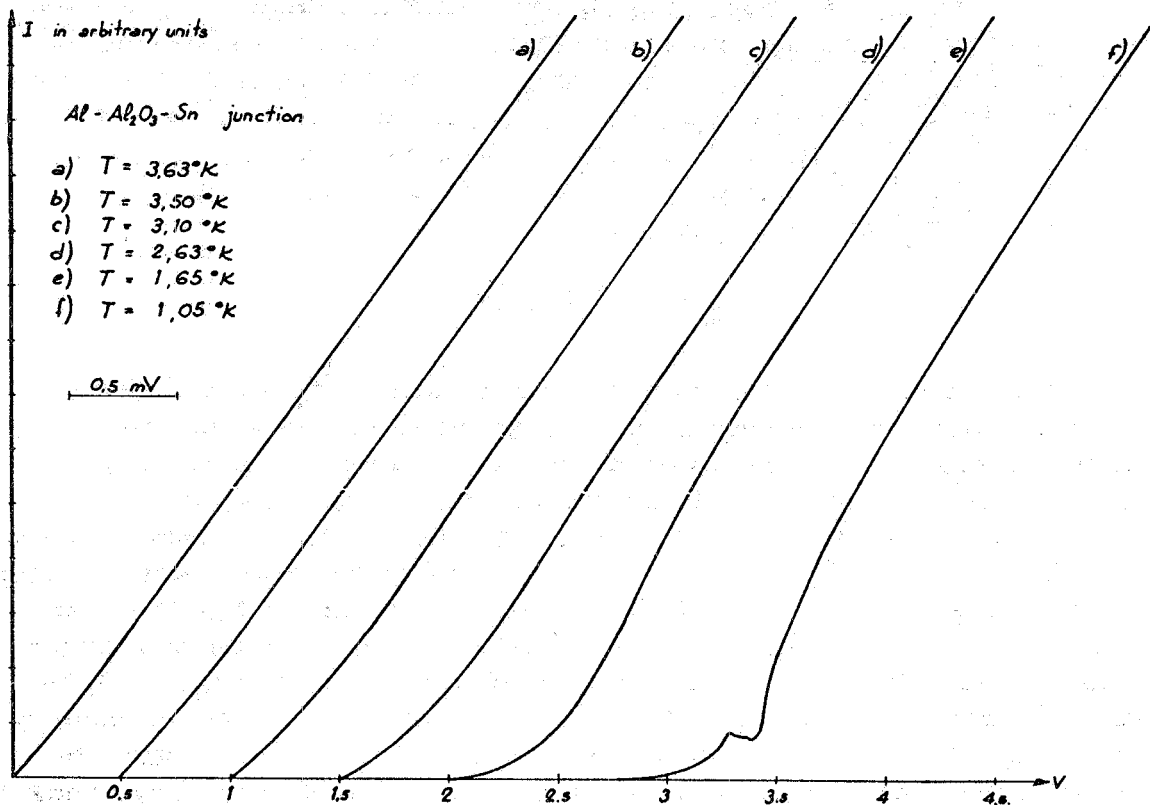


FIG. 8 - Experimental characteristics of an Al-Al₂O₃-Sn junction. The curves from a) to e) are relative to temperatures less than $T_c(\text{Sn})$ but higher than $T_c(\text{Al})$ (S-I-N case); the curve f) is relative to both Al and Sn in the superconducting state (S₁-I-S₂ case). For clarity the origin is displaced along the V axis (after ref. (6)).

at temperatures as low as possible; however we can calculate dI_{SN}/dV as function of V at temperatures different from 0°K by introducing a suitable expression $n^{\text{S}}(\mathcal{E})$ and we can get useful informations on the validity of this expression from measurements of dI_{SN}/dV . In fig. 9⁽⁷⁾ we show a number of dI_{SN}/dV v. s. V curves for a Sn-MgO-Mg tunneling junctions. The comparison with the theoretical curve is made on the basis of B. C. S. theory for $n^{\text{S}}(\mathcal{E})$.

More generally we can say that measurements of dI_{SN}/dV are a very sensitive method to put in evidence structures in $n^{\text{S}}(\mathcal{E})$ which are not described by the B. C. S. theory. In some cases it is also useful to measure d^2I_{SN}/dV^2 as a function of V to reach a better localization of the structural details. We will see in the following more exactly what kind of physical information we can get by means of these methods.

Before concluding this section we want to discuss briefly the single tunnel processes in relation to the dependence of the quasi particle energy on the wave vector k in a superconductor. This is an important point because we can understand in a simple way why the coherence factors

like u_k^2 or similar^(x), which usually have strong influence on the quantum transitions involving superconductors (ultrasonic attenuation, microwave absorption, etc.), do not appear in the tunneling current. We limit for simplicity to the case of a S-I-N junction at $T = 0^\circ\text{K}$. We remember that, following B. C. S., the quasi particle energy E_k in the superconducting state is related to the corresponding energy \mathcal{E}_k in the normal state by the expression:

$$(18) \quad E_k = (\mathcal{E}_k^2 + \Delta^2)^{1/2}$$

if we measure the energies from the Fermi level \mathcal{E}_F . In fig. 10 we show the quasi particle energy v. s. k curves for a S-I-N junctions; two tunnel processes are also shown by means of which an electron starting from the same state α in the metal 1 (normal) can go in the final state β or β' in the metal 2 (superconducting) with the condition $\mathcal{E}_\beta = -\mathcal{E}_{\beta'}$. As it is well known if we add a quasi particle to a superconductor by putting it in the state β the excitation energy is E_β (positive). On the other hand, owing to the modification of the electron distribution in the superconductor, we can add a quasi particle by putting it in the state β' with the condition $\mathcal{E}_\beta = -\mathcal{E}_{\beta'}$ obtaining an excitation energy $E_{\beta'} = E_\beta$. In conclusion a quasi particle starting from the state α can go in the final states β or β' and in both cases the energy conservation is expressed by the same term $\delta(\mathcal{E}_\alpha + E_\beta - V)$. Now the probability of finding the state β empty is given by:

$$u_\beta^2 = \frac{1}{2} \left(1 + \frac{E_\beta}{E_\beta} \right)$$

while, for the state β' we have:

$$u_{\beta'}^2 = \frac{1}{2} \left(1 + \frac{E_{\beta'}}{E_{\beta'}} \right) = \frac{1}{2} \left(1 - \frac{E_\beta}{E_\beta} \right) = v_\beta^2$$

The total probability is then:

$$u_\beta^2 + u_{\beta'}^2 = u_\beta^2 + v_\beta^2 = 1.$$

In this way the coherence factors add up to the unity and disappear from the current expression. Moreover the presence of the factor $\delta(\mathcal{E}_\alpha + E_\beta - V)$ and the fact that the minimum excitation energy is Δ accounts for the zero current when $V < \Delta$. Analogous considerations hold for all the other cases of tunneling already discussed and can be extended to temperatures different from 0°K .

(x) - See ref. (8) for a definition and a discussion of the coherence factors.

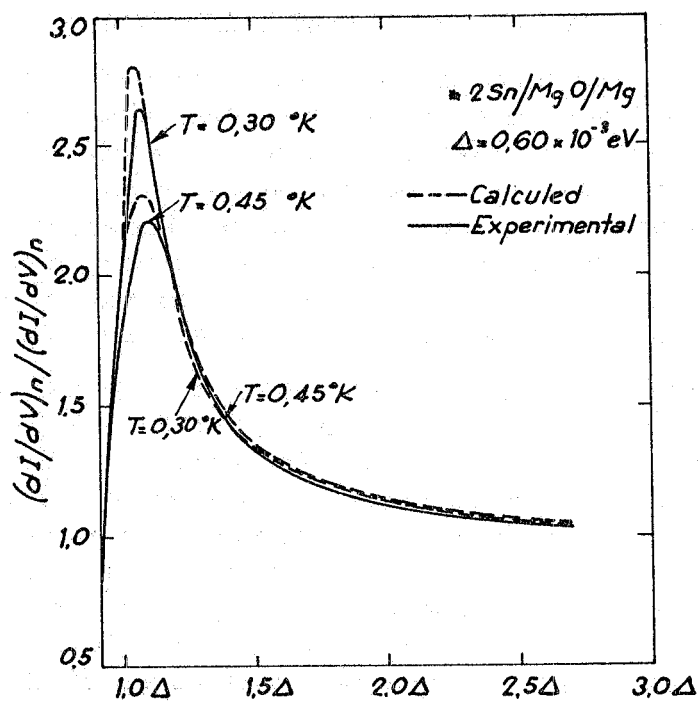


FIG. 9 - Experimental and theoretical curves of the relative conductivity as a function of the energy for two temperatures. The theoretical conductivity has been calculated using the B. C. S. model (after ref. (8), p. 335).

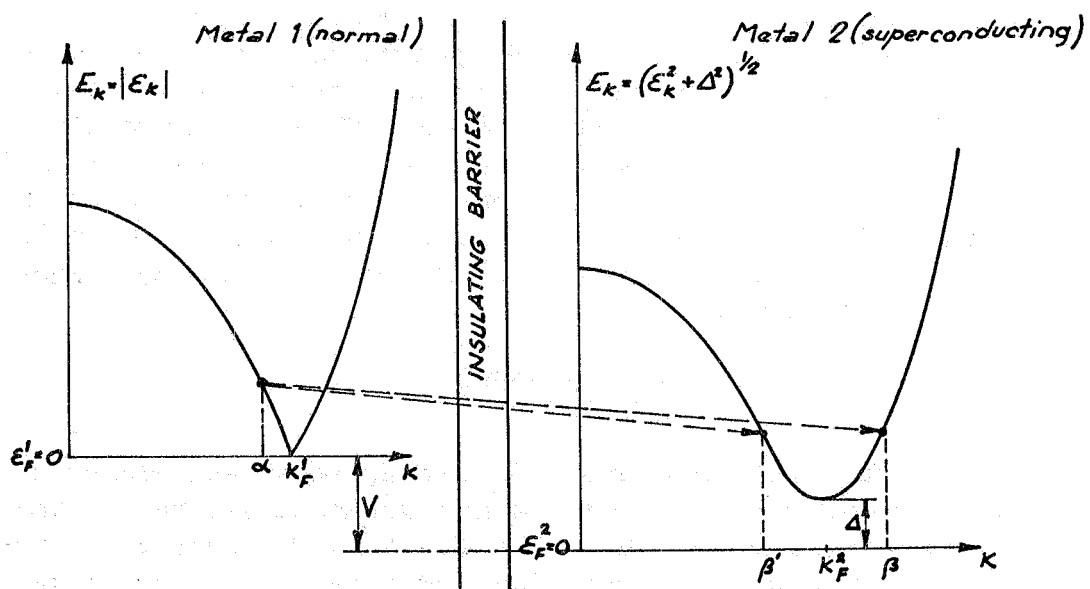


FIG. 10 - Schematic drawing of single tunnel process between a normal and a superconducting metal.

