impurities results entirely from the difference between Eqs. (4.10) and (4.29), and in particular from the fact that the second term on the right-hand side of (4.29) is proportional to τ_4 rather than τ_3. Because of (4.27), it is still possible to take b_k and Δ real, and to assume that $K(0,0;H_2)$ and $K(l,l;H_2)$ contain nothing proportional to τ_2 and something proportional to $\omega\tau_4$. However, it is necessary to modify (4.12) by taking *different* coefficients for the two terms $\Delta\tau_1$ and $\hbar\omega\tau_4$. This leads to the results discussed in detail in Ref. 12.

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Destruction of Superconductivity in Disordered Near-Monolayer Films*

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Severe decreases are observed in the superconducting transition temperatures of metallic films as they are made thinner and more disordered. Explanations for these decreases in the transition temperature are discussed. These include changes in the phonon spectrum, the effect of the metal-insulator boundary, size quantization in small particles, the effect of an activated conduction mechanism in the normal state, and, finally, the effect of order-parameter fluctuations.

I. INTRODUCTION

In recent years, there has been much speculation about the properties of ultrathin film superconductors and, especially, the possibility of achieving higher transition temperatures T_c than those presently attained in such systems. Buckel and Hilsch[1] and Zavaritsky[2] initially showed that soft metals deposited at cryogenic temperatures had T_c's significantly above the bulk value in fairly thick films, which electron diffraction work indicated were composed of small metallic grains. With recent work[3–5] on the effects of softening the phonon spectrum, we seem to understand why T_c goes up, and a discussion of this work will not be presented here. Instead, we consider the problem of the decreasing T_c found in the thinnest films. Throughout the literature, there have been various reports that T_c decreases in the very thinnest metallic films.[6,7] In this paper, we present a systematic experimental investigation of this problem along with the effect of dielectric overlayers, and a discussion is given of the physical mechanisms that can affect T_c in this regime.

As mentioned, the general substance of this paper is the severe decrease in the T_c of superconducting films

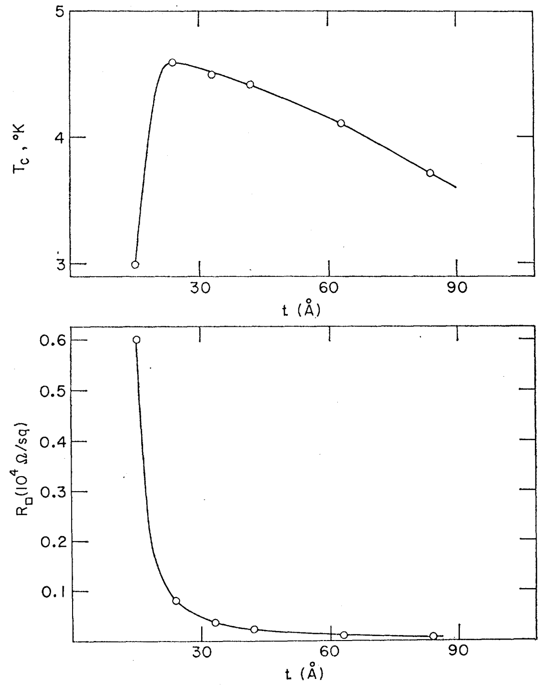

FIG. 1. T_c versus thickness for Al film deposited on previously deposited SiO. Lower graph shows sharply increased resistance at small thicknesses.

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* Work performed under the auspices of the U. S. Atomic Energy Commission.

[1] V. Buckel and R. Hilsch, Z. Physik **132**, 420 (1952); **138**, 109 (1954).

[2] N. V. Zavaritsky, Dokl. Akad. Nauk SSSR **86**, 501 (1952).

[3] W. L. McMillan, Phys. Rev. **167**, 331 (1968).

[4] M. Strongin, O. F. Kammerer, J. E. Crow, R. D. Parks, D. H. Douglass, Jr., and M. A. Jensen, Phys. Rev. Letters **21**, 1320 (1968).

[5] J. M. Dickey and A. Paskin, Phys. Rev. Letters **21**, 1441 (1968).

[6] N. V. Zavaritsky, Dokl. Akad. Nauk SSSR **82**, 229 (1952); H. Vogel, thesis, University of North Carolina, 1962 (unpublished).

[7] M. Strongin and O. F. Kammerer, J. Appl. Phys. **39**, 2509 (1968).

