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# Review of the Present Status of the Theory of Superconductivity

**Abstract: Theory and experiment are compared for a number of phenomena in superconductors. While the agreement is generally good, there are some discrepancies for which there is no adequate explanation.**

The field of superconductivity is in a period of rapid growth. This is in part due to the fact that we now have a microscopic theory to predict and interpret results of experiments, and in part due to interest in possible practical applications. The theory which Leon Cooper, J. R. Schrieffer and I gave about four years ago[1] has been further developed by many people to improve the mathematical foundations, to apply it to new phenomena, and to generalize it so as to be able to treat problems not accessible by the original method. Mathematical methods have been applied to other Fermi systems such as nuclear matter, liquid helium 3, and even to the theory of elementary particles. Many experiments have been carried out to test various predictions of the theory and to measure the various parameters involved. In most cases the agreement between theory and experiment is surprisingly good, particularly in view of the simplicity of the model on which most of the theoretical calculations have been based, but there are a number of problems which remain unsolved. Thus in these comparisons between theory and experiment, the transition temperature is taken to be an empirical parameter. Not very much progress has been made on the very important problem of developing criteria to distinguish between superconductors and nonsuperconductors and to predict values for the critical temperature of real metals from first principles. There is more known empirically from studies of Matthias and others on superconducting compounds and alloys. These studies have led to the discovery of superconductors with unusual properties, such as the superconductors which will withstand very high critical fields; and some aspects of this are not yet completely understood by theory.

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This paper mainly concerns applications of the theory rather than the mathematical formulation. I shall try to give an over-all picture of the present status and will emphasize the areas where difficulties remain. You will hear, of course, in much more detail during the progress of the conference about the topics I take up. The talk I am giving today is based in part on a review article which Schrieffer and I wrote and which has been published very recently in the third volume of Gorter's series *Progress in Low Temperature Physics*.[2]

In the first couple of years after the initial formulation of the theory, it was applied to a large number of phenomena with considerable success but discrepancies were found in a few cases, such as thermal conduction where scattering is dominated by phonons, the Knight shift and other things. Most of these were problems at the time of the Cambridge Conference two years ago and still remain as problems. In the meantime the experimenters have kept busy and have found new results. Some of these newer experiments, such as tunneling, have given additional and striking confirmations of the theory; others, such as ferromagnetic superconductors and low-temperature specific heats, have created new problems for the theorists. To give an over-all assessment, I think the experimenters have been running ahead of the theorists for the last couple of years.

The remarkable properties of superconductors, as well as superfluid flow in liquid helium, are consequences of quantum effects operating on a truly macroscopic scale. The general lines along which an explanation might be found were suggested by the late Fritz London;[3] the present theory is in accordance with his ideas. The superconducting state has the characteristics of a single quantum state extending throughout the volume. There is a long-range order which maintains the value of the momentum constant over large distances in space. As stated by London, "a superconductor is a quantum structure on a macroscopic scale, which is a kind of solidification or condensation of the average momentum distribution." I think this is a good description of the present microscopic theory. As you know, the basis for the current theory was suggested by Fröhlich[4] in 1950 and confirmed by the simultaneous discovery of the isotope effect.[5] It is an effective long-range attractive interaction between the electrons which results from interactions between the electrons and the lattice vibrations. The criterion for occurrence of superconductivity is essentially that this attractive interaction dominate the repulsive screened coulomb interaction.

It is not too easy to see on the basis of the present microscopic theory why one should have an isotope effect with $T_c \sim M^{-1/2}$ when one considers both the coulomb and the phonon interaction. Also we have a recent discovery of Geballe and Matthias, et al[6] that there is practically no observable isotope effect in ruthenium. This suggests the possibility that there may be another mechanism for superconductivity besides the electron-phonon interaction, or possibly the explanation for the case of ruthenium is that the coulomb interactions have such a strong influence that they spoil the isotope effect.

One should regard these interactions which give rise to superconductivity as occurring not between the free electrons but between the quasi-particle excitations of the normal state. As a result of coulomb and phonon interactions there are strong correlations between the positions of the electrons in the normal state. Nevertheless the low-lying excitations which correspond to exciting particles out of the Fermi sea are similar to those of the Bloch independent-particle model and can also be described in terms of occupation of states in $k$ space. As a result of the electron-phonon interactions and interactions between the excited particles and the Fermi sea, the quasi-particles can be scattered and thus have a finite lifetime $\tau$. One may regard the quasi-particle excitations as reasonably well defined if the uncertainty in energy $h/\tau$ is smaller than the excitation energy above the Fermi sea. I think it is quite important to take this lifetime into account, particularly in the cases where the electron-phonon interaction is strong, such as lead and mercury. This problem has been treated theoretically recently by Eliashberg[7] in Russia, and Schrieffer and others[8] have been also considering this problem; Schrieffer will discuss this problem in his talk.