III. - GENERAL THEORY OF THE TUNNEL EFFECT.

Although the results of the semiphenomenological theory are in good accordance with the experimental data the question concerning the connections of the tunnel phenomena with the microscopic theory of superconductivity cannot be neglected. We need of such a justification from a general point of view; but, letting aside this argument, the point is that there does exist a series of tunnel phenomena which the semiphenomenological theory cannot explain. We are explicitly referring to the Josephson effects and to the weakly connected superconductors.

We will give here a general account of the microscopic theory while for a more detailed description the reader is referred to the bibliography. First we could try to establish a theory of the tunnel effect by introducing a suitable approximation of independent quasi particles according to which the electronic states of the whole system (metal-barrier-metal) would be, say, a superimposition of Bloch states with wave vectors of opposite sign and suitable continuity conditions in the region of the barrier. However it has been shown⁽⁹⁾ that this approximation leads to an expression of the current which is substantially independent from the density of states.

Conversely the problem can be handled starting by some hamiltonian in which the many body effects are included. The first thing we want to discuss is the relation between the hamiltonian of the whole system and the hamiltonian of the two metals when they are completely far apart. For an isolated piece of normal or superconducting metal we are able to write, although within certain approximations, a hamiltonian which describes in a satisfactory way the different properties of the metal. In the other hand when we put together two pieces of metal to form a tunnel junction it is quite obvious that the properties of one of the metals must be influenced to a certain extent by the presence of the other. This means simply that we cannot affirm that the hamiltonian, e. g. of the right metal, is the same as that of the isolated metal. From a quite rigorous point of view we could not distinguish between right and left hamiltonian but we would consider the total hamiltonian of the system. However the structure of our system suggests the following schematization could be reasonable

$$(19) \quad H = H_1 + H_2 + H_T$$

where H is the total hamiltonian, H_1 and H_2 refer respectively to the two metallic parts and H_T is the term responsible for the electron transfer from one side to the other. We note that (19) is much more useful if H_1 and H_2 can be chosen coincident with the hamiltonian of the isolated metals. This problem has been discussed in detail by Prange⁽¹⁰⁾ by examining the properties of the eigenfunctions of H . From his analysis it results that a reasonable justification of (19) is obtained when we introduce a suitable set of wave functions distinguished as right and

left wave functions. These functions localize an electron essentially in the left (right) metal but have an amplitude different from zero also in the right (left) metal. This set is chosen in such a way that the orthogonality conditions are not satisfied but the states are as orthogonal as possible and the left (right) states obey the completeness conditions. We can then rewrite eq. (12) in the second quantization formalism by introducing "right" and "left" creation and annihilation operators. In this way the hamiltonian can be expressed as a sum of terms containing only "left" or "right" operators and of terms where the operators are mixed together. The total hamiltonian reduces to the (19) if it is possible to neglect the mixed terms. In fact it can be shown that, as a first approximation, such terms are negligible and this is equivalent to assume that all the "right" operators anticommute with the "left" ones and vice versa. From this it follows immediately that the tunnel current is proportional to $|(H_T)_{rs}|^2$. Now we proceed to evaluate the tunnel current. First we consider the matrix element $|(H_T)_{rs}|^2$ which gives the transition probability per unit time between the states r and s . To calculate $(H_T)_{rs}$ we need the knowledge of the eigenfunctions in the region of interest, that is the metallic sides and the barrier. However even if we do not know the exact analytic form of the eigenfunctions we can discuss some properties of $(H_T)_{rs}$ ^(11,12). Let ψ_r and ψ_s be the wave functions relative to states of the system in which an electron is in the state r on the left and s on the right respectively. It can be shown that the expression for $(H_T)_{rs}$ is:

$$(20) \quad (H_T)_{rs} = -i J_{rs}(x_B)$$

where x_B is any point in the interior of the barrier and $J_{rs}(x)$ is the matrix element of the x component of the current density operator defined by:

$$J_{rs}(x) = -\frac{i}{2m} \sum_i \int \dots \int \left[\psi_r^* \frac{\partial \psi_s}{\partial x_i} - \psi_s \frac{\partial \psi_r^*}{\partial x_i} \right] x \delta(x-x_i) d\tau_1 \dots d\tau_N$$

Eq. (20) constitutes an important result because it shows that $(H_T)_{rs}$ depends essentially on the behaviour of the wave functions in the barrier. It follows that $(H_T)_{rs}$ does not change when one of the metals undergoes the superconducting transition. In fact if we take into account the possibility of spatial variations of the "energy gap" Δ ⁽¹³⁾ we see that Δ goes to zero very quickly in the insulating barrier. As a consequence the wave functions of electrons in the barrier are insensitive to the state of the metals and the coherence factors do not appear in the matrix element $(H_T)_{rs}$. Moreover $(H_T)_{rs}$, as the electron states are roughly independent from the energy at least in the range of interest, is in practice independent from the energy. Let us turn now to the expression of

the hamiltonian :

$$H = H_1 + H_2 + H_T.$$

If c and c^\star are the creation and annihilation operators of electrons in the metal 1 and d and d^\star are the analogous operator for the metal 2, H_1 and H_2 can be expressed in the second quantization formalism as products of c and d operators respectively. We are mainly interested in the term H_T for which the explicit expression is :

$$(21) \quad H_T = \sum_{r, s, \sigma} \left[(H_T)_{r, s} c_{r\sigma}^\star d_{s\sigma} + (H_T)_{r, s}^\star d_{s\sigma}^\star c_{r\sigma} \right]$$

Remembering that the operator for the total number of electrons in the metal 1 is :

$$(22) \quad N^1 = \sum_{k, \sigma} c_{k\sigma}^\star c_{k\sigma}$$

the tunneling current at the time t ^(14, 15, 16) can be evaluated by computing the mean value of the time derivative of (22). Taking into account the equation of motion for N^1 it follows immediately :

$$\begin{aligned} |I| &= e \langle \dot{N}^1 \rangle = \frac{ie}{\hbar} \langle [N^1, H] \rangle = \\ &= \frac{ie}{\hbar} \langle [N^1, H_T] \rangle = \frac{ie}{\hbar} \langle N^1 H_T - H_T N^1 \rangle \end{aligned}$$

as N^1 commutes with H_1 and H_2 .

The mean values can be calculated by the methods of quantum statistical mechanics according to which the following expression for I holds :

$$(23) \quad |I| = e \langle \dot{N}^1(t) \rangle = e \text{Tr} \left(\frac{e^{-\beta H} \dot{N}^1(t)}{Z} \right)$$

where $Z = \text{Tr} e^{-\beta H}$ is the partition function.

On the other hand remembering the expressions (21) and (22) for H_T and N^1 we get :

$$(24) \quad \dot{N}^1(t) = i \sum_{r, s, \sigma} \left[(H_T)_{rs} c_{rs}^\star d_{s\sigma} - (H_T)_{rs}^\star d_{s\sigma}^\star c_{r\sigma} \right].$$

If we consider H_T as a perturbation and putting :

$$H = H_1 + H_2 + H_T = H_0 + H_T$$

the first order perturbation theory gives :

$$(25) \quad I = ie \int_{-\infty}^t dt' \langle [\hat{N}(t'), \hat{H}_T(t')] \rangle =$$

$$= ie \int_{-\infty}^t dt' \text{Tr} (\rho_0 [\hat{N}^1(t'), \hat{H}_T(t')])$$

with $\rho_0 = \frac{e^{-\beta H_0}}{Z_0}$ and $Z_0 = \text{Tr} e^{-\beta H_0}$, while the time dependence of the operators appearing in (25) is :

$$\hat{A}(t) = e^{iH_0 t} A_{op} e^{-iH_0 t}.$$

From eqs. (24) and (21) we can rewrite eq. (25) as follows :

$$(26) \quad |I| = 2e \text{Re} \int_{-\infty}^t dt' \left\langle \sum_{r, s, \sigma} \left\{ | (H_T)_{rs} |^2 \right. \right. \times$$

$$\times \left[c_{r\sigma}^\dagger(t) d_{s\sigma}(t), d_{s\sigma}^\dagger(t') c_{r\sigma}(t') \right] +$$

$$\left. \left. + (H_T)_{rs} (H_T)_{-r-s} \left[c_{r\sigma}^\dagger(t) d_{s\sigma}(t), c_{-r-\sigma}^\dagger(t') d_{-s-\sigma}(t') \right] \right\} \right\rangle$$

The right member of eq. (26) is composed by two terms: the first represents the tunneling processes already discussed with the semiphenomenological theory, the second one is a new term which, when both metals are in the superconducting state, describes Cooper pairs tunneling through the barrier without destroying the coherence of the superconducting state. The order of magnitude of this term can be comparable with that of the first one and its presence gives rise to new effects (d. c. and a. c. Josephson effects). We point out also in the S-I-N case this term is rigorously zero because Cooper pairs cannot exist in a normal metal.

We want now to evaluate⁽¹⁷⁾ explicitly the expression (26) to deduce the results of the semiphenomenological theory neglecting the existence of the second term in (26).