(particularly Pb and Bi) with thicknesses of the order of a few monolayers. We have already indicated that Al and Sn films, prepared on previously deposited SiO, increase in T_c as the thickness t decreases down to about 30 Å; then, below about 30 Å, T_c decreases.[7] This nonmonotonic behavior is shown in Figs. 1 and 2. In order to concentrate on the regime where T_c decreases without the complication of T_c enhancement, we have studied Pb, whose T_c only decreases as t is made smaller. In the regime where the films first become electrically continuous, the resistance in the normal state is extremely high (greater than about 10 000 Ω/sq), and T_c is drastically reduced and is usually below the lowest temperature achievable with our cryostat. Also, in this regime where the films first become continuous, the normal-state resistance usually increases with decreasing T according to $R_0e^{+\langle E\rangle/kT}$. This, of course, is in contrast to the usual metallic behavior where R decreases with decreasing T. The exponential dependence is characteristic of an activated conduction mechanism which is expected to occur in the regime where the film first becomes electrically continuous, where the metal might be composed of separate grains and conduction is obtained by electron tunneling. It is also possible that, because of the extreme atomic disorder in this regime, the usual band conduction is destroyed and electrons can only move through the lattice by an activated conduction mechanism.[8,9]

In Sec. II, we discuss our methods of sample preparation. Then, in Sec. III, we present our experimental results. A discussion of the various factors which could influence T_c and their relative importance for our films is given in Sec. IV, where we decide that the presence of the metal-insulator boundary probably dominates the decrease in T_c.

II. EXPERIMENTAL TECHNIQUE

The films are prepared at cryogenic temperatures in an oil-free vacuum system composed of a Turbomolecular pump backing two vac-ion pumps. During evaporation, the pressure in the system rises to about 5×10^{-7}–1.5×10^{-6} Torr, and usually the pressure during evaporation is somewhat below 10^{-6} Torr. Normal evaporation rates were near 10 Å/sec. Because of the He and N shields, which have solenoid-operated shutters to allow the metal to reach the slide, we would expect the ambient pressure in the vicinity of the slide to be much lower than the above pressures and probably to be near the ambient He pressure, which is about 10^{-9} Torr. During evaporation, it seems reasonable that most of the gas in the films must come from the gases in the metal itself, since the solid angle through the shutters for gas coming from the evaporator walls is extremely small. In general, we have seen no behavior attributable to gases in the range from 5×10^{-7} to about 2×10^{-6} Torr. For instance, from work with gases in cryogenically deposited Al films, it appears that system pressures near 10^{-4} Torr are necessary before the T_c of the Al films changes drastically from the usual value for cryogenically deposited films. The ambient pressure in the system before evaporation is usually well below 10^{-6} Torr and is sometimes near 2×10^{-7} Torr. The effect of the substrate will be discussed in detail later, but we should mention that, on almost all runs, Pb is deposited simultaneously on the glass slide while the other film is made on the substrate with previously deposited Ge, Al_2O_3, SiO, or LiF. In the cases of Ge, Al_2O_3, and SiO, the film becomes continuous well before the film deposited on glass. If oxygen were important, we would not expect to see the remarkable difference in the nucleation properties with the various substrates. Before leaving the question of gases in the system, it is probably worth mentioning that water vapor is the principal gas in the ambient pressure reading. Nitrogen and oxygen pressures are significantly lower.

The general features of the shutter system are shown in Fig. 3. The shutters on the N and He shields are controlled by solenoids which are cooled by contact to the shields. The slides, in this case glass, have Au strips previously deposited to provide electrical contact when the film comes on. On most of the runs, masking tape was placed over the Au strips, perpendicular to the strip direction and parallel to the film direction. When the film is deposited, the edge of the film falls on the

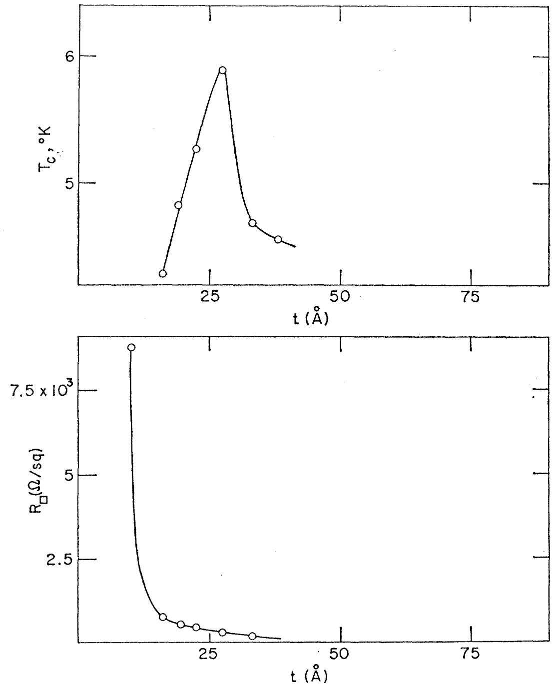

FIG. 2. T_c versus thickness for Sn film deposited on previously deposited SiO. Lower graph shows sharply increased resistance at small thicknesses.

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[8] P. W. Anderson, Phys. Rev. **109**, 1492 (1958).

[9] N. F. Mott, Phil. Mag. **17**, 1259 (1968).