Cooper, Schrieffer and I discussed a simplified model in which only quasi-particle excitations within a cutoff energy, $\hbar\omega_c$, above and below the Fermi surface are considered. This zone is chosen so that within it the quasi-particles are reasonably well defined and the phonon interaction is attractive. As pointed out by Anderson and Morel[9] the choice of this cutoff energy is somewhat arbitrary, at least in the weak-coupling approximation. The effective interaction may depend on the cutoff but the over-all results do not. An outstanding problem is just what one should take for the screened coulomb interaction within this cutoff. Most of the applications, as you know, have been based on the model, in which one just takes a constant interaction within the cutoff, and then the value of this interaction is determined empirically from the energy gap at the absolute zero or from the critical temperature. This procedure works reasonably well for the so-called "weak coupling" superconductors for which the cutoff energy is large compared with the energy gap. It probably does not work so well for the so-called "strong coupling" superconductors for which the cutoff is probably not much greater than the energy gap. This may account for some of the anomalous properties of lead and mercury for which the electron-phonon interaction is particularly strong, and the excitations have a short lifetime so that it is necessary to take a cutoff which is not very much larger than the gap.

One can form states with current flow by displacing the whole distribution of electrons corresponding to the ground state in $k$ space so that the ground state pairs have a common net momentum. At some finite temperature there will be a thermal distribution of quasi-particles appropriate to this common momentum of the pairs, but, contrary to a normal metal, these do not destroy the current. Scattering of the individual quasi-particles will not change this common value of the momentum of the pairs so that this residual current persists in time. The common momentum of the paired states gives the long-range correlation of the average momentum, of the sort envisaged by London.[3] I will say a little more about this later on, particularly on what determines the critical current density, which is a problem of considerable interest.

Most of the applications have been based on the simplified model, which involves basically three parameters – one is the density of states of the normal metal at the Fermi surface, which is usually estimated from the electronic specific heat in the normal state; another parameter is the average velocity of the electrons at the Fermi surface of the normal metal which, as shown by Pippard and Chambers,[10] can be estimated from the surface impedance in the extreme anomalous limit; and the third parameter is the one involving the effective interaction, which is usually determined from the critical temperature.

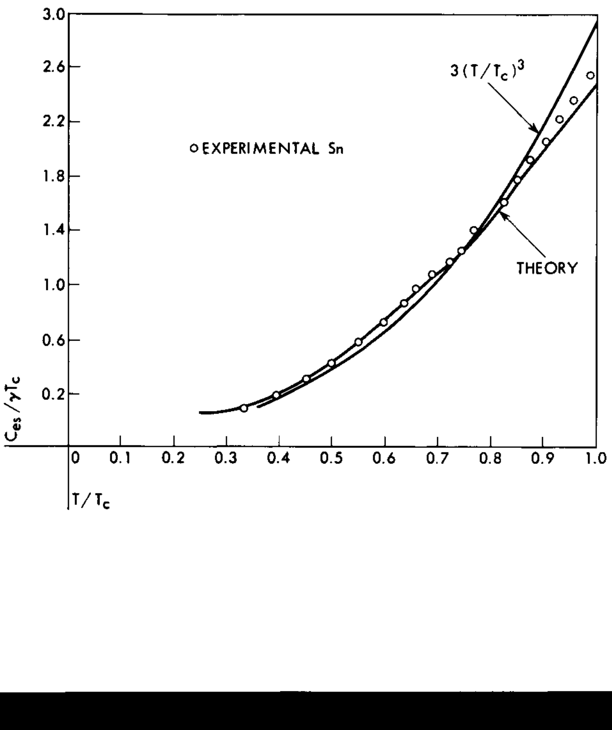
The topics which I will give a brief discussion of are specific heats, infrared transmission and absorption, tunneling, electrodynamics (penetration depths and surface impedance), ultrasonic absorption, nuclear spin relaxation times, thermal conductivity, Knight shift and critical fields and currents. Infrared transmission and absorption experiments, first done by Glover and Tinkham,[11] gave direct evidence for an energy gap. The energy gap, of course, is now shown much more strikingly by the tunneling experiments of Giaever and others.[12] The agreement between theory and experiment is particularly good for the electrodynamics. One of the experiments for which the theory gives particularly simple results, ultrasonic absorption, states that the ratio of the absorption coefficient of the superconducting to the normal state depends just on the energy gap according to this simple Fermi-Dirac sort of expression,

$$\frac{\alpha_s}{\alpha_n}=\frac{2}{1+\exp[\Delta(T)/kT]}, \tag{1}$$

so that one can use such experiments to estimate the gap; recently this has been done on single crystals to show that the energy gap may be anisotropic in certain materials such as tin.[13] Another problem in which there is current interest is the nuclear spin relaxation times. As you know, the relaxation rate increases, rather than decreases, as you go from the normal to the superconducting state, as first shown by Hebel and Slichter[14]; more recently experiments have been carried out by Redfield and Masuda, which will be discussed at this conference.

Another way in which the energy gap may be estimated is from experiments on thermal conductivity, in which the theory seems to be reasonably reliable if the scattering is by impurities rather than by phonons. The theory can be used to estimate the value of the gap and the way it changes with temperature and with fields; Tinkham is going to give some discussion of this later on in the Conference. One of the problem areas, of course, is to try to account for thermal conductivity when the scattering is dominated by phonons rather than by impurities. Another problem area is the Knight shift, which gives evidence about the electron spin paramagnetism. A simple theory indicates that it should go to zero, i.e., that the electron spin paramagnetism should go to zero at the absolute zero in the superconducting state. However the experiments indicate that it drops only a little bit from the normal value and this has been rather difficult to understand. Anderson[15] and Ferrell[15] have suggested that this can perhaps be understood from the lifetime of the quasi-particles from scattering involving a spin flip, which in turn depends on the spin-orbit interaction. There is some doubt as to whether it is the correct explanation, particularly in view of the recent experiments of Noer and Knight[16] on vanadium, which detect practically no change at all in the spin paramagnetism of vanadium when it becomes superconducting.