Summing up with respect to the spin index σ and using the Wick's theorem we can rewrite eq. (26) as follows :

18.

$$(27) \quad |I| = Ae |H_T|^2 \operatorname{Re} \sum_{r,s} \int_{-\infty}^t dt' \left\{ \langle c_r^*(t) c_r(t') \rangle \langle d_s(t) d_s^*(t') \rangle - \langle d_s^*(t') d_s(t) \rangle \langle c_r(t') c_r^*(t) \rangle \right\}$$

where we have substituted for $|H_T|_{rs}$ a suitable mean value $|H_T|$ independent from the indices r and s and from the energy. On the other hand the mean values appearing in (27) are related to the so-called correlation functions in the following way:

$$(28) \quad \begin{aligned} G^>(r, t'-t) &= \frac{1}{i} \langle c_r(t') c_r^*(t) \rangle; & G^<(r, t'-t) &= -\frac{1}{i} \langle c_r^*(t) c_r(t') \rangle \\ G^>(s, t-t') &= \frac{1}{i} \langle d_s(t) d_s^*(t') \rangle; & G^<(s, t-t') &= -\frac{1}{i} \langle d_s^*(t') d_s(t) \rangle \end{aligned}$$

Introducing eq. (28) in (27) we get:

$$(29) \quad I = 4e |H_T|^2 \operatorname{Re} \sum_{r,s} \int_{-\infty}^t dt' \left\{ G^<(r, t'-t) G^>(s, t-t') - G^>(r, t'-t) G^<(s, t-t') \right\}$$

We can develop in Fourier series the G functions:

$$(30) \quad G^>(r, t) = \pm \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega e^{-i\omega t} G^>(r, \omega)$$

and express $G(r, \omega)$ in terms of the spectral functions $A(r, \omega)$ by means of the following relations:

$$(31) \quad \begin{aligned} G^>(r, \omega) &= A(r, \omega) [1 - f(\omega)] \\ G^<(r, \omega) &= A(r, \omega) f(\omega) \end{aligned}$$

with $f(\omega) = \left\{ \exp[\beta(\omega - \mu)] + 1 \right\}^{-1}$, $\beta = (kT)^{-1}$ and $\mu =$ chemical potential. Introducing now eq. (30) and (31) in (29) we get:

$$(32) \quad \begin{aligned} I &= 4e |H_T|^2 \operatorname{Im} \sum_{r,s} \int_{-\infty}^{\infty} \frac{d\omega d\omega'}{(2\pi)^2} \left\{ [1 - f_1(\omega)] - \right. \\ &\quad \left. - [1 - f_2(\omega')] \right\} \frac{A(r, \omega) A(s, \omega')}{\omega - \omega' + i\eta} \end{aligned}$$

We give now the explicit expressions for the spectral functions:

$$(33a) \quad A(r, \omega) = 2\pi \left[\left(1 + \frac{\varepsilon_r}{E_r}\right) \delta(\omega - E_2 - \mu) + \left(1 - \frac{\varepsilon_r}{E_r}\right) \delta(\omega + E_r - \mu) \right]$$

for a superconducting metal in the B. C. S. model, and

$$(33b) \quad A(r, \omega) = 2\pi \delta(\omega - \varepsilon_r - \mu)$$

for a normal bulk metal. Then by putting (33a) and (33b) in (32) we can calculate the tunneling current for the various cases already discussed, with a good accordance with the semiphenomenological theory.

Before closing this section we point out that in the preceding treatment the detailed properties of the insulating barrier have been neglected. In other words the only important effect of the barrier we have considered is the fact that the intensity of the tunneling current is determined by the barrier itself, but other possible effects which influence the form of the $I(V)$ curves have been neglected. However there is experimental and theoretical evidence⁽¹⁸⁻²³⁾ of anomalies in the tunnel characteristics which are due essentially to some properties of the barrier. A more general microscopic theory of the tunnel effect taking into account the properties of the barrier, has been recently given by Zawadowski⁽²⁴⁾.

From the considerations worked out in the preceding sections it is evident the importance of the tunnel effect as a tool to study the properties of the superconducting state, mainly the energy gap and the density of states. We have already shown in fig. 5 the dependence of Δ on the temperature as deduced from zero bias conductivity measurements. A number of analogous data can be found in the literature^(4,7,25,26). Of course it is possible in the same way to get informations on the dependence of Δ from other physical parameters. The effect of a magnetic field is a rather complicated question. Its influence on Δ depends on the orientation of the plane of the superconducting films with respect to the direction of the field as well as on the purity and the thickness of the film. Such a problem has been worked out rather extensively from the theoretical point of view⁽²⁷⁻³⁰⁾ and examined experimentally by means of the tunnel effect technique by various researchers^(7,31,32,33).

As we have already pointed out the density of states is directly obtainable from differential conductivity measurements for a S-I-N junction. In this way informations on the influence of various "depairing" mechanisms, such that magnetic impurities, superconducting currents, etc. can be available. When a depairing factors is present a full account of the physical situation is possible if we distinguish between order parameter and excitation gap; under certain conditions the excitation gap goes to zero while the order parameter is different from ze-

ro, i. e. the metal is still superconducting. In these conditions we are dealing with the so-called "gapless" superconductivity. Recently the argument has been reviewed by Maki⁽³⁴⁾ while experimental data concerning the influence of the depairing factors on the density of states have been reported by many authors^(33, 35, 36, 37, 38, 39).

IV. - HIGHER ORDER EFFECTS.

The tunnel processes we have considered up to this point involve the proportionality between the current and $|H_T|^2$. However there have been observed experimentally⁽⁴⁰⁾ a number of anomalies in the $I(V)$ characteristics relative to S_1 -I- S_2 and S-I-S junctions. These anomalies consist mainly in an excess current for voltage values corresponding to Δ_1 and Δ_2 in the S_1 -I- S_2 case and 2Δ in the S-I-S case. They have been interpreted⁽⁴¹⁾ by means of the hamiltonian formalism introducing tunnel processes for which the transition rate is proportional to terms like $|H_T|_{rm} |H_T|_{ms}$, i. e. processes which go from the initial state \bar{s} to the final r through an intermediate state m . The resulting current is then proportional to $|H_T|^4$ and this can explain the low intensities of the excess currents. We can visualise these processes by means of the diagrams introduced in fig. 10. The first process is shown in fig. 11a and consists in the tunneling of an electron pair from the metal 1 through the barrier, dissociation of the pair and creation of two quasi particle excitations in the metal 2 with wave vectors β_1 and β_2 respectively. The energy conservations, written in this case in the form $\delta(E\beta_1 - V)\delta(E\beta_2 - V)$, gives $V = \Delta_2$ as minimum voltage for which this process takes place. A similar process is shown in fig. 11b. In this case two Cooper pairs in the metal 1 dissociate giving rise to two quasi particle excitations with wave vectors α_1 and α_2 in the same metal while the other two electrons tunnel into the metal 2 and recombine as a Cooper pair. The energy conservation expressed as $\delta(E\alpha_1 - V)\delta(E\alpha_2 - V)$ gives as minimum voltage for this process the value $V = \Delta_1$.

The jumps in the currents can be calculated by the hamiltonian formalism and the following expression hold:

a) S-I-S junctions ($\Delta_1 = \Delta_2 = \Delta$) - when $V = \Delta$ we get:

$$(34) \quad J(\Delta) = \left(\frac{\Delta}{4\pi}\right) \frac{eK_F^2}{\hbar} \exp(-4 \langle K_{\perp} \rangle d)$$

where $\langle K_{\perp} \rangle$ is a suitable average value of the component of K perpendicular to the junction surface whose value is about $(3/8)K_F$. We can make a comparison between this jump and the discontinuity in the current for $V = 2\Delta$. It results:

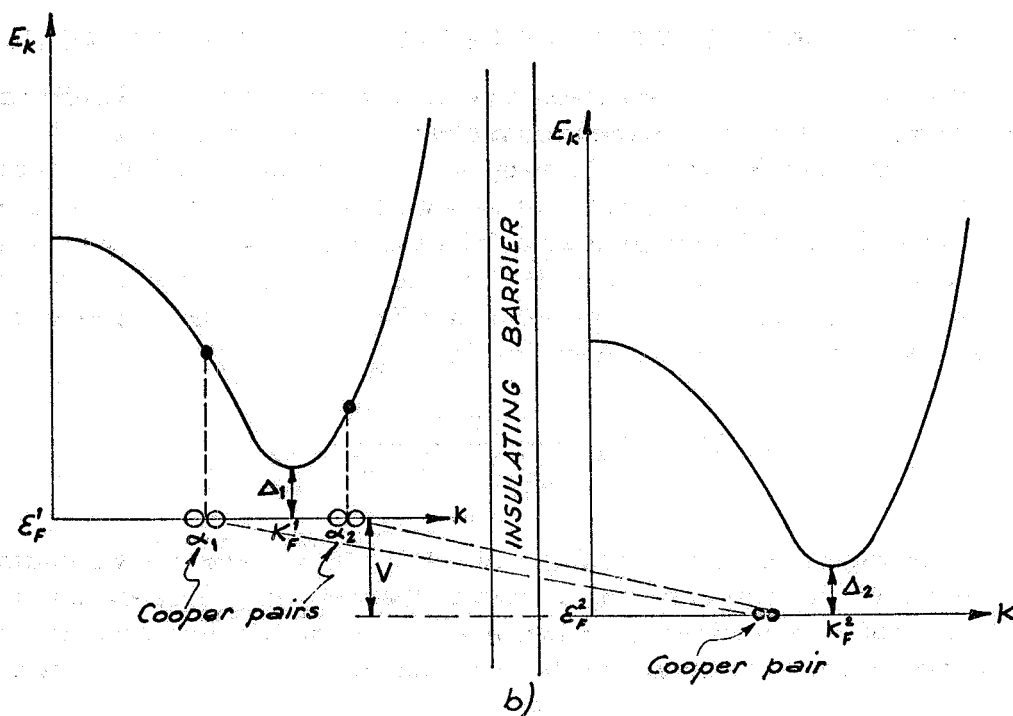
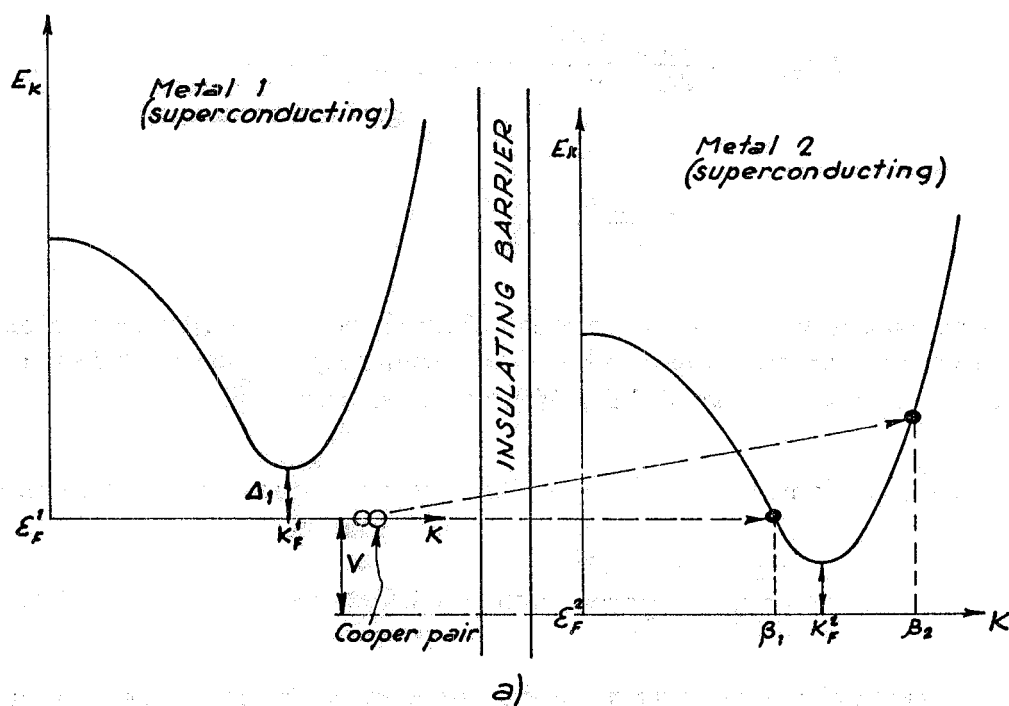


FIG. 11 - Schematic drawing of higher order tunneling processes.