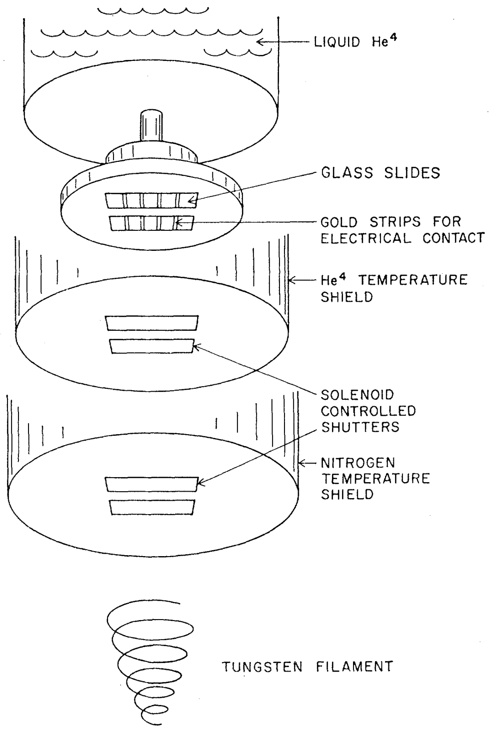

FIG. 3. General experimental setup for evaporating samples.

masking tape and is discontinuous to the main part of the film. Hence, the section of the film we are measuring is fairly uniform. This is also due in part to the slide being about 22 in. from the filament source, which makes angular corrections small and which also allows the substrates to stay quite cool during deposition. In fact, Pb stays superconducting as more Pb is deposited, which shows that the film stays below 7°K during deposition.

The bottom section of the He Dewar is held together with Pb O-rings. This seal remains tight even with atmospheric pressure pushing out on the flange. With superfluid He in the Dewar, we have achieved pressures in the high 10^{-9}-Torr range in the vacuum system. This flange arrangement allows the bottom of the He Dewar to be changed for inclusion of a superconducting magnet. Electrical leads were initially brought through the He bath. However, we have found that bringing the leads in through the vacuum space provides a more convenient method. When this is done, the wires are wrapped around both the N and He Dewars and are ballasted with GE 7031 cement. All regions with volatile cements are cooled to N or He temperatures.

The film thickness is determined with a Sloane crystal oscillator thickness monitor corrected by the geometrical factor relating the position of the crystal to the position of the slide. After the run, the film thickness is checked with an interferometer.

A question that comes to mind is the effect of magnetic impurities in the initial decrease in T_c. There are two sources of this contamination of, say, Fe. There can be some impurities on the deposition surface and there can also be impurities coming from the metal itself. It is very implausible that magnetic impurities in the substrate play an important role, since deposited Ge, SiO, and Al_2O_3 about 20 Å thick are used as the substrate. The conditions and evaporation technique involved in these depositions are relatively different; Ge and Al_2O_3 are evaporated from an electron beam gun while SiO is evaporated from a special Ta boat, and, yet, greatly depressed T_c's are obtained for all these substrates.

Spectrographic analysis of the actual Pb samples indicates 5–10 ppm of Fe which is larger than the 1-ppm value claimed by the supplier. Even with relatively large amounts of Fe, such as 0.01% in the sample, and making the pessimistic assumption that Fe comes off at approximately 0.01% of the Pb rate, there is not enough Fe to significantly depress T_c. If Raoult's law is obeyed in any reasonable sense, almost no Fe should come off, since the partial pressure of Fe would be the concentration multiplied by the bulk vapor pressure, which is about 10^5 times smaller than Pb. Also, if any Fe comes off, it should be towards the end of the run, which certainly would not account for the large decreases in T_c at the beginning of the run when the films are thinnest. Finally, when the films are thick enough, the T_c compares well with the usual value for Pb made on cryogenic substrates. Hence, any Fe impurities, even by this test, must be negligible.

III. EXPERIMENTAL RESULTS

A. General

In Fig. 4, we show an over-all plot of the data. This shows the decrease in T_c with increasing R of the Pb films. Of course, the regime of increasing R is also the regime where the thickness of the films is rapidly decreasing. The T_c's are the values where the extrapolated "Curie-Weiss" resistance would be zero. This will

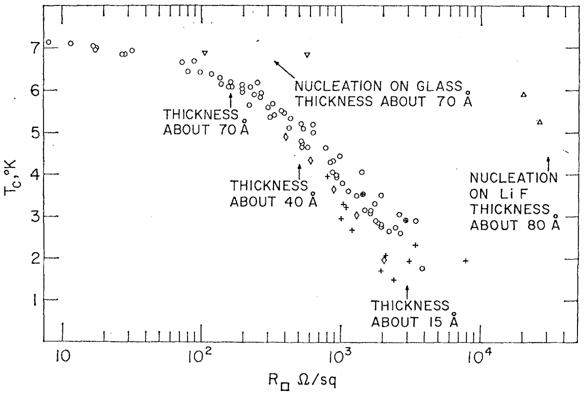

FIG. 4. T_c versus $R_\square$ (log plot), where $R_\square$ is the resistance/sq area: ○—Pb on SiO; ◇—Bi on SiO; +—Pb on Ge; ⊕—Pb on Al_2O_3.