*Figure 1* **Electronic specific heat as a function of temperature.**
*The tin data are those of Corak and Satterthwaite[22] at the high temperatures and Goodman[23] at the low temperatures.*




An important area in which recently there has been considerable interest, both theoretically and experimentally, is that of boundary effects. The earlier theories, one by Pippard[17] which involved in a qualitative way a coherence distance, and a semi-empirical theory by Ginsburg and Landau,[18] attempt to account for such things as the boundary between the normal and superconducting domains in the intermediate state and size effects. Gor'kov[19] has shown that one can derive the Ginsburg-Landau theory from the microscopic theory near the critical temperature; however, the theory gets rather complicated at the lower temperatures where Pippard's nonlocal equations,[20] rather than the London equations,[21] are valid. Another problem of current interest is the one involving critical currents and fields and possible changes in energy gap with currents and fields. I will say a little more about this later on.

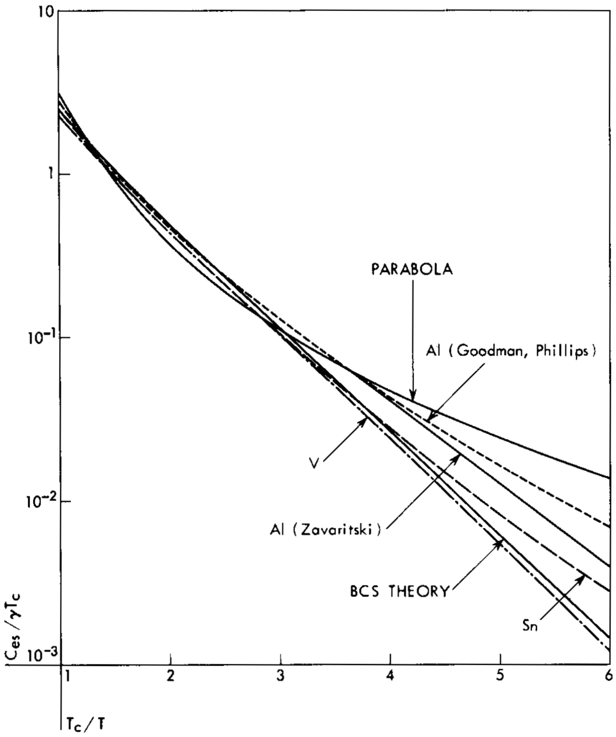
The state of the agreement or disagreement between theory and experiment can best be illustrated by means of Figures. Figure 1 shows the electronic specific heat as a function of the reduced temperature. One of the anomalies which has turned up recently comes from observations at low temperatures, where one expects the electronic specific heat to drop out and leave only the lattice specific heat in the superconducting state. It has been found, surprisingly, that the lattice specific heat in the superconducting state is lower than in the normal state,[24] which has created problems for the theorist. The problem will be discussed by Schrieffer in his talk, who will give possible explanations. Figure 2 shows the specific heat of a number of superconductors, plotted on a reciprocal temperature scale so as to bring out the low-temperature part of the curve. The electronic specific heat is plotted on a logarithmic scale against the reciprocal of the absolute temperature so that low temperatures are to the right. In this region there are discrepancies from the theory, with the experiments usually giving larger specific heats than predicted by the theory. Cooper and others[27] have suggested that this may be due to anisotropy of the energy gap, and this is the most likely explanation for such discrepancies.

Another way of showing up the thermodynamic properties is in terms of the critical fields. Figure 3 shows the departure of the critical fields of a number of superconductors from the parabolic law. Note that most of them give a departure which falls below the parabola. This plot was made by Mapother and some of his associates.[28] The theory follows along the group of so-called weak-coupling superconductors for which the gap is small compared to the cutoff energy. Notice that the departure from parabolic is in the opposite direction for Hg and Pb. This indicates that some modification is required for the theory of these so-called strong-coupling superconductors such as Pb and Hg.

Figure 4 shows the experiments of Glover and Tinkham,[11] which gave the first direct evidence for the energy gap based on infrared transmission through thin films. The absorption, which is plotted here as a function of the frequency, drops to zero at low temperatures when the quantum energy is less than the gap. Then, as the quantum energy becomes greater than the gap, the absorption rises rapidly to that appropriate to the normal state. In more recent work there has been found a precursor absorption; Fig. 5 is based on results of Ginsberg and Tinkham[29] for Pb. This precursor absorption may be the result of absorption by collective or exciton-like states which have energies within the gap. The true explanation for this is still rather uncertain. Ginsberg has been carrying out some experiments on alloys in which he finds this precursor absorption showing up, and this will be discussed later on in this conference.