22.

$$(35) \quad J(2\Delta) = \left(\frac{\Delta}{4\pi}\right) \frac{eK_F}{\hbar} \exp(-2 \langle K_{\perp} \rangle d)$$

and

$$\frac{J(2\Delta)}{J(\Delta)} = e^2.$$

However, owing to unavoidable disuniformities in the barrier thickness it can happen that the mean value of d appearing in (34) is different from that of (35) and the ratio $J(2\Delta)/J(\Delta)$ is less than e^2 .

b) S_1 -I- S_2 junctions ($\Delta_1 \neq \Delta_2$). - The jumps in the current are now :

$$(36) \quad J(\Delta_i) = \left(\frac{\Delta_i}{8\pi}\right) \frac{e(K_F^i)^2}{\hbar} \exp(-4 \langle K_{\perp} \rangle d) \quad (i=1, 2)$$

We point out that there is same disagreement with experience because usually we observe, superimposed to the current jumps already discussed, excess currents which depend on the temperature and on the voltage. Possibly these excesses are due to photon or phonon assisted tunneling processes.

V. - THE PHONON SPECTRUM AS RELATED TO THE TUNNEL EFFECT.

We have already discussed how it is possible to get informations on the density of states of superconductor by measuring dI/dV as a function of V in the N-I-S case. It is easy to realize that any "structure" which is present in the density of states will be reflected in the dI/dV v. s. curves. Experimentally a careful analysis of such curves is achieved by plotting simultaneously d^2I/dV^2 v. s. V . The physical reasons of the origin of structures in the density of states can be understood if we remember the B. C. S. expression for $n_s(E)$:

$$(37) \quad n_s(E) = n_N \frac{E}{(E^2 - \Delta^2)^{1/2}}$$

Such expression comes from the B. C. S. theory if we assume the simple form of the gap equation in which the details of the electron-phonon interaction are neglected. However it is possible to introduce explicitly the phonon spectrum in the theory and the modified gap equation is:

$$(38) \quad \Delta(E) = \frac{dn}{d\varepsilon} \int_0^{\infty} dE' V(E-E') \operatorname{Re} \frac{\Delta(E')}{[E'^2 - \Delta^2(E')]^{1/2}}$$

where E is the quasi particle energy, $dn/d\varepsilon$ is the density of states in the normal state and $V(E-E')$ describes the electron-electron interaction. $\Delta(E)$ depends on the quasi particle energy and $V(E-E')$ contains in some way the phonon spectrum. From (38) we can deduce the following expression for the tunneling density of states:

$$(39) \quad n_s(E) = n_N \operatorname{Re} \left[\frac{E}{[E^2 - \Delta^2(E)]^{1/2}} \right]$$

Clearly by measuring $n_s(E)/n_N(E)$ we can gain informations on the phonon spectrum if we resolve eq. (38) to get $\Delta(E)$ as a function of $V(E-E')$ while, if we know independently the phonon spectrum, it is possible to study the term $V(E-E')$ and the exact form of the gap equation (38). We give now the more interesting experimental results.

a) Evidence of peaks in the phonon spectrum. - Anomalies in $n_s(E)/n_N$ have been observed in Al-Al₂O₃-Pb junctions (aluminum in the normal state) which are related to the presence of two peaks in the phonon spectrum of lead⁽⁴²⁾ (see fig. 12) localized at 4.4 and 8.5 mV respectively. Such a spectrum has been also used to resolve the gap equation⁽⁴³⁾ and to obtain the density of states. A comparison between theoretical and experimental data is shown in fig. 13. To get some idea of the diffe

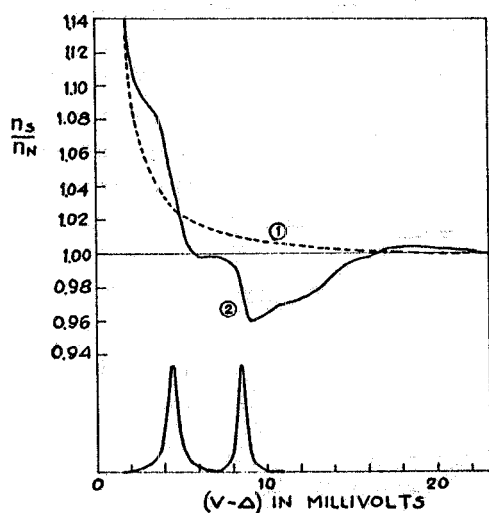


FIG. 12

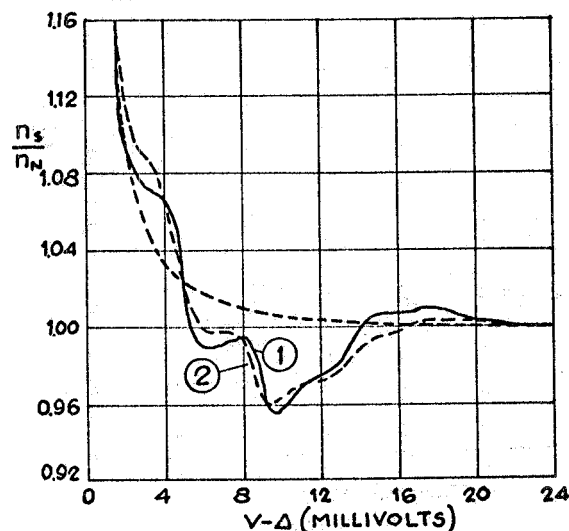


FIG. 13

FIG. 12 - The variation with energy of the ratio of density of states in superconducting lead to that in the normal state. Curve 1 is the B. C. S. plot, curve 2 the tunneling measurement. Also shown is the phonon spectrum suggested by the experimental density of states plot (after ref. (42)).

FIG. 13 - Comparison of: (1) The density of states v. s. energy variation calculated by Schrieffer et al. - solid line, and (2) the tunneling result - long dashed line. The B.C.S. variation is shown as the short dashed line.

rence between the simple B. C. S. model and the calculations of ref. (43) and of the way by which the phonon spectrum influences the density of states we remember that the phonon density of states $F(\omega)$ which gives the good fitting reported in fig. 13 has the following forms:

$$F(\omega) = 2f_T(\omega) + f_L(\omega)$$

where

$$f_T(\omega) = \frac{W_T/\pi}{(\omega_T - \omega)^2 + W_T^2} ; \quad f_L(\omega) = \frac{W_L/\pi}{(\omega_L - \omega)^2 + W_L^2}$$

$W_T = 0.75$ mV, $\omega_T = 4.4$ mV, $W_L = 0.50$ mV and $\omega_L = 8.5$ mV.

We note that to resolve the gap equation it is necessary to introduce different branches of the phonon spectrum, ω_L and ω_T referring to longitudinal and transversal branches respectively.

b) The Van Hove singularities. - A general theorem established by Van Hove states that in a tridimensional crystal there exist a number of singular points in the phonon spectrum. Namely if we consider the phonon density $g(\nu)$ as a function of ν it can be shown that there are at least two infinite discontinuities in $dg/d\nu$ and, at the upper limit of the spectrum, $dg/d\nu = -\infty$. Usually the number of singularities is much larger than two and for a complete discussion of this argument the reader is referred to ref. (45). Owing to their general nature, the occurrence of Van Hove singularities is superimposed to the particular phonon spectrum of a metal and can give rise to some effect in the superconducting density of states. However such effects are quite weak and cannot be put in evidence by measurements of dI/dV and d^2I/dV^2 for N-I-S junctions. A method to overcome this difficulty makes use of S-I-S junctions in which the singularities of the phonon spectrum are present in both sides of the junction so that their effect is accentuated in the dI/dV and d^2I/dV^2 curves. Once we introduce a reasonable model for the phonon spectrum we can evaluate dI/dV and d^2I/dV^2 (46) for S-I-S junction explicitly. In fig. 14 it is shown a plot of d^2I/dV^2 v. s. V for a Pb-I-Pb junction with a comparison between observed and calculated singularities (47, 48).

c) Harmonic structures. - It has been pointed out (49) that the presence of an Einstein peak in the phonon spectrum at a certain energy E_E gives rise to anomalies in the superconducting density of states for the values of the energy $\Delta + E_E$, $\Delta + 2E_E$, ... $\Delta + nE_E$. In fig. 15 we reported measurements of d^2I/dV^2 v. s. V for a Pb-I-Pb junction showing the occurrence of such an harmonic structure.

We point out that, in general the influence of the phonon spectrum on the density of states is better studied in so-called "strong cou-

pling" superconductors like lead and mercury⁽⁵⁰⁾ owing to the fact that the electron-electron via phonon interaction is relatively intense in this case. However effects of this kind have been pointed out also for weak coupling superconductors like tin by using a sufficiently sensitive technique^(42, 51, 52, 53). Recently measurements on the phonon spectra⁽⁵⁴⁾ of

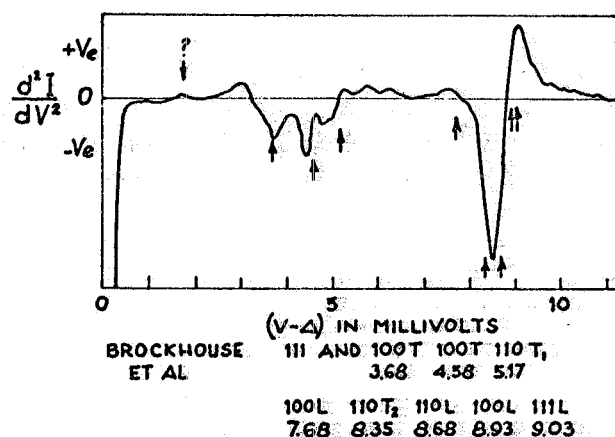


FIG. 14

FIG. 14 - d^2I/dV^2 v. s. V (measured from Δ) for a Pb-Pb junction at 1.3°K. Arrows indicate the bias for Van Hove singularities expected from the data of Brockhouse et al. (after ref. (48)).