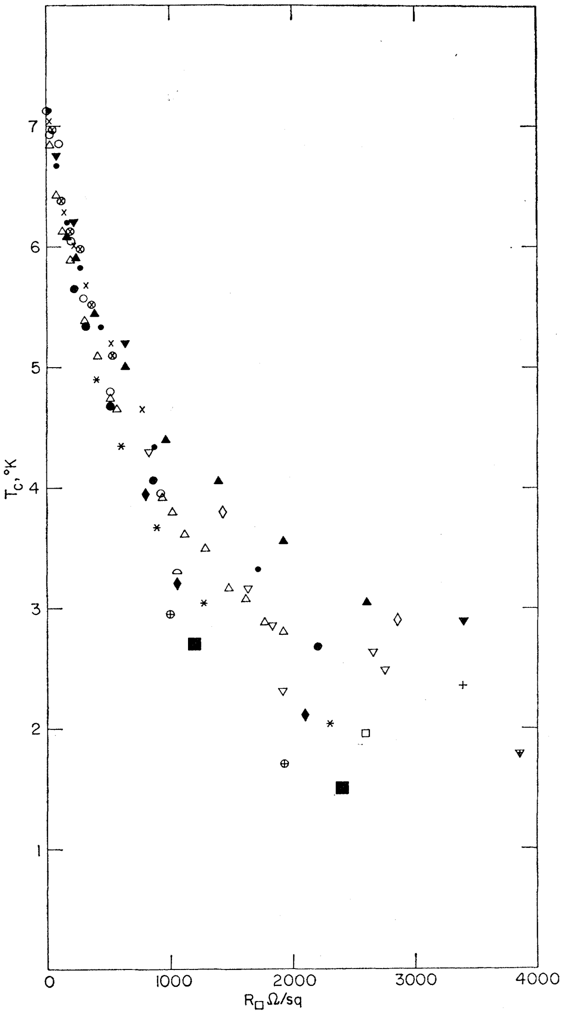

FIG. 5. T_c versus $R_\square$ where $R_\square$ is the resistance/sq area: ⊕, ■—Pb on Ge; +—Pb on Al_2O_3; ♦, ◊—Pb on Ge (deposited at room temperature); ∗—Bi on SiO; ∇, ⊗, ○, •, ●, △, ▲, ▼—Pb on SiO.

be discussed where the nature of the transition is discussed. It is clear that films deposited on previously deposited SiO, Ge, and Al_2O_3 can be made much thinner than films deposited on LiF or glass, immediately showing the important effect of the substrate. In Fig. 5, we show the data on a linear plot with T_c again plotted against $R_\square$; in Fig. 6, T_c is plotted against thickness for those runs where there are reasonable thickness values; and in Fig. 7, T_c is plotted against the resistivity ρ. It is clear that T_c correlates much better with $R_\square$ than with thickness or ρ. Although certainly not conclusive, there seems to be some indication that Pb on Ge has somewhat lower T_c's than Pb on SiO. This might certainly be expected from the different properties of the substrate. Figures 8 and 9 also show how both $R_\square$ and ρ vary with thickness. While the data show a lot of scatter, which undoubtedly shows that the nucleation conditions are delicate, it is interesting that in the ρ-versus-t plot some of the curves show kinks at about 50 Å that might indicate changes in the nature of the films. It is also clear that most runs show steep rises in ρ at about 10 Å, which must indicate where the film starts to break up. A few runs indicate rises near 30 or 40 Å.

When Pb is deposited on glass or LiF, the films do not become continuous until they are about 50–100 Å thick and T_c is not lowered nearly as much, even for very high resistances. This is easy to understand since the high R is probably due to poorly connected particles, and since the particles are relatively large they can stay superconducting individually and will have nearly the bulk T_c.

It is probably well to mention that, at least with SiO and Al_2O_3, it is not completely clear whether there is decomposition and, hence, what material is present when about 20 Å of this material is deposited onto the glass. At any rate, these materials provide a substrate on which films become continuous at only a few monolayers thickness.

B. Nature of Transition for Ultrathin Pb Films on Previously Deposited SiO or Ge

The resistance of the films in the transition region reflects the Curie-Weiss law for the pair conductivity above T_c.[10,11] The pair conductivity in two dimensions

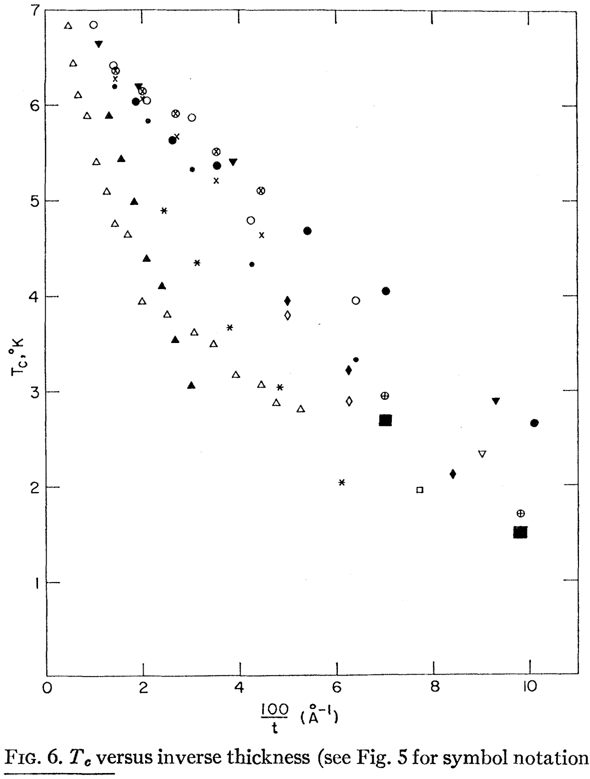

FIG. 6. T_c versus inverse thickness (see Fig. 5 for symbol notation).