Figure 6, which was taken from the paper of Giaever and Megerle,[30] illustrates the phenomenon of tunneling. The agreement between theory and experiment is remarkably good if it is assumed that the only difference between the tunneling probability in the superconducting and

*Figure 2* **Electronic specific heat as a function of the reciprocal of the temperature.**
*The vanadium data is from Goodman[23]. The experiments on aluminum by Zavaritskii[25] differ from those of Goodman[23] and Phillips[26] at the lowest temperatures.*



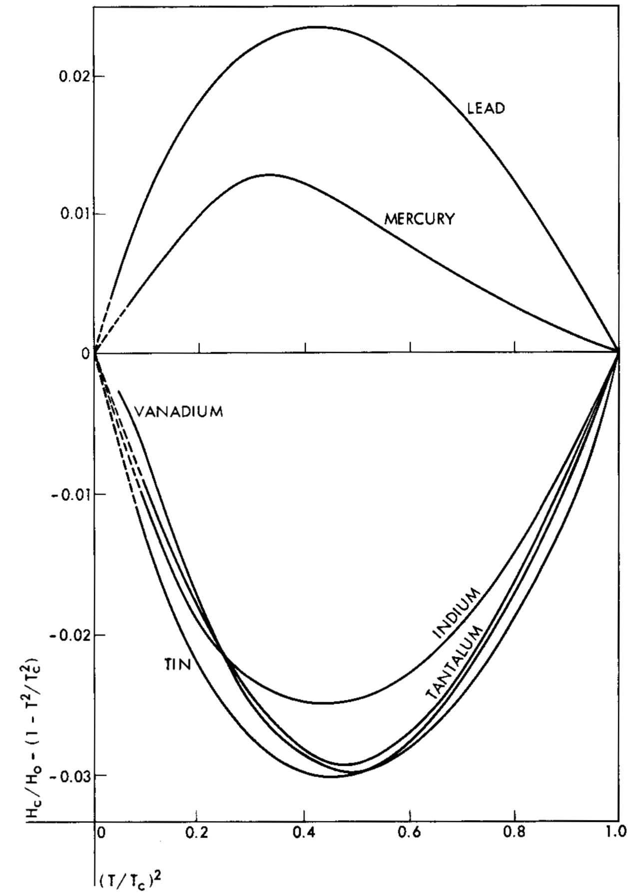




*Figure 3* **Deviation of the critical field from a parabolic law.**
*The plot is based on one made by Mapother and co-workers.*

normal states arises from the density of states in energy. Now this assumption is certainly physically reasonable. But it is not true for the normal metal and one has to look into the theory rather deeply, taking into account the many-particle aspects of the superconducting wave functions, to see why this applies to the superconductor and not to the normal metal.[31] Figure 7 shows that from the tunneling experiments one can determine the energy gap as a function of temperature, and gives a comparison between the results of Giaever and Megerle[30] and the simple theory, with an extremely good fit.

Let us turn now to a brief discussion of the electrodynamics. The theory (Eq. 2) gives an expression for current density very similar to that suggested by Pippard[20] on phenomenological grounds:

$$\mathbf{j}(r,t) = \sum_{\omega} \frac{e^2 N(E_F) v_0 e^{i\omega t}}{2\pi^2 \hbar c} \int \frac{\mathbf{R}(\mathbf{R}\cdot\mathbf{A}_{\omega}(r'))I(\omega, R, T)e^{-R/l}}{R^4}\, d\tau' , \qquad (2)$$

where $\mathbf{R} = \mathbf{r} - \mathbf{r}'$.

This expression is similar to Chambers' equation[10] for

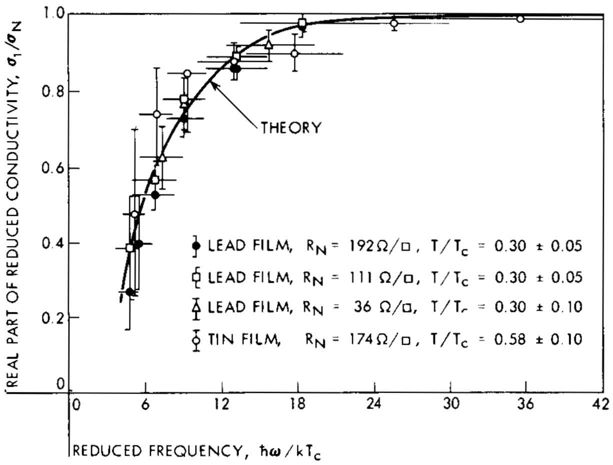



*Figure 4* **Electromagnetic absorption as a function of frequency.**
*The data are from Glover and Tinkham.*

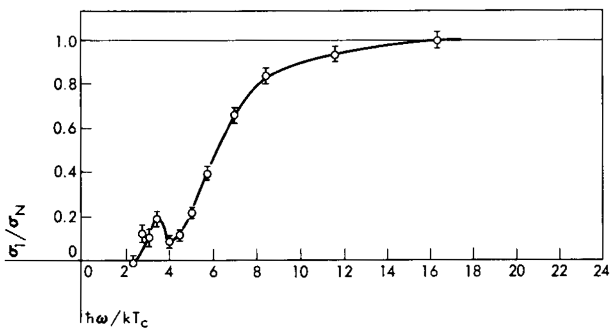



*Figure 5* **Infrared absorption in lead thin films as a function of frequency.**
*The data from Ginsberg and Tinkham.*