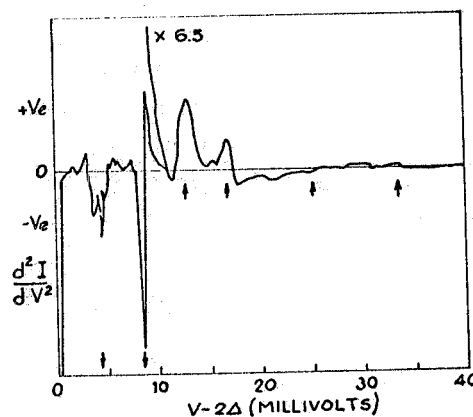


FIG. 15

FIG. 15 - d^2I/dV^2 v. s. V for a Pb-I-Pb junction at 1.3°K. Arrows mark fundamental, sum, and harmonic structures (after ref. (42)).

Pb-Bi, Pb-Tl, Pb-In alloys have been reported. A rather interesting result is that as the concentration of solutes in lead increases the electronic concentration decreases and at the same time the phonon spectrum changes in the sense that the amplitudes of peaks in d^2I/dV^2 decrease and their position in energy changes with respect to the localization in the pure lead case. This is connected with the fact that (especially for Pb-Bi and Pb-Tl alloys) either $\Delta(0)$ or $2\Delta(0)/kT_c$ decrease by increasing the solute concentration; in other words there could be a gradual transition from a strong coupling to a weak coupling superconductor. Moreover phonon spectra of films of bismuth condensed at very low temperature (4.2°K) have been studied by tunneling technique⁽⁵⁵⁾. It is well known in these conditions the bismuth is superconducting with a transition temperature of the order of 6°K and with $2\Delta(0)/kT$ nearly 4.6. This suggests that under these circumstances the bismuth is a strong coupling superconductor. The phonon spectrum exhibited in this modification is quite different from that relative to its usual semi-metal structure.

VI. - ENERGY GAP ANISOTROPY.

The energy gap depends on the crystallographic direction. This effect is better pointed out by tunnel effect measurements in very pure samples otherwise the anisotropy effects are averaged by the impurities⁽⁵⁶⁾. Anisotropy studies can be made either on single crystals and on polycrystalline films.

a) Measurements on single crystal samples. - Such measurements are usually made by realizing a number of tunneling junctions in the various crystallographic directions. In this way the dependence of the energy gap on the crystallographic direction is obtained. It is useful to introduce the following quantity :

$$(40) \quad \langle \alpha^2 \rangle = \frac{\langle (2\Delta_i - \langle 2\Delta_i \rangle)^2 \rangle}{\langle 2\Delta_i \rangle^2}$$

where the index i refer to the crystalline direction and the symbol $\langle \rangle$ denotes an average on such directions. A number of results are available in the literature^(57, 58, 59) and we can get an idea of the possible values for $\langle \alpha^2 \rangle$ remembering that $\langle \alpha^2 \rangle = 0.006$ for niobium⁽⁵⁷⁾ while $\langle \alpha^2 \rangle = 0.019$ for tin⁽⁶⁰⁾. The physical origin of the energy gap anisotropy is related to lattice anisotropies which in turn gives rise either to Fermi surface anisotropy and to phonon spectrum anisotropy. It is not clear up to date what kind of anisotropy determines the energy gap anisotropy. An experimental attempt to correlate Fermi surface anisotropy and superconducting energy gap has been not completely successful. On the other hand a model according to which the energy gap anisotropy is due essentially to phonon spectrum for strong coupling superconductors has been proposed⁽⁶¹⁾.

b) Measurements on polycrystalline films. - Measurements on polycrystalline films have been made essentially in the case of strong coupling superconductors. The theory⁽⁶¹⁾ predicts that the presence of different values of the energy gap due to anisotropy effects gives rise to structures in dI/dV v. s. V curves analogous to those found in studying the phonon spectra effects. Remembering the gap equation :

$$(41) \quad \Delta_k = \sum_{k'} \frac{V_{kk'} \Delta_{k'}}{2E_{k'}}$$

the anisotropy is introduced in the term $V_{kk'}$ which can written as :

$$(42) \quad V_{kk'} = V_{kk'}^{\text{phon}} + V_{kk'}^{\text{coul}}$$

$V_{kk'}^{\text{phon}}$ in turn has the following expression⁽⁶²⁾ :

$$(43) \quad V_{kk'}^{\text{phon}} = \frac{2(E_{k'} + \hbar \omega_{k-k'}) |g_{kk'\lambda}|^2}{(E_{k'} + \hbar \omega_{k-k'})^2 - E_k^2}$$

where $\hbar \omega_{k-k'}$ is the energy of the phonon which couples the states k and k' and $g_{kk'\lambda}$ is the matrix element for such a coupling. Any isotropy in the phonon spectrum reflects, through $\hbar \omega_{k-k'}$, on $V_{kk'}^{\text{phon}}$ ($g_{kk'\lambda}$ is usually treated as an isotropic term). Starting then from (43) and introducing a suitable "distribution function" for the energy gap values it is possible to evaluate the effects of such a number of different energy gap values on the tunneling characteristics of polycrystalline samples. Data concerning I v. s. V and dI/dV v. s. V curves for Pb-I-normal metal, Pb-I-Al (superconducting) and Pb-I-Pb junctions are available in the literature⁽⁶³⁾. As an example we reported in fig. 16 a plot of dV/dI v. s. V for an Al-Al₂O₃-Pb at 1.037°K. The anisotropy

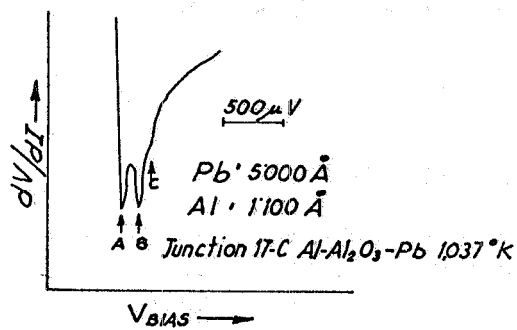


FIG. 16 - The dV/dI characteristic of a Pb-I-Al junction in the vicinity of $eV = \Delta_{\text{Pb}} + \Delta_{\text{Al}}$ showing anisotropy effects (after ref. (63)).

effects are characterized by the points A, B and C. A and C correspond to saddle and maximum values of the distribution function whereas B is correlated to the mean value of the energy gap.

Another interesting feature is the observation of subharmonic structure (SHS) (see fig. 17). They consist of a series of peaks in the dV/dI v. s. V plot which occur for $V < 2\Delta$. Such peaks are located at voltage values Δ , $2\Delta/3$, ..., $2\Delta/n$... However to classify all the observable peaks it is necessary to introduce a number of different values of Δ each of which gives rise to a series Δ_i , $2\Delta_i/3$, ..., $2\Delta_i/n$... Experimentally there have been identified up to seven different values of the energy gap arising from the anisotropy in lead. The origin of the subharmonic structures is quite unclear. They could arise in some way by the interaction between tunneling electrons and photon at Josephson frequency ($\omega = (2neV)/\hbar$) which could be present in the junction owing to the fact that the occurrence of subharmonic structures is always associated with the presence of strong d. c. Josephson currents at zero bias. Alternatively the existence of micro shorts in the barrier giving rise to the so-called weak-linked superconductors could account for this phenomenon. Recently the argument has been reviewed by Rowell and Feldmann⁽⁶⁴⁾.

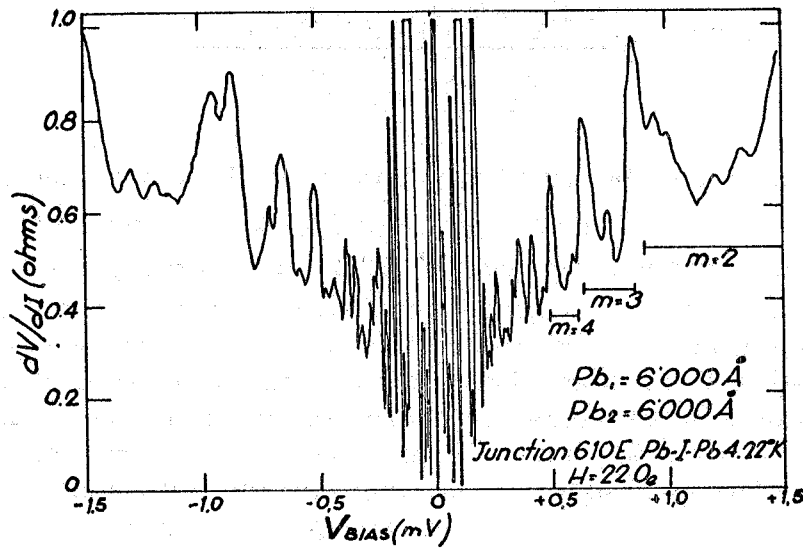


FIG. 17 - The dV/dI characteristic of a Pb-I-Pb junction at 4.22°K , showing the complex fine structure in SHS (after ref. (63)).

VII. - PHOTON AND PHONON ASSISTED TUNNELING.

We will deal now with the interaction between tunneling currents and electromagnetic waves or elastic waves. Experimentally such interactions take place in the first case by putting a tunneling junction inside a resonant cavity while in the second case the junction is realized on an oscillating quartz in which elastic waves are excited through coupling with a resonant cavity.

a) Photon assisted tunneling. - It has been observed experimentally in S_1 -I- S_2 junctions the existence of two series of peaks in the $I(V)$ curve given by the following values of the applied voltage^(65, 66, 67):

$$eV_0 = \Delta_1 + \Delta_2 \pm n\hbar\omega \quad (44)$$

$$eV_0 = \Delta_1 - \Delta_2 \pm n\hbar\omega$$

where $\Delta_1 > \Delta_2$ and ω is the frequency of the microwave field. Moreover the intensity of these peaks decreases as n increases and increases along with the microwaves power. We can understand qualitatively these phenomena considering the simple case of a S_1 -I- S_2 junction at $T = 0^\circ\text{K}$ (see fig. 18). As it has been already shown that in absence of radiation $I = 0$ until V reaches the value $\Delta_1 + \Delta_2$. Supposing now we turn on a radiation field of frequency $\nu = \omega/2\pi$. An electron whose energy is at the lower gap edge of the metal 1 can absorb a photon $\hbar\omega$

and make a tunnel transition to the upper gap edge of the metal 2 provided the energy conservation :

$$eV + \hbar\omega = \Delta_1 + \Delta_2$$

is satisfied.

