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"CURIE-WEISS" BEHAVIOR AND FLUCTUATION PHENOMENA IN THE RESISTIVE TRANSITIONS OF DIRTY SUPERCONDUCTORS*

Myron Strongin, O. F. Kammerer, J. Crow, R. S. Thompson, and H. L. Fine
Brookhaven National Laboratory, Upton, New York
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By making very small mean-free-path films we have been able to measure the intrinsic nature of resistive transitions as a function of mean free path. Analysis based on the concepts of Anderson and Josephson leads to an estimate of the smearing of the transition near zero resistance.

Very recently, experimental studies of the nature of the superconducting transition temperature[1] have shown "Curie-Weiss" behavior above T_c and the possibility of a critical region about 3 mdeg away from T_c. The usual estimates for the natural widths of the superconducting transition have ranged from[2] 10^{-14} to 10^{-8}°K in pure superconductors, and in view of these estimates little hope was given to observing the nature of the transition in ideal superconductors. However, Glover,[1] following a suggestion of Anderson,[3] was able to achieve a measurable transition region by studying amorphous Bi, a system with a very small mean free path (l). In these films l was about two atomic spacings, which is about as small an l as can be achieved in pure metallic systems. Hence the study of the transition region as a function of l is difficult in these films, since larger l's would make the width prohibitively small.

In this note we wish to report measurements on thin Al films[4,5] prepared in vacua of $\sim 10^{-6}$ Torr at room temperature and then exposed to air. In this type of system the film is probably composed of grains of metal surrounded by oxide, or possibly weakly linked to each other through Josephson barriers or fine metallic links. The crucial points we wish to make are the following:

(a) The effective mean free path (l_{eff}) can be made much smaller in a "granular" system than in pure metal systems, thereby leading to a larger intrinsic transition region. This is because of the high resistance of the tunneling barriers between particles, or the fine metallic links.

(b) The dependence of the transition width on l_{eff} can therefore be studied.

(c) Towards the end of this paper a model is given which discusses the smearing of the transition near $R/R_n \sim 0$.

In Figs. 1 and 2 the data are shown for two different films with mean free paths of about 0.2 and 5 Å, respectively.[6] The heavy line in both cases is a fit at high temperatures, near 4°K, to the function $R/R_N = (1+\tau_0/\tau)^{-1}$. τ is defined as $(T-T_c)/T_c$ and τ_0 is the value of τ at $R/R_N = 0.5$. The fact that this "Curie-Weiss" dependence might describe the nature of the resistive transition above T_c has been suggested by Schmidt[1] and discussed by Glover.[1] Although the data are fitted extremely well by this dependence, it is not clear why this analogy to the magnetic case holds. (See Note added in proof.) From our measurements it is clear that τ_0, which differs by about a factor of 10 in the two films, goes inversely as l_{eff}.

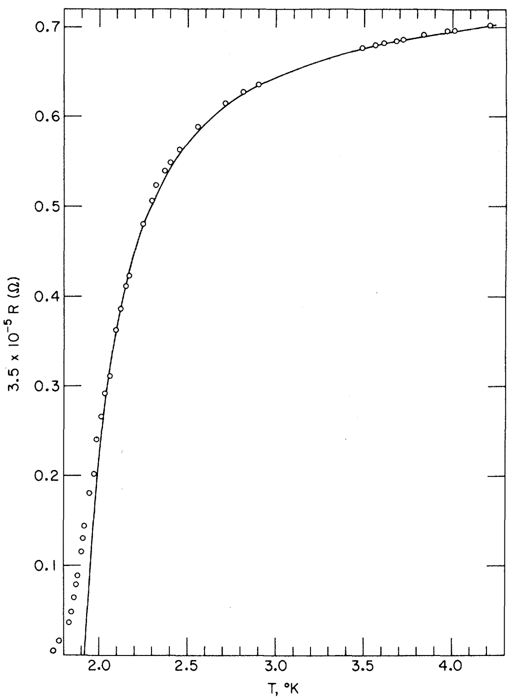

FIG. 1. R vs T for film with mean free path estimated to be about 0.2 Å. τ_0 from high temperature fit to "Curie-Weiss" law is 0.1. Thickness of film about 100 Å.