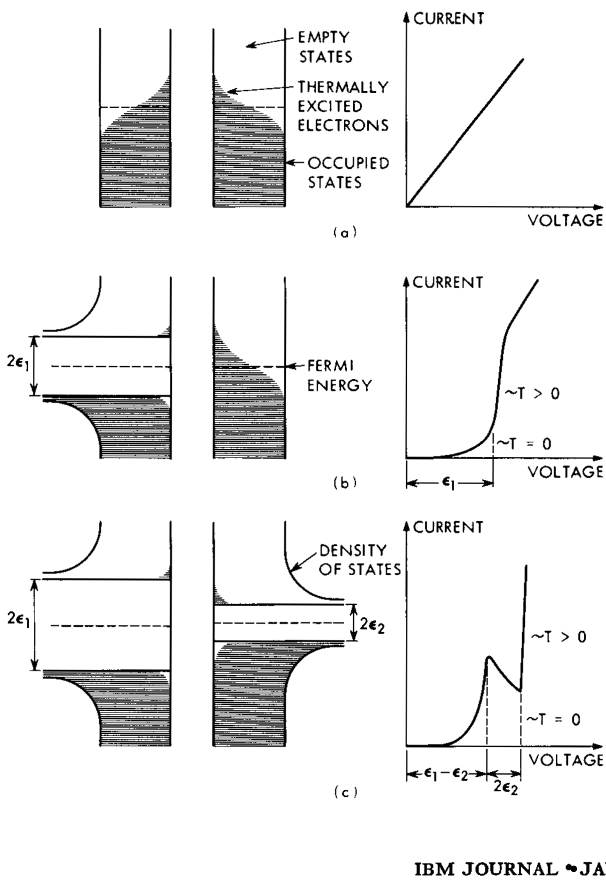
the current density in the normal metal when the electric field may vary over a mean free path. The difference comes in the kernel, which in a superconductor, of course, may depend on the frequency and the temperature as well as the distance between the observation point and the point of integration. This theory was worked out by D. C. Mattis and myself[32] some time ago and independently by Abrikosov, Gor'kov and Khalatnikov.[33] It gives an extremely good fit to the experiments.

Perhaps the most striking fit is shown in Fig. 8, which gives the surface resistance of Al as measured by Biondi and Garfunkel[34] as a function of the energy in units of $kT_c$. These values of the surface resistance were obtained by measuring the absorption of energy, using microwaves in the range of 2 mm to 2 cm, covering a wide range of frequency and temperature. They represent the most complete set of measurements of the surface impedance.

When plotted in this way as a function of the energy or frequency of the radiation, it is seen that at very low temperatures there is no absorption until the quantum energy is greater than the gap. Then it starts rising rapidly to that of the normal metal, as indicated. At higher temperatures there is absorption by quasi-particles in the superconductor which are thermally excited, and this gives increased absorption as the temperature increases. The knee in the curve corresponds to the frequency at which the quantum energy is sufficient to excite particles across the gap. You can see qualitatively that the energy gap decreases with increasing temperature. I would like to emphasize that the solid curve is the experimental one and that the points were calculated by Peter Miller[35] on the basis of the microscopic theory. The only "fudging" done is to take for the gap 3.35 $kT_c$ instead of 3.5 $kT_c$ as the simple model indicates; otherwise there are no undetermined parameters in getting this fine agreement between theory and experiment. Figure 9 is a similar plot for the reactive part of the surface impedance which was deduced from the real part by the use of the Kramers-Kronig relations; again the fit between the theory and experiment is extremely good. The points again are those calculated.

Figure 10 illustrates a similar sort of agreement for Sn. While Al is a very good case for a weak-coupling superconductor, being almost at the extreme Pippard limit where the penetration depth is small compared to the coherence distance, this is not true for Sn. Peter Miller, who made the calculations[35] for Sn as well as Al, had to use a more involved theory than that for the extreme

*Figure 6* **Density of states and current-voltage tunneling characteristics for (a) both metals normal conducting, (b) one metal superconducting and the other metal normal, and (c) both metals superconducting — from I. Giaever and K. Megerle[30].**



anomalous limit. Pippard showed that you can account for the data over a reasonable range of frequency and temperature by giving the surface resistance as a product of frequency alone times a function of temperature alone. Figure 10 gives the frequency factor. The points represent the data of various investigators on Sn. The

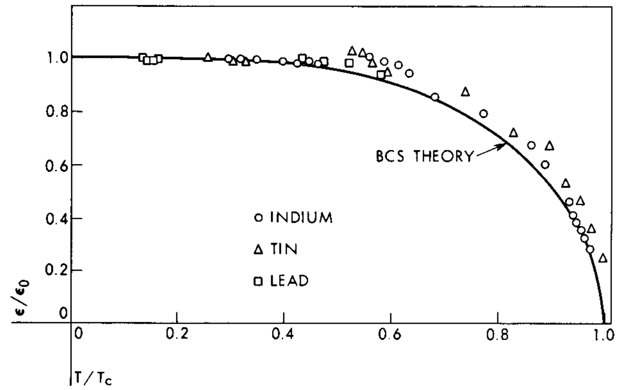



*Figure 7* **The reduced energy gap as a function of reduced temperature of lead, tin, and indium films as determined by tunneling experiments by I. Giaever and K. Megerle[30].**