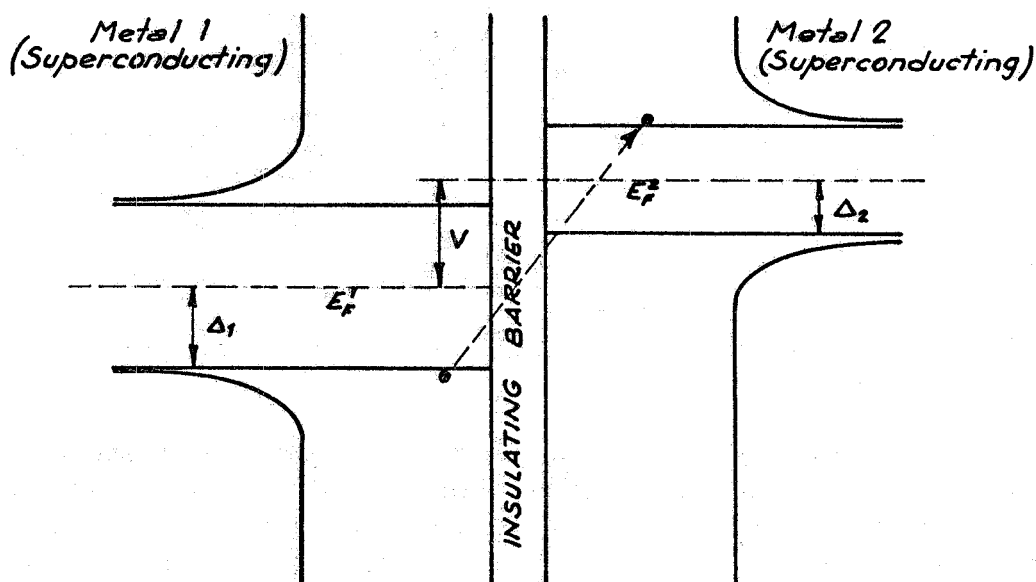


FIG. 18 - Schematic representation of a tunneling junction at $T = 0^{\circ}\text{K}$ showing an electron which, after absorption of a phonon $\hbar\omega$, can tunnel through the barrier also when $eV < \Delta_1 + \Delta_2$.

In other words the current will be zero until the voltage will reach the value $eV = \Delta_1 + \Delta_2 - \hbar\omega$. In these conditions owing to the high density of empty states at the upper edge of the gap in the metal 2 a sudden rise in the current will occur. By increasing further the voltage when $eV = \Delta_1 + \Delta_2$ the usual rise in the current will be noted while for $eV = \Delta_1 + \Delta_2 + \hbar\omega$ another peak will be present corresponding to transitions in which an electron goes from the lower gap edge of the metal 1 to the upper edge of the metal 2 by emitting a photon $\hbar\omega$. The possibility of observing the series of peaks given by the relation $eV = \Delta_1 + \Delta_2 \pm n\hbar\omega$ arises from simultaneous absorption or emission of n phonons. Of course these multi-photon processes depend on the number of phonons, i. e. on the microwave power. This accounts, almost qualitatively, of the dependence of the peak intensities on the microwave power. At finite temperatures there is qualitatively the same behaviour; moreover if we remember the maximum in the current for $eV = \Delta_1 - \Delta_2$, we can understand in an analogous way the existence of the series of peaks given by the relation $eV = \Delta_1 - \Delta_2 \pm \hbar\omega$. In figures 19 and 20 we reported, as an example, some experimental results relative to the behaviour of Sn-I-Pb junctions in a microwave field at 36.000 GHz⁽⁶⁷⁾.

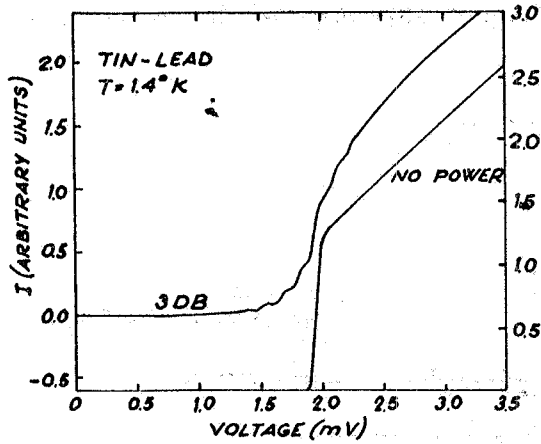


FIG. 19

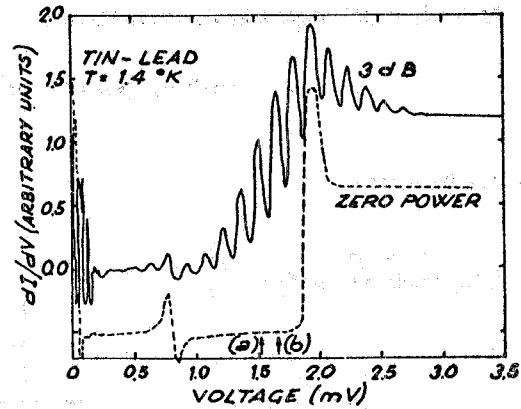


FIG. 20

FIG. 19 - Current v. s. voltage plot for a Sn-I-Pb junction in a microwave field (after ref. (67)).

FIG. 20 - Conductance v. s. voltage plot for the same junction as in fig. 19 (after ref. (67)).

All these effects can be calculated in a rigorous way starting from the hamiltonian formulation⁽⁶⁶⁾. The oscillating field is introduced as an extra term giving rise to an oscillating potential in the unperturbed superconducting hamiltonian. It results in a modified time dependence for the electronic wave functions while the spatial dependence is unaffected because it is assumed that the microwave field penetrates uniformly inside the films. Of course this is valid for very thin films. Avoiding further details the term which modifies the time dependence can be written as follows :

$$\sum_{n=-\infty}^{+\infty} B_n e^{-in\omega t}$$

and the resulting quasi particle energy in both superconductors contains terms such as :

$$E \pm \hbar\omega ; \quad E \pm 2\hbar\omega ; \quad \dots \quad E \pm n\hbar\omega ; \dots$$

This means that an electron can make a transition from one energy level to another by absorbing or emitting the right number of photons. We then get that in the integral of the tunneling current it appears a modulated density of states

$$(45) \quad n_s^!(E) = \sum_{n=-\infty}^{n=+\infty} n_s(E + n\hbar\omega) J_n^2(\alpha)$$

where $\alpha = eV_M/\hbar\omega$ (V_M is the maximum value of the microwave potential in the modified hamiltonian $H = H_0 + eV_M \cos \omega t$), n_s is the usual B. C. S. density of states and J_n is the n order of the Bessel function of

the first kind. The resulting current has the following expression :

$$(46) \quad I'(V) = A \sum_{m, n=-\infty}^{m, n=+\infty} J_m^2(\alpha) J_n^2(\alpha) \int_{-\infty}^{\infty} \left[f(E + m\hbar\omega - eV) - f(E + n\hbar\omega) \right] n_s^1(E + m\hbar\omega - eV) n_s^2(E + n\hbar\omega) dE$$

or, in a more compact form :

$$(47) \quad I'(V) = \sum_{n, m=-\infty}^{n, m=+\infty} J_n^2(\alpha) I[eV + (n - m)\hbar\omega]$$

with

$$I = A \int_{-\infty}^{\infty} \left[f(E - eV + (n - m)\hbar\omega) - f(E) \right] n_s^1(E - eV - (n - m)\hbar\omega) n_s^2(E) dE$$

The difference $n - m = N$ corresponds to all the possible N photons processes and the total current can be rewritten as a sum of partial terms :

$$(48) \quad I' = \sum_N I_N$$

with

$$(49) \quad I_N = \left\{ J_0^2(\alpha) J_N^2(\alpha) + \sum_{m=-\infty}^{m=+\infty} J_m^2(\alpha) \left[J_{n+m}^2(\alpha) + J_{n-m}^2(\alpha) \right] \right\} I(eV + N\hbar\omega)$$

Eq. (48) and (49) are in good accordance with the experiments as long as we are concerned with the location of the peaks and the dependence of various terms on the microwave power; there exists however a discrepancy between the theoretical and experimental values of α ($\alpha_{\text{theor}} \sim 10^2 \alpha_{\text{exp}}$).

b) Phonon assisted tunneling. - In a similar way we can treat the interaction between phonons and a tunneling junction. The more detailed results are relative to the case of longitudinal phonons with wave vector \vec{q} perpendicular to the junction plane^(68, 69, 70). The theoretical treatment makes use also in this case of an additional term $H' = v \cos \omega t$ in the hamiltonian. The factor v , analogous to V_M previously introduced, has the following expression :

$$(50) \quad v = c_1 s_1 - c_2 s_2$$

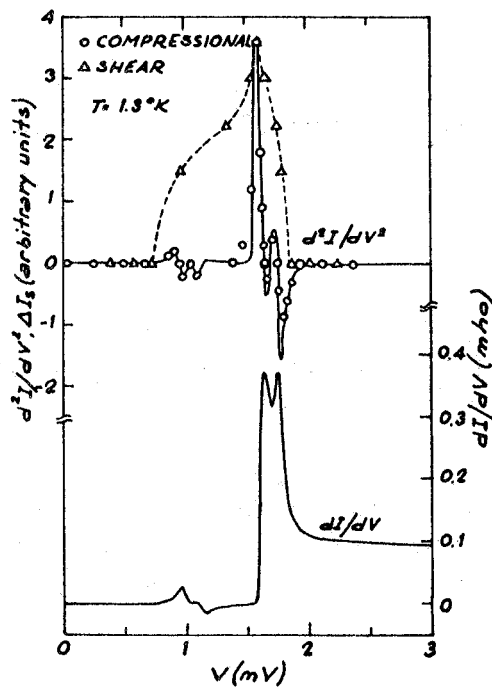
where c_i and s_i are, respectively, the deformation potentials and strains in the two metals. The term H' leads to a modulation of the energy levels $E + cs \cos \omega t$ (where $c = 2E_F/3$ in the free electron model). The resulting expression for the current is then:

$$(51) \quad I'(V) = \sum_{n=-\infty}^{n=+\infty} J_n^2(\alpha) I(eV + n\hbar\omega)$$

with $\alpha = (c_1 s_1 - c_2 s_2)/\hbar\omega$. Usually, owing to the small power available, $\alpha \ll 1$ and from (51) we get as a reasonable approximation:

$$(52) \quad \Delta I_s \approx \left(\frac{c_1 s_1 - c_2 s_2}{2\hbar} \right)^2 \frac{d^2 I(V)}{dV^2}$$

where ΔI_s is the extra current with respect to the current in absence of interaction. In fig. 21 are shown



some experimental results confirming the validity of approximation (52). In the same figure are shown also the extra current resulting from the interaction with transverse phonons. In this case eq. (52) is no longer valid and this may be due to the existence of a magnetic field associated to the shearing waves which is not screened by the Meissner effect⁽⁷¹⁾.