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[10] R. E. Glover, Phys. Letters 25A, 542 (1967).

[11] M. Strongin, O. F. Kammerer, J. E. Crow, R. S. Thompson, and H. L. Fine, Phys. Rev. Letters 20, 922 (1968).

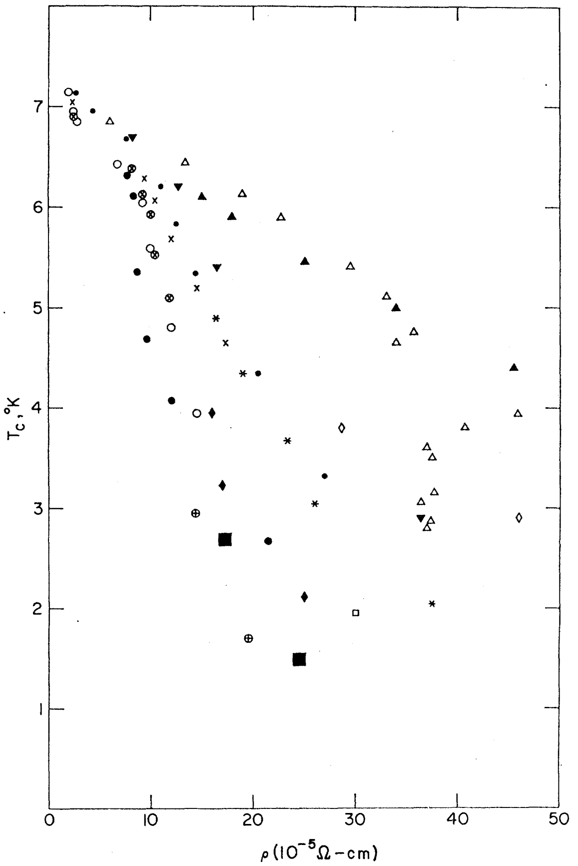

FIG. 7. T_c versus resistivity ρ (see Fig. 5 for symbol notation).

is given by $C/(T-T_c)$ above T_c, and is in this respect analogous to the magnetic susceptibility of a ferromagnet above its Curie point. However, the analogy is not exact since the susceptibility, in contrast to the conductivity, is a static property. When this pair conductivity is combined with the normal conductivity, the law for the resistance becomes $R/R_n=(1+\tau_0/\tau)^{-1}$, where $\tau=(T-T_c)/T_c$ and τ_0 is the value of τ at $R/R_n=0.5$. In Fig. 10, we show some typical transition curves for the very thin Pb films with greatly depressed T_c's. An important parameter of the theory of the pair conductivity is $\tau_0/R_\square$. According to the theory of Aslamazov and Larkin,[12] $\tau_0/R_\square$ is $1.5\times10^{-5}\ \Omega^{-1}$. We believe that this result is approximately valid for very dirty systems, but does not hold in general. This will be the subject of other work. It is clear from the results in Fig. 10 that the experimental curves are closely related to the computer fits which are represented by the solid lines. The values of $\tau_0/R_\square$ for the three curves average to about $1.3\times10^{-5}\ \Omega^{-1}$. Other values of $\tau_0/R_\square$ in similar films range from about $1\times10^{-5}\ \Omega^{-1}$ to about $2.5\times10^{-5}\ \Omega^{-1}$.

At small R/R_n, large deviations from the Curie-Weiss behavior are observed. We believe this is characteristic of critical behavior in these two-dimensional systems. In Ref. 11, we have given a simple estimate of the width of this region, which agrees fairly well with the present data and is equivalent to the Ginzburg criterion when applied to two dimensions. This result gives a width $\Delta T/T_c\approx\tau_0$.

Of course, in this regime where $R_\square$ is so extremely large and where the conduction mechanism starts to change (to be discussed in Sec. IV) the film is probably composed of many small metallic particles. Electrons probably pass from region to region through metallic filaments or tunnel through a nonconducting barrier. If the tunneling model is used, the expression for the effective mean free path would then involve a transmission coefficient. In this regime, we think the result of Abeles, Cohen, and Stowell applies, and one can write an effective l_{eff} given by $Md/(1-M)$, where M is the transmission coefficient and d is the particle diameter. Of course, this assumes that the particle boundaries are the main scattering mechanism, although a finite l in the particle can be easily included. They now attempted to show that the Ginzburg-Landau-Gorkov theory applies with l replaced by l_{eff}. We think this result is true, but it is not clear the proof of Abeles, Cohen, and Stowell[13] is meaningful, since the initial assumption of treating barriers as random scattering centers implies that the answer obtained will be analogous to the impurity result. In practice, we would expect small discontinuities in the order parameter for particles with