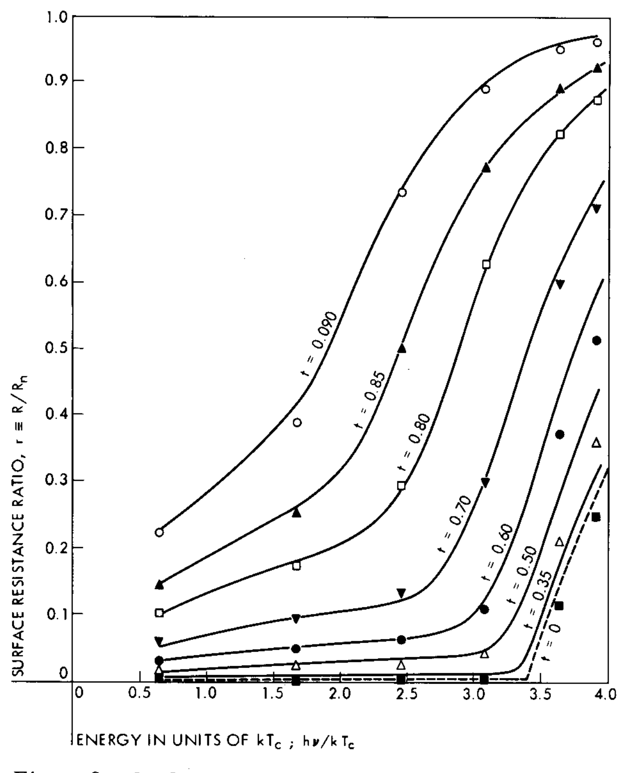



*Figure 8* **Surface resistance of aluminum as a function of frequency.**
*The solid lines are from the experiments of Biondi and Garfunkel[34] while the points are calculated from the theory by Miller[35].*

lower curve gives the theory for the extreme anomalous limit, while the upper curve gives the theory, taking into account the actual coherence distance and penetration depth of the complete theory. You can see that the agreement is extremely good, and there are no undetermined parameters in getting this agreement.

Figure 11 illustrates the two coherent contributions to the matrix element for transition probabilities in a superconductor which may add destructively or constructively. In the case of ultrasonic absorption (Fig. 12), there is a very rapid drop when going from the normal to the superconducting state, following approximately the Fermi-Dirac type of expression of Eq. (1) involving the energy gap.[36] The coherence can come in with either sign, and for the nuclear relaxation (Fig. 13) it is opposite, giving an increase in the interaction between the electrons and the nuclei in the superconducting state. In comparing the theory with the experiments it is necessary to take some sort of width for the levels; the actual energy involved in the nuclear spin flips is much smaller than one-hundredth of $kT_c$ and it has been uncertain as to just what causes the observed width of the levels. The theoretical curve with a width of one-hundredth of $kT_c$ fits roughly with the data of Hebel and Slichter[14,37] and of Redfield and Anderson.[38] This is earlier data – there is much more accurate data now. As we will hear later on in the Conference from Masuda, the width apparently decreases when impurities are introduced. Impurity scattering tends to average out the Fermi surface and reduces the anisotropic effects; at least this is presumably the explanation. Thus the width in the more pure metal is due mainly to anisotropy.

Figure 14 shows that there is good agreement between experimental and theoretical values of the thermal conductivity when scattering is dominated by impurities. There is still no satisfactory theory when thermal scattering is important.

Kadanoff and Martin[43] have shown that you get a reasonably good fit for superconductors such as Sn and In if it is assumed that the relaxation time for scattering is the same in the superconducting as in the normal state. There is no basic microscopic justification for this assumption and, further, this explanation does not apply to Pb and Hg, for which the drop near $T_c$ is even more abrupt. There is a problem here for the theorist.

The final thing I want to talk about is what determines the critical current. There are two criteria which might be used to determine the critical current in a thin film or other specimen as a function of the temperature. There is an increase in free energy as a result of current flow, which is essentially one-half of $\rho_s$, the density of superconducting electrons in the two-fluid model, times $v_s^2$, the square of the velocity with which the pairs are moving. This must be superimposed on the usual free energy. If one assumes that the critical current is determined when this additional free energy, $1/2\ \rho_s v_s^2$, becomes greater than the energy difference between superconducting and normal state, one gets the criterion given by the upper curve in Fig. 15. But if you look at the theory more closely you see that as $v_x$ is increased you reach a state where it is favorable for electrons to be scattered from one side of the Fermi surface to the other, in spite of the gap. As the Fermi distribution is displaced in $k$ space, the energy in one side of the Fermi distribution is increased and on the other side decreased. Eventually that energy difference becomes greater than the gap, so that there is a kind of catastrophic formation of electron-hole pairs, starting at a given critical current. This is the so-called "depairing criterion" which gives, surprisingly, not a very much lower critical current than the free energy criterion.