FIG. 21 - Typical bias dependence of the current pulses, ΔI_s , due to compressional and shear sound waves, obtained with Al-Pb tunnel diodes. The first and second derivatives are also shown (after ref. (69)).

VIII. - DECAY OF QUASI PARTICLES IN A SUPERCONDUCTOR AS RELATED TO THE TUNNEL EFFECT.

a) Decay and recombination of quasi-particles. - Two quasi-particles in a superconductor can recombine to form a Cooper pair losing their excitation energy by means of various processes. However there are several reasons^(70, 73, 74, 75, 76) to say that the most likely process is the following (see fig. 22): 1) a quasi-particle of energy E relaxes to the energy Δ emitting a phonon of energy $E - \Delta$; 2) two quasi-particles

of energy Δ recombine together giving rise to a Cooper pair and emitting a phonon of energy 2Δ .

b) Injection of quasi-particles in a superconductor. - If we consider a S-I-S tunneling junction at $T = 0^\circ\text{K}$ the current is zero for $V < 2\Delta$ while for $V > 2\Delta$ there is a finite current from the metal 1 to the metal 2 with creation of quasi particles in the superconductor 2 (see fig. 23).

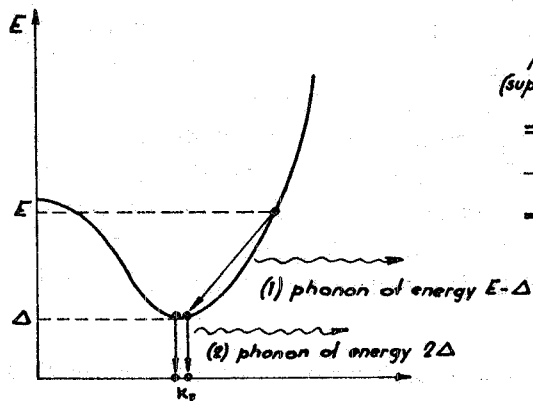


FIG. 22

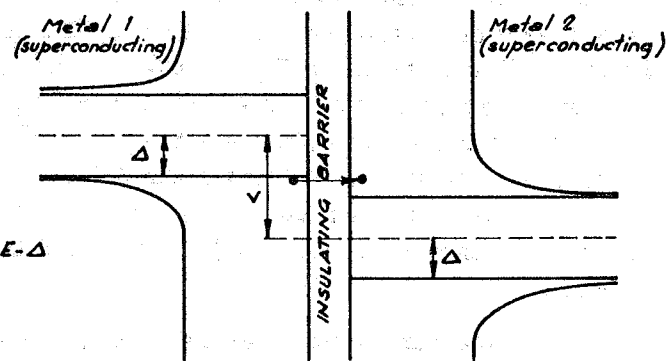


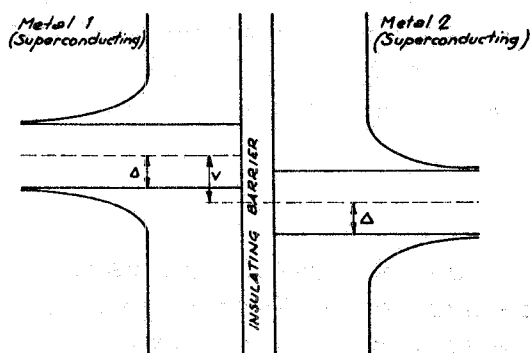
FIG. 23

FIG. 22 - Schematic representation of the relaxation and recombination of two quasi-particles.

FIG. 23 - Quasi-particles injection in a superconductor.

Such quasi-particles decay following the process sketched before with emission of two phonons of energy $E - \Delta$ and 2Δ respectively. At $T \neq 0^\circ\text{K}$ we will have quasi-particles injection also when $V < 2\Delta$ but their number is rather small. In these conditions a tunneling junction acts as a phonon generator. Besides the theoretical importance the interest of such a generator is in the fact that the emitted phonons are in a frequency range (100-300 GHz) which is difficult to obtain by other means.

c) Phonon detection. - To detect the phonons generated by a tunneling junction we can use another S-I-S tunneling junction biased at $V < 2\Delta$ (see fig. 24). In these conditions the current is nearly zero but, if in



the first superconductor are generated phonons of suitable frequency they can break Cooper pairs creating quasi-particles which can tunnel in the second superconductor giving rise to an excess current. On the basis of these considerations a device has

FIG. 24 - A tunneling junction biased to detect phonons.

been realized by means of which it is possible to generate and detect phonons⁽⁷⁷⁾. Both the "generator" and the "detector" are constituted by Sn-SnO₂-Sn junctions evaporated on the two opposite sides of a single crystal sapphire rod. Pulses whose duration is in the range 0.2-5 μ -sec are applied to the generator at a repetition frequency of 10 KHz. Correspondingly current pulses in the "detector" are observed with delays due to the propagation of the phonons through the sapphire in the longitudinal, fast transverse and slow transverse modes. It is interesting to take into consideration the behaviour of the amplitude V_2' of the pulses in the detector as a function of the current I_1 in the "generator", keeping fixed the bias V_2 ($< 2\Delta$) of the detector. The principal experimental results are: 1) the amplitude V_2' relative to the detected phonons increases linearly as a function of the current I_1 of the generator until the voltage V_1 is less than 4Δ ; 2) when $V_1 = 4\Delta$ a sharp increase of a factor 2.5 in the slope occurs while the dependence of V_2' on I_1 is still linear up to $V_1 = 6\Delta$ whereupon the dependence is no longer linear.

This behaviour can be interpreted qualitatively in the following way: 1) First of all the detector pulses correspond essentially to the absorption of phonons of energy $\geq 2\Delta$ which give rise to the breaking of Cooper pairs and the subsequent increase (pulse) of the tunneling current for $V_2 < 2\Delta$; 2) The contribution of the phonons of energy $< 2\Delta$ can be treated in the same way as the phonon assisted tunneling and is negligible because of the low power available; 3) It is clear then, if the energy of injected quasi particles give rise to two phonons of energy $E - \Delta$ and 2Δ respectively, V_2' will increase linearly with I_1 until $V_1 < 4\Delta$; 4) When $V_1 \geq 4\Delta$ the energies of the two phonon will be now 2Δ and $\geq 2\Delta$ respectively so that we can explain the change in the slope at $V_1 = 4\Delta$ if the excess current is essentially due to breaking of Cooper pairs (see fig. 25); 5) The deviations from linearity observed when $V_1 > 6\Delta$ can be due to other relaxation processes like electron-electron interaction and photon emission.

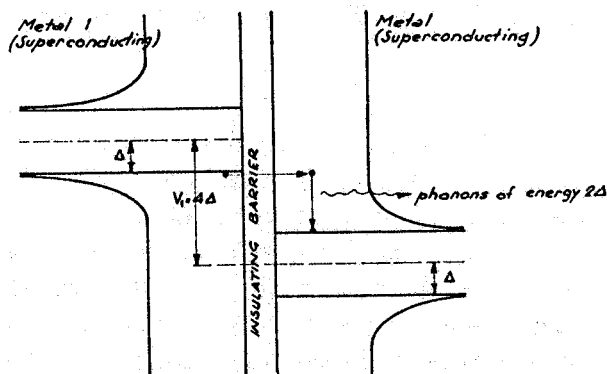


FIG. 25 - A tunneling junction biased to generate phonons of energy 2Δ .

On the other hand we remember that the change in slope is not exactly a factor 2 but about 2.5 and this suggests the possibility of other relaxation mechanisms although that previously described is the predominant one.

d) Quasi-particles relaxation and recombination times. - By using an analogous technique it is possible to measure the relaxation time τ' (mean life time for quasi-particles at the energy E before they decay to

the energy Δ) and the recombination time τ'' (mean life time for quasi-particles at the energy Δ before they recombine to form a Cooper pair). In this case the experimental device is made by two tunnel junctions with a common metallic element⁽⁷⁸⁾. In practice experiments have been made with the pair of junctions Al-Al₂O₃-Al-Al₂O₃-In (Al and In both superconductors) realized by the usual technique of successive evaporations and oxidations of the elements. To understand how it is possible to get a measure of τ' let us consider the fig. 26. The Al-Al₂O₃-Al junction is biased at a voltage $V_1 > 2\Delta_{Al}$. In these conditions