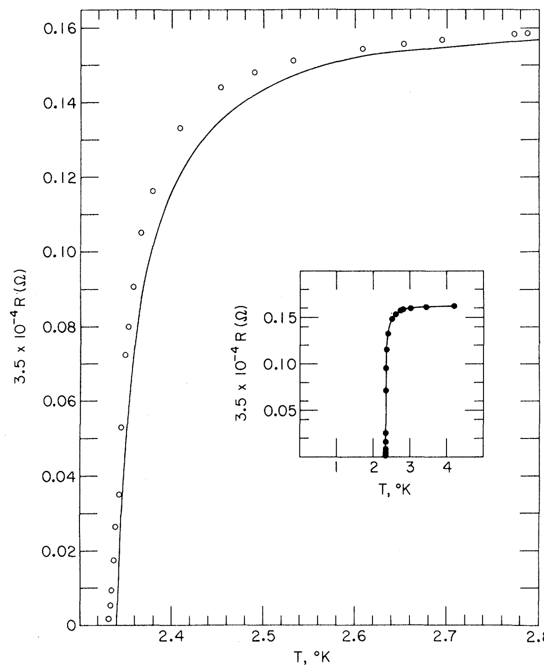

FIG. 2. R vs T for film with mean free path estimated to be about 5 Å. τ_0 from high temperature fit to "Curie-Weiss" law is about 0.011. The earth's field was balanced to about 0.1 Oe. Thickness of film about 100 Å.

An $l_{\rm eff}$ of ~0.2 Å is somewhat surprising, since it is much less than the interatomic spacing. This result, however, is not inconsistent with the analysis of the conduction mechanism in granular superconductors as analyzed by Parmenter[7] and by Abeles, Cohen, and Stowell.[8] The expression they give[8] for the effective transport mean free path is $l_{\rm eff}=dt/(1-t)$, where t is the transmission coefficient of the barrier between particles and d is the particle size. Physically one might expect this analysis to be meaningful as long as ξ, the coherence length, extends over many particles and as long as $P_{\rm F}l_{\rm eff} > 1$. For Al, with this high T_c, we might expect ξ_0 to be of the order of 10^4 Å, and hence $\xi \sim [\xi_0 l_{\rm eff}T_c/(T_c-T)]^{1/2}$ is ~150 Å at about $0.9T_c$. Since the particle size is probably of the order of 20 Å for films with such high resistivities, ξ extends over many particles. In this particular case with $l_{\rm eff} \sim 0.2$ Å, the condition $P_{\rm F}l_{\rm eff} > 1$ is not satisfied, although there is experimental evidence[8] that this is not crucial.

Models[4,5] of the T_c in these small systems suggest that one would expect variations in T_c with particle size, or film thickness. An analysis of the transition similar to that given by Pippard[2] shows that a fit cannot be obtained with any realistic distribution of particles, but instead a large asymmetric tail is required to explain the high-temperature region. We suspect that because the coherence length extends over many particles, especially near T_c, the transition broadening due to inhomogeneities is small compared with the higher temperature features of the transition such as the "Curie-Weiss" behavior. Hence the good fit to the "Curie-Weiss" behavior is an intrinsic feature of the transition. When $R/R_n < 0.5$, inhomogeneities might be expected to be more important.

Ferrell and Schmidt[9] have discussed the effect of small l on the phase transition and they have compared the predictions of their arguments with the experiments of Glover.[1] Recent calculations by Ferrell[10] from the microscopic theory indicate that the critical region is much smaller than the qualitative estimates of Ferrell and Schmidt[9] and essentially yield, as the earlier estimates did,[2] that this region will be too narrow to observe experimentally in the three dimensional case. This would imply that the deviations from the "Curie-Weiss" fit in Ref. 1 and the present results are due to inhomogeneities.