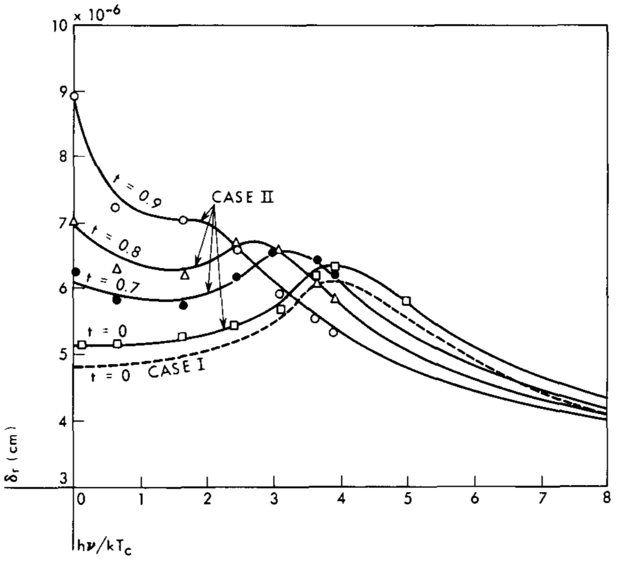



*Figure 9* **Reactive part of the surface impedance of aluminum.**
*The solid lines are derived from the experimental surface resistance by the Kramers-Kronig relations*[34] *and the points are calculated from the theory by Miller*[35].

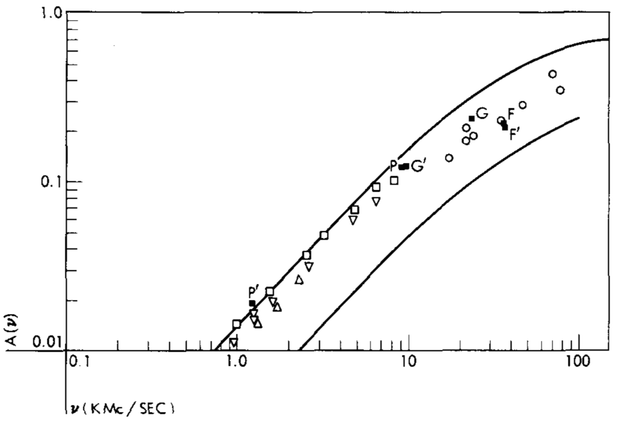



*Figure 10* **The frequency-dependent part of the surface resistance of tin.**
*The points are experimentally determined and curves are calculated from the theory*[35]. *The lower curve is for the extreme anomalous limit while the upper curve is for the actual coherence distance of tin.*

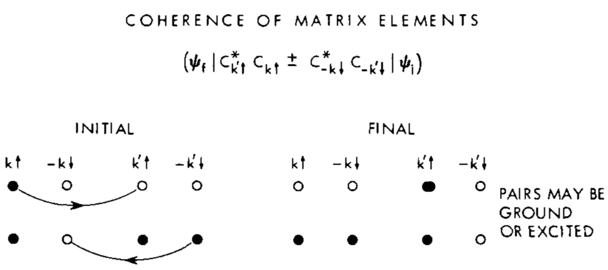



*Figure 11* **Configurations which enter when a quasi-particle makes a transition from a singly occupied state in $k$ to one in $k'$.**
*This shows the coherence effects that are involved because of the electron pairing.*

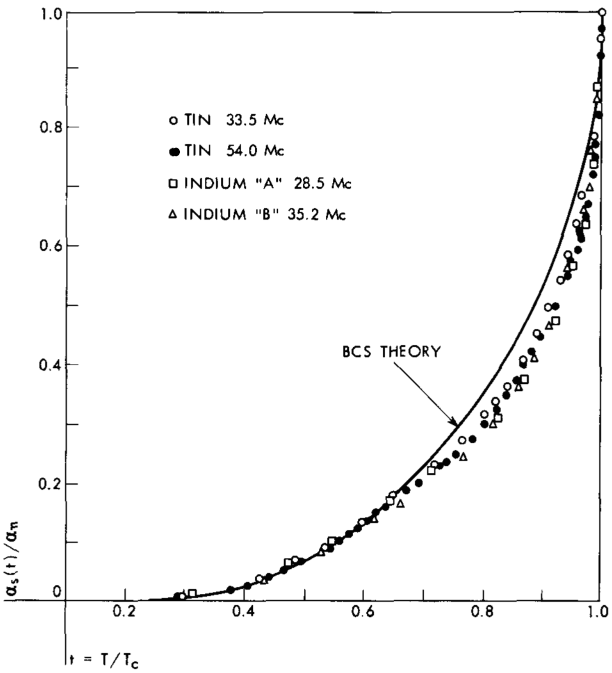



*Figure 12* **Ultrasonic attenuation in the superconducting state compared to the normal state as a function of temperature.**
*The experiments are those of Morse and Bohm*[36].