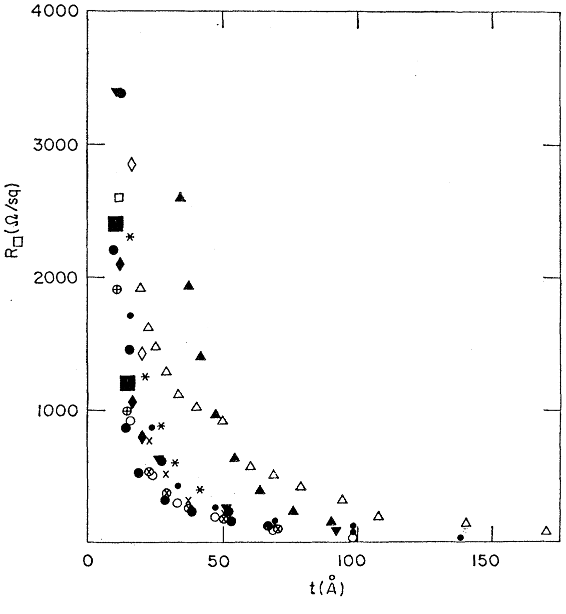

FIG. 8. Resistance $R_\square$ versus thickness (see Fig. 5 for symbol notation).

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[12] L. G. Aslamazov and A. I. Larkin, Phys. Letters **26A**, 238 (1968).

[13] B. Abeles, R. W. Cohen, and W. R. Stowell, Phys. Rev. Letters **18**, 902 (1967).

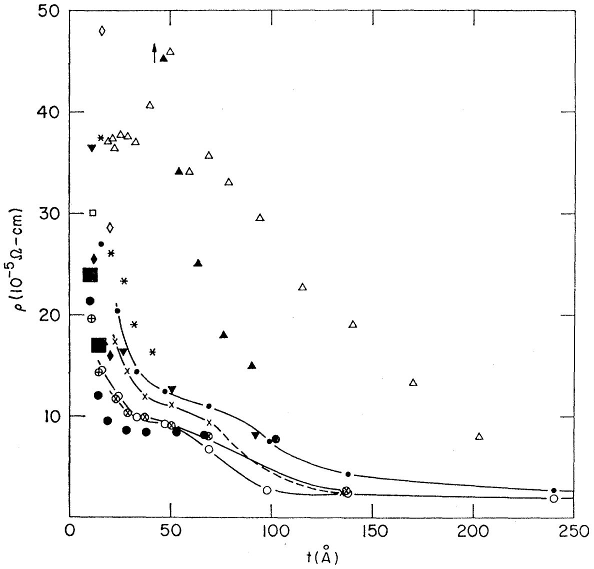

FIG. 9. Resistivity ρ versus thickness (see Fig. 5 for symbol notation).

slightly different T_c's. However, if the particle sizes are smaller than the coherence length, we would expect that the concept of an average wave function over this region is a good one. We think this is why the transition curves appear fairly ideal and are in reasonable agreement with the mean-field theory. For a typical film, we would estimate that M is not too small. The typical $R_\square$ of a film about 20 Å thick is about 3000 Ω/sq, which yields a resistivity of about 60×10^{-5} Ω cm. Hence, this would correspond to an approximate l in the 3 Å range if we use the result for Pb [14] that $\rho l=1.5\times10^{-11}$ Ω cm. Hence, the l of even the most disordered films with a measurable T_c is of the order of the interatomic spacing, as in a liquid metal. In some of the even higher-resistance films, near say 10 000 Ω/sq, l becomes even smaller than an interactomic spacing, and it is reasonable for the conduction mechanism to change from metallic to nonmetallic in this regime.

C. Nature of "Normal-State" Conduction Mechanism

Our films of Pb first show electrical continuity at near 10–15 Å thickness on about 20 Å of previously deposited SiO, Ge, or Al_2O_3. In this regime where continuity is first obtained, $R\geq 10\,000$ Ω/sq, superconductivity is essentially gone, and we find a normal-state resistance which goes as $R=R_0e^{+\langle E\rangle/kT}$, with an activation energy of about 2°K. Herman and Rhodin[15] have indicated that, when metallic films prepared at 100–300°K first become electrically continuous, they are composed of weakly coupled particles 10–20 Å in diameter, and a Coulomb activation energy $E_0\sim100$°K influences the conduction process. In view of the very much smaller activation energy that we observe, we assume particles, if they exist, are much more strongly coupled and it is likely that the energy levels or bands in the various regions are only slightly shifted from one another, so only the very small ~2°K activation energy, even in the thinnest films, is necessary for the electrons to hop or tunnel from one region to the next. Another model of the conduction mechanism that would be consistent with the normal-state conduction mechanism, and which would affect superconductivity, is severe local disorder at an atomic scale. Under certain conditions, this can lead to localization of the electronic states and would lead to the resistive behavior we observe in the highest-resistance films. The effects of extreme disorder and the condition for localization of electrons was discussed by Anderson[8] and by Mott.[9] Although the properties of electrons in this quasi-metallic state have just barely been theoretically investigated, it appears likely that when the electrons become localized superconductivity would be destroyed.