In order to provide some insight into the region where resistance disappears we have developed the argument below. In this analysis it is assumed that the natural distance for phase fluctuations is ξ, when $\xi > d$ and $\xi > l_{\text{eff}}$. The effect of particles and barriers is included in l_{eff} as mentioned previously.

Following Anderson and Rowell[11] and Josephson[12] we use the concept of a coupling energy between the phases of the gap function on two sides of a "barrier." The magnitude of this energy is $\Delta E = (\hbar/e)J$, where J is the maximum Josephson current. This coupling energy also maintains the internal coherence of a continuous superfluid.[13] In our analysis we assume resistance will appear when $kT \gtrsim (\hbar/e)J$. J will be the product of the maximum supercurrent density given by $[n_s e(\hbar/m)\nabla\varphi]_{\max}$ multiplied by the area of the region through which it flows. For our dirty sample, n_s, the number of superfluid pairs per cm^3, is reduced relative to the clean case by l_{eff}/ξ_0. This can easily be shown by referring to de Gennes,[14] where it is shown that $\psi = (2mC/\hbar^2)^{1/2}\Delta$. For a clean material $C \to \xi_0^2$, and for a dirty material $C \to l\xi_0$. Hence $n_s(\text{dirty})/n_s(\text{clean}) = \psi^2(\text{dirty})/\psi^2(\text{clean}) = l/\xi_0$. This result is well known and has been used by Ferrell and Schmidt.[9] It is now argued that for the clean material at 0°K the characteristic distance for a phase change is ξ_0 and for a dirty material at temperature T it is ξ. Hence for a dirty material at temperature T, and for a given phase change, $\nabla\varphi$ will be $(\xi_0/\xi)\nabla\varphi(0)_{\text{clean}}$. Thus we can estimate the current density for the dirty material at temperature T as $j_{c\ \text{clean}}(0)(l_{\text{eff}}/\xi)[n_s(T)/n_s(0)]$, where the last factor gives us the temperature dependence of n_s. For a first approximation, the two-dimensional case is considered. It is assumed that kT causes a change of phase in cells characterized by ξ, resulting in the flow of supercurrents. For simplicity we assume that this change occurs in a disk of diameter $\sim\xi$ and thickness $t \lesssim \xi$ near T_c, and thus currents flow into or out of a region of area $\pi\xi t$. In reality many of these regions must rapidly appear and disappear throughout the sample. If we use the two-fluid dependence of n_s near T_c and use the above result for the current density with $j_{c\ \text{pure}}(0) \sim 10^7\ \text{A/cm}^2$, we get for the two-dimensional case that $kT \gtrsim 4\pi(\hbar/e)10^7 l_{\text{eff}} t(1-T/T_c)$ is the condition for which the maximum supercurrents are no longer sufficient to keep phase coherence. At this point we assume that any small measuring currents flowing in this region will encounter resistance, as in the flux flow regime of type-II superconductors. Our estimate of the regime in which fluctuations may cause resistivity is similar to comparing kT with the condensation energy Δg in a volume $\xi^2 t$ because the critical current density[15] is determined by $(\hbar/e)j_c = (\frac{4}{3})^{3/2}2\xi\Delta g$. The numerical calculations from the above result give $(T_c-T)/T_c \sim 0.2$ for $l_{\text{eff}} \sim 0.2$ Å, and $(T_c-T)/T_c \sim 0.008$ for $l_{\text{eff}} \sim 0.5$ Å. We briefly discuss some interpretations of this result: (a) If we consider the "tail" region to be significant and not due to inhomogeneities, we can interpret T_c-T as the distance between the zero resistance point and the T_c from the extrapolation of the "Curie-Weiss" fit. This region is ~0.2°K for Fig. 1, compared with the above calculation of ~0.4°K, and for the data of Fig. 2 we get about 0.015°K compared with a calculated value of ~0.016°K. (b) We can consider this calculated difference in temperature to be the depression of the whole "Curie-Weiss" curve below what T_c would be if there were no fluctuations. Hence for the data in Figs. 1 and 2 the observed shift of T_c from a supposed original value of 2.36°K are 0.44 and 0.02°K, respectively, in agreement with the above estimates. (c) Lastly, we mention that our calculation might indicate the strength of the "Curie-Weiss" fit, and should be related to the τ_0's. Again there is approximate agreement. Further theoretical and experimental work will be necessary to clarify these points. The above analysis can be extended to the thicker film results of Glover.[1] We assume the phase changes over a spherical region of area $\pi\xi^2$. The previous arguments give $\frac{3}{2}kT \gtrsim 4\pi(\hbar/e)10^7 l_{\text{eff}}^{3/2}\xi_0^{3/2} \times [(T_c-T)/T_c]^{1/2}$ as the condition for resistance and we obtain $(T_c-T)/T_c \sim 2\times 10^{-3}$ in agreement with Glover.[1]