One way of making the calculations is to take the energy gap as a free parameter of the theory and to see how the energy gap varies with current density, as has been done by K. T. Rogers.[44] The energy gap will decrease with increasing current. The free energy difference between superconducting and normal states is given by

$$F_s - F_n = g(x) + \tfrac{1}{2}\rho_s v_s^2\ ,$$

where $x$ is the energy gap parameter, which may be taken in reduced units as $x = \Delta(T, v_s)/\Delta(0, 0)$. If there is no current flow, $v_s = 0$, then $x$ is determined by taking $dg/dx = 0$; this determines how $x$ varies with $T$. Near $T_c$ one can expand out the free energy difference in a power series in $x$:

$$g(x) = -\tfrac{1}{2}a_2(l-t)x^2 + \tfrac{1}{4}a_4 x^4\ .$$

This is equivalent near $T_c$ to the Ginsburg-Landau theory,[18] and is in agreement with Gor'kov's formulation.[19] The above method is somewhat simpler and can be used as long as the energy gap does not vary in space, as it does not in a sufficiently thin film. The parameters $a_2$ and $a_4$ are determined first of all from knowing how $x$ varies with $T$ in the absence of current flow and from the free energy difference which is given in terms of the critical field; so $a_2$ and $a_4$ are known. Now the problem is to add the $\rho_s v_s^2$ and then to determine the free energy as a function of the current or $v_s$. Taking into account the variation of $\rho_s$ with $x$, we find that the current as a function of $v_s$ increases to a maximum and then decreases to zero again so that there is a maximum current density. At this maximum the gap is decreased only slightly from the gap at $v_s = 0$. Near $T = 0$ the decrease in $x$ from zero to the maximum current is only a few percent; it is perhaps 20% near $T_c$.

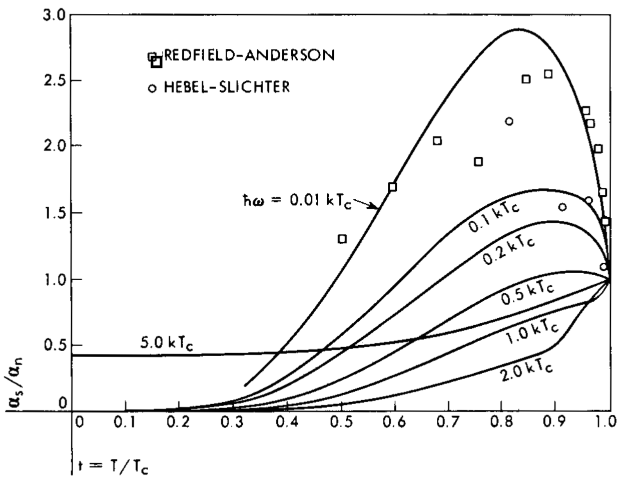



*Figure 13* **Nuclear spin relaxation rate in aluminum as a function of temperature.** *The curve for $\hbar\omega = 0.01kT_c$ was calculated by L. C. Hebel[37] for level broadening.*

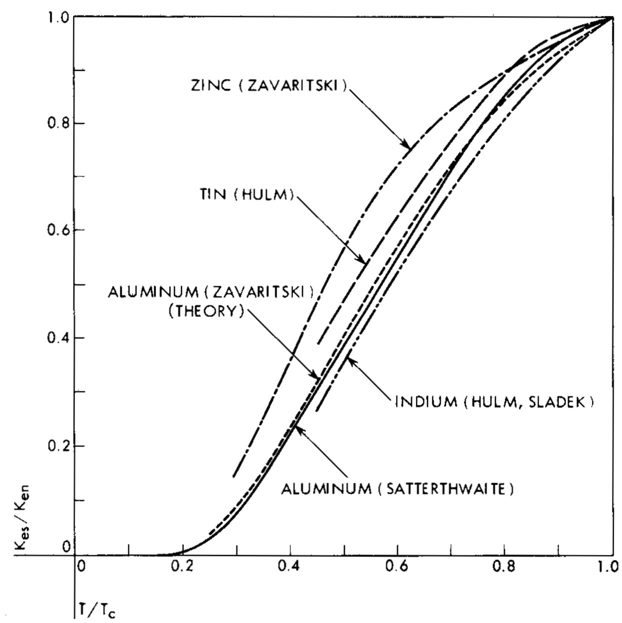
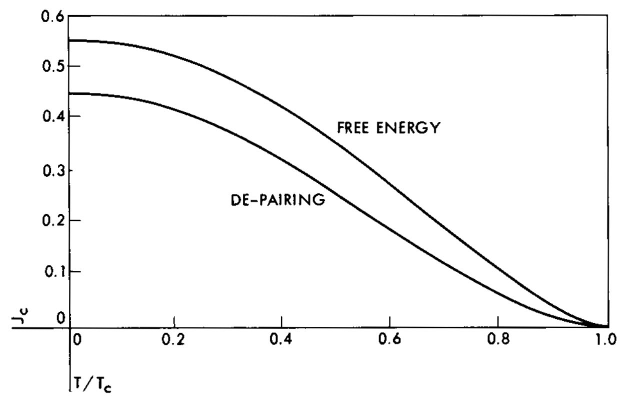



*Figure 14* **The ratio of the electronic thermal conductivity in the superconducting state, $K_{es}$, to that in the normal state, $K_{en}$, when impurity scattering is predominant.** *The experiments have been performed by Zavaritskii[25] (Zn, Al), Satterthwaite[40] (Al), Hulm[41] (Sn, In), and Sladek[42] (In).*

*Figure 15* **Calculated critical current in a thin film as a function of temperature.** *The upper curve is based on the equality of the free energy in the two states at the transition. The lower curve is the criterion for de-pairing of the electron pairs in the supercurrent, taking into account the change of gap. The curves are based on calculations of K. T. Rogers.[44]*



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