In Fig. 11, we show a representative transition, showing the film as initially deposited, with the nonmetallic conduction mechanism which goes as $R=R_0e^{+\langle E\rangle/kT}$. As more metal comes on, $\langle E\rangle$ gets smaller and a transition appears. Note that superconductivity coexists with a small $\langle E\rangle$ in the normal state.

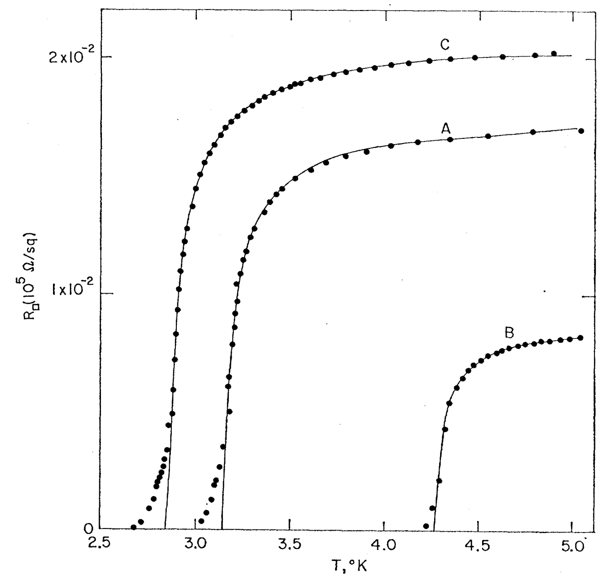

FIG. 10. Transition curves for thin Pb films on SiO. Curve A is film as initially deposited on ~20 Å of previously deposited SiO. Thickness of film A ~10 Å. Curve B is film after an additional 3 Å of Pb was deposited. Curve C is film after annealing overnight to N_2 temperature at pressure of about 5×10^{-6} Torr. Curve C was also taken at a factor of 10 less current than the usual measuring current of 3.5×10^{-6} A, and there was no change in behavior. Hence, at our measuring currents, the transitions are essentially current-independent. At 35×10^{-6} A, the T_c is shifted by ~0.03°K.

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[14] G. D. Cody and R. E. Miller, Phys. Rev. **173**, 481 (1968).

[15] D. S. Herman and T. N. Rhodin, J. Appl. Phys. **37**, 1594 (1966). Also, see C. A. Neugebauer and R. H. Wilson, in *Basic Problems in Thin Film Physics*, edited by Needermayer and Mayer (Vandenhoeck and Ruprecht, Göttingen, 1966).

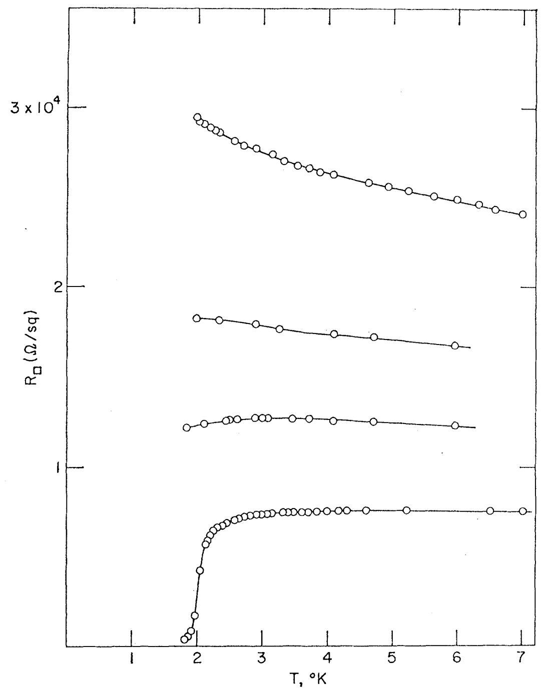

FIG. 11. Resistive behavior as Pb film is built up. First stages show nonmetallic conduction where film resistance increases as temperature is decreased. As more metal is deposited, the resistance decreases and metallic behavior and superconductivity appear. In the middle two curves, there is nonmetallic conduction in the normal state and the beginning of a superconducting transition. When the full transition appears, the film thickness, as determined by the Sloane thickness monitor, is usually from 10 to 20 Å.

D. Substrate Effects

It is clear that any understanding of the conduction mechanism and superconductivity in these ultrathin films must involve the details of what happens at the metal-substrate interface.