We conclude by suggesting that one search for superconductivity in metals such as Cu, by making dirty films and searching for small changes at temperature above T_c, in a similar way to the paramagnetic salt case. Of course, one has the worry that metals prepared in this way are not always indicative of the bulk material.[4,5]

We have benefited from discussions with Dr. R. A. Ferrell, Dr. L. P. Kadanoff, and our colleagues at Brookhaven, especially Dr. Paskin and Dr. Lee.

Note added in proof.—Since the submission of this paper we have seen the work of Aslamazov and Larkin,[16] which derives the $(1+\tau_0/\tau)^{-1}$ dependence from a microscopic analysis. A feature of their argument is that $\tau_0/R_{\text{square}} = 1.5$

$\times 10^{-5}\ \Omega^{-1}$ for all materials. We find that our experimental results are in extremely good agreement with this result which predicts that τ_0 will go inversely as l for films of a given thickness. For the data in Fig. 1, $R_{\rm square}$ is $8.7 \times 10^3\ \Omega$ and therefore τ_0/R is $1.15\times 10^{-5}\ \Omega^{-1}$; for the data in Fig. 2, $R_{\rm square}$ is $\approx 2.5\times 10^2\ \Omega$ with $\tau_0/R_{\rm square} \sim 4\times 10^{-5}\ \Omega^{-1}$. We consider this to be good agreement with the value of Aslamazov and Larkin of $\tau_0/R_{\rm square} \sim 1.5\times 10^{-5}\ \Omega^{-1}$, especially since our τ_0 values were obtained from a fit to the data near 4°K.

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ACCURATE CALCULATION OF LOW-ENERGY ELECTRON-DIFFRACTION INTENSITIES BY THE PROPAGATION-MATRIX METHOD

Paul M. Marcus and Donald W. Jepsen
IBM Watson Research Center, Yorktown Heights, New York
(Received 26 February 1968)

A necessary step in relating low-energy electron-diffraction (LEED) observations to crystal structure is the calculation of accurate values of the intensities of electrons scattered coherently from a given periodic potential (or pseudopotential) terminating at a plane surface. Several methods have been discussed in recent papers,[1-3] but they do not seem to give complete and accurate results, which we believe the method described here can provide. Our method uses the "mixed" (Fourier and coordinate) representation of von Laue,[4] employed recently by Hirabayashi and Takeishi,[5] but develops a systematic computational procedure whose convergence toward the correct solution can be estimated. The calculation of a "propagation" matrix P defined later is central to this procedure, since the problem is then reduced to finding the eigenvectors of P, for which new high-speed computer techniques are available.

The calculation has a natural division into two parts, as is emphasized by Heine[6] and also adopted here. First, solutions are required of the energy-band problem for the infinite crystal, but just for the particular discrete set of Bloch functions with the same energy ϵ and the same (reduced) component of wave number parallel to the surface $\vec{k}_\rho$ as the incident electron has; this set includes solutions which attenuate. Second, the reflection coefficients are found from linear equations which match the wave function and its normal derivative at the surface. In the crystal,