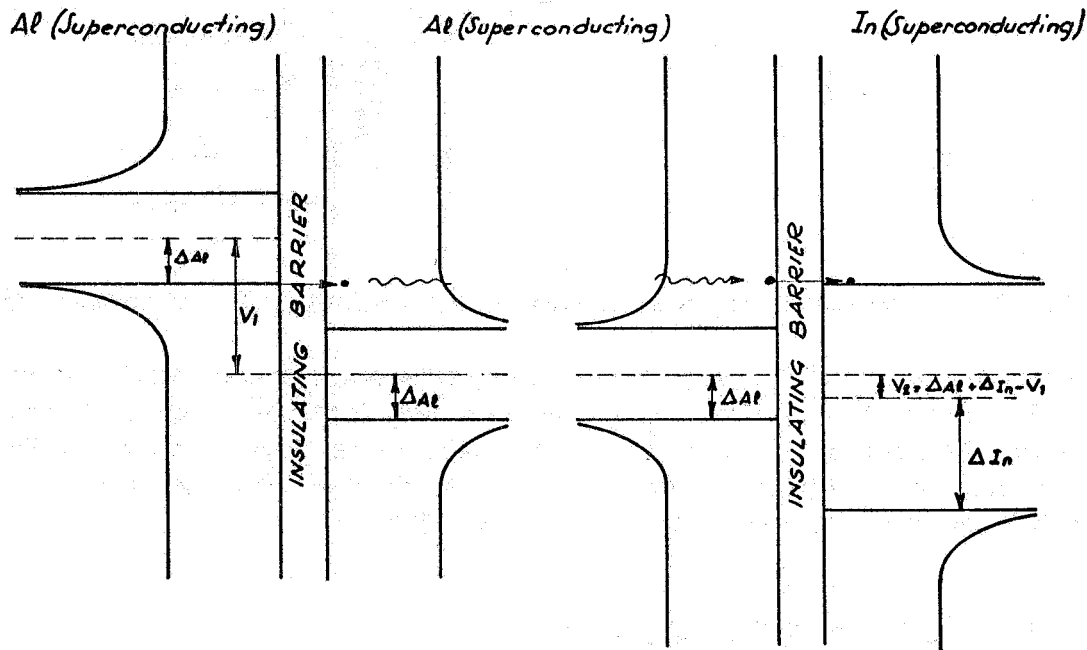


FIG. 26 - Schematic representation of the technique for measure τ' .

quasi-particles are injected in the central film of aluminum. If the thickness of this film is sufficiently small the injected quasi-particles can propagate through the film without decay and make a tunnel transition through the Al-Al₂O₃-In junction giving rise to an excess current at the voltage V_2 applied at the junction. We point out that choosing $V_2 = \Delta_{Al} + \Delta_{In} - V_1$ it results $V_2 < \Delta_{In} - \Delta_{Al}$ if $V_1 > 2\Delta_{Al}$. That is the current through the Al-Al₂O₃-In junction is very small and this facilitates the observation of excess currents. It is intuitive that the excess current is proportional in some way to the number of quasi-particles which propagate through the central film of aluminum before to decay from E to Δ i. e. it must be proportional to τ' .

To measure τ'' we use still the same device with the difference that the first junction is biased at a voltage $V_1 = 2\Delta_{Al}$ while the second is biased at a voltage $\Delta_{In} - \Delta_{Al} < V_2 < \Delta_{In} + \Delta_{Al}$. The experimental situation is sketched in fig. 27. In this case the injected quasi-particles are at the upper edge of the gap of the aluminum and the excess current in the second junction is in some way proportional to τ'' (the

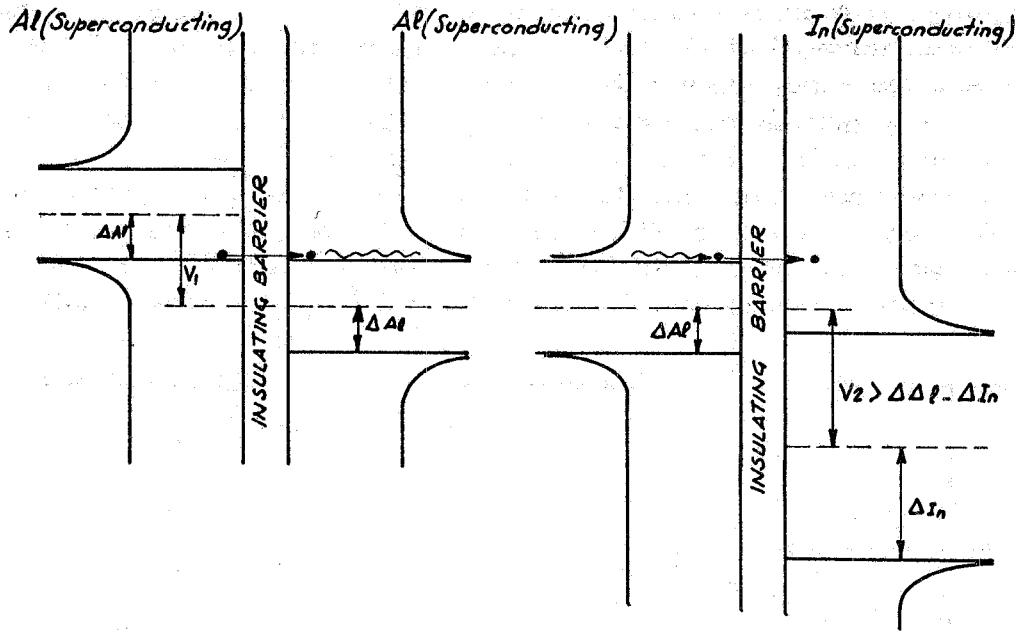


FIG. 27 - Schematic representation of the technique for measure τ'' .

value of V_2 used in ref. (78) (~ 0.6 mV) corresponds to a stable point of the $I(V)$ curve of the Al-Al₂O₃-In junction and for this value the indium density of states at the injected quasi-particles energy is only 1.4 times the normal state density of states). Without further details we will give here the explicit expressions for τ' and τ'' :

$$\begin{aligned}
 \tau' &= \tau'(E) = \tau'(V_1 - \Delta_{Al}) = \\
 (53) \quad &= \frac{\Delta I_2(V_2) e^2 [n_N(0)]_{Al} v}{W \sigma_1(\infty) \sigma_2(\infty)} \frac{A_1}{A_{12}}
 \end{aligned}$$

where $\Delta I_2(V_2)$ is the measured increase of the current at the voltage V_2 , $[n_N(0)]_{Al}$ is the aluminum normal density of states, W is a quantity proportional to the current I_2 whose expression is given by the tunnel theory (see ref. (78) for further details), $\sigma_1(\infty)$ and $\sigma_2(\infty)$ are the normal state conductivities of the two junctions respectively, A_1 and v are the surface and the volume of the aluminum central film common with the first junction and A_{12} is the surface of the central film common to both the junctions.

$$\tau'' = \frac{\Delta I_2(V_2) 2 e^2 v [n_N(0)]_{Al}}{1.4 \sigma_2(\infty) (I_1 - I_1^0)} \frac{A_1}{A_{12}}$$

where $(I_1 - I_1^0)$ is the difference between the injection current I_1 in the first junction and the current I_1^0 due to the thermally excited quasi particles. The experimental results show that τ' is an exponential decreasing function of $(E - \Delta_{A1})/\Delta_{A1}$ and its value is about 0.5×10^{-8} sec for $(E - \Delta_{A1})/\Delta_{A1} \sim 1$. On the contrary τ'' is about 10^{-6} sec at 0.37°K and decreases by increasing T until T reaches the value 1.2°K , afterward increasing slightly. The fact that τ' is at least an order of magnitude less than τ'' gives a good support to the proposed decay scheme.

IX. - SOME APPLICATIONS OF THE SUPERCONDUCTING TUNNEL EFFECT.

a) Oscillators, amplifiers, detection and mixing. - It is obvious the analogy between the $I(V)$ curves relative to a S_1 -I- S_2 tunnel junctions and those referring to an Esaki diode (tunnel diode). On this basis we can think of making amplifiers and oscillators by means of such junctions. Applications in this sense have been made by a number of researchers. Miles et al. (79) have studied the experimental behaviour of an Al- Al_2O_3 -Sn junction. The circuit analysis is the same as that of a Esaki diode taking into account the difference of the voltage values for which the minimum and the maximum of current occur. The series inductance and the parallel capacity are usually larger than the corresponding quantities for an Esaki diode, their values being of the order of 5×10^{-8} h and 100 pF respectively. The series resistance instead is quite zero. In this way a 72.5 Mc/sec oscillator has been realized while, as an amplifier, a gain power of 23 db has been reached. On the other hand there is not a large amount of experimental work in this sense and probably some parameters of the superconducting diodes must be optimized before making a significant comparison with the Esaki diode. A real advantage is the strong reduction of the noise (at least a factor 20) as the major contribution arises from the shot noise and, with the same impedance level, the current in a superconducting tunnel diode are about 400 times less than those in an Esaki diode (see also ref. (80) for more details). Other electronic applications are the strip transmission lines, distributed amplifiers and quarter-wave distributed oscillators (81). Also in this case the useful property is the existence of a negative resistance region. The tunneling junctions is still in the form of evaporated films but one of the dimensions is usually much larger than the other. This involves some technical problem because, increasing the junction area, it is difficult to control the thickness of oxide and the absence of short circuits through the barrier. However Sn-SnO₂-Pb junctions have been realized, whose length was about 95 mm, with propagation and distributed oscillations at 77 MHz. The theoretical limit of the frequency is about 1 GHz (82).

It is also possible to employ tunneling junctions for the detection of modulated signals (with detected powers of the order of $30 \mu\text{W}$) (83)

and for the mixing of modulated signals. It is reported in the literature the mixing of two microwave signals in the X band obtaining a signal at 30 MHz⁽⁸⁴⁾.

b) Microwave and sub-millimeter wave radiation detection. - We have already discussed the interaction between a tunnel junction and a microwave field. It is intuitive that it is possible to obtain a "photo current" if a S-I-S junction interacts with a radiation field of frequency $\nu \geq 2\Delta/\hbar$. Such a detector has been discussed in the literature⁽⁸⁵⁾. The limits of the detectable wavelengths depend on 2Δ and therefore on the superconducting metal and on temperature. For aluminum at 0°K this limit is 3.9 mm, while for lead is 0.46 mm.

On the other hand the photon assisted tunneling has been used to detect microwave radiation. In this case the minimum detectable frequency is given by the relation $\hbar\omega = 2\Delta - eV$ but, owing to the strong increase of the current when $V = 2\Delta$, it is convenient to work at biases less than 2Δ and this put a limit in the minimum frequency of about 10 GHz (x band). In the ref. (66) are reported measurements of radiation at 36 GHz with detected power of the order of $2\mu\text{W}$.

Analogous considerations can be made in the case of the phonon assisted tunneling.

c) Low temperature thermometry. - An S_1 -I- S_2 tunnel junction can be used as a sensitive and low capacity thermometer. In this case when $V < 2\Delta(T)$ the tunneling current depends on the number of excited quasi-particles which in turn depends on T roughly like $\exp(-\Delta/kT)$. The current then will depend roughly exponentially on T. The exact expression of the current is a rather complicated function and must be evaluated numerically. Temperature measurements performed by an Al- Al_2O_3 -Al junction are reported in ref. (7). There is a good accordance with the data taken by a carboresistor in the range 0.8-0.3°K. The range of temperatures in which such a thermometer can be useful is from $0.9 T_c$ to $0.2 T_c$ where T_c is the critical temperature of the superconductor.

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