In general, the nucleation properties vary between different substrates. In Fig. 4, it is clear that nucleation on previously deposited LiF and glass leads to very different results than nucleation on previously deposited SiO, Al_2O_3, and Ge. It appears likely that "acceptor" levels could account for a significant movement of electrons from the metal into the substrate. Almost any estimate of the relative change in $\Delta T_c/T_c$ is of the order a/d, where the width of the surface region a is of the order of a few atomic spacings, several Å. Detailed results have been previously obtained by Glover.[16] An estimate of the size of this kind of effect is obtained where SiO and Ge are deposited over ultrathin films of Pb, Sn, Al, or Bi. The recent results we have taken in this regard are shown in Fig. 12. The initial rise is quite interesting and has been previously interpreted as evidence for surface interactions.[17] However, in the results shown in Fig. 12, the initial increase in T_c as about a monolayer of Ge is deposited is accompanied by a decrease in R. Hence, it appears that the initial rise in T_c is associated with a decrease in R due to the increased conductivity provided by the Ge layer. This effect of the initially decreased R yields a T_c rise that is consistent with the data showing T_c as a function of R in Figs. 4 and 5. Hence, at least in our case, there is no conclusive evidence for surface interactions increasing T_c. Finally, as more Ge is added, T_c starts dropping and then finally levels off at about 20 Å of Ge. In the regime where T_c starts going down as the overlay is added, R stays essentially constant. The drop in T_c is probably related to boundary effects where part of the electron gas is lost into the Ge.

E. Properties of Pb Films Nucleated on Glass and LiF

It is clear, from Figs. 4 and 13, that the T_c and resistance of Pb films nucleated on glass or previously deposited LiF are entirely different from the films nucleated on SiO, Ge, and Al_2O_3. These films can have extremely high resistance (near 50 000 Ω/sq), and, yet, there is still a T_c not too depressed from the bulk value.[18,19] The reason for this probably lies in the fact that the films do not become electrically continuous until the thickness of the film is from 50 to 100 Å. In this case, the particles are large enough so that each grain has its own T_c, and fluctuations are unimportant in any particular grain if $(H_c^2/8\pi)V>kT_c$. Hence, we postulate that the extremely high film resistance is

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[16] R. E. Glover, S. K. Gosh, and W. E. Daniels, Jr., in *Proceedings of the International Symposium on Basic Problems in Thin Film Physics* (Vandenhoeck and Ruprecht, Göttingen, 1965), p. 536.

[17] D. G. Naugle, Phys. Letters **25A**, 688 (1967).

[18] L. H. Palmer and M. Tinkham, Phys. Rev. **165**, 588 (1968), have studied the properties of ultrathin Pb films deposited on crystalline quartz substrates held at 78°K. They find that films with about 250 Ω/sq resistance have essentially the bulk value of T_c. Our results, shown in Fig. 4, for films deposited on glass are in agreement with these results. We have found that the T_c's of 100 Å films are quite similar when deposited onto quartz or glass substrates. This appears reasonable, since the films are many monolayers thick and the film is probably being deposited on adsorbed layers of gas or solid O_2, N_2, or H_2O. In Fig. 4, we show that, for resistances up to 800 Ω/sq, T_c is only depressed a few tenths of a °K. Films on previously deposited LiF also show only small changes in T_c, even for very high $R_\square$.

There is some apparent disagreement with Palmer and Tinkham on the film thicknesses. We would estimate film thicknesses of 50–100 Å when our films become electrically continuous, whereas Palmer and Tinkham estimate their films are 10 Å thick and electronically continuous. Professor Tinkham has emphasized to us that these numbers are nominal thicknesses as stated in their paper, and that larger thickness values are certainly possible. In estimating their thicknesses, Palmer and Tinkham have used the bulk resistivity at 78°K and Matthiessen's rule. While this procedure may give an approximate thickness value, it is probably better to assume that the film resistance at 78°K is related to the bulk value by the formula $\rho_F/\rho_B=1+\frac{3}{8}(l/d)(1-p)$, where p is a factor describing the fraction of electrons specularly scattered. [For a discussion, see K. L. Chopra, *Thin Film Phenomena* (McGraw-Hill Book Co., New York, 1969), pp. 351 and 360.] With these corrections and expected deviations from Matthiessen's rule expected in films, we can estimate thicknesses near 50 Å for the films of Palmer and Tinkham. Hence, our results are in general agreement with Palmer and Tinkham.

[19] R. S. Thompson, Myron Strongin, O. F. Kammerer, and J. E. Crow, Phys. Letters **29A**, 194 (1969).

tunneling resistance between the independently superconducting grains. Finally, below the T_c of the grains, there is pair tunneling and the resistance decreases. In contrast to the case of the thinner films, we find that the resistance never becomes zero in certain films. In Fig. 13, we see that there is an extremely large tail region, which would be expected from an analysis of the shape of the resistive transition as a function of the film resistance. It is not clear whether this is an intrinsic property associated with long-range order in these systems, or whether this transition is indicative of different particle sizes going superconducting. In these films where the particle size is of the order of ξ, we would not expect averaging of the order parameter, and these broad transitions may be indicative of different regions of the film. Even though the tail region is extremely large, it is worth mentioning that the steep part of the transition is actually narrower than that predicted from the Aslamazov-Larkin result that $\tau_0/R_\square \sim 1.5\times10^{-5}\ \Omega^{-1}$. We think that this result can be explained by the weak coupling between particles whose size is larger than the effective coherence length. This problem has been considered elsewhere.[19]

Although the transitions in Figs. 13 and 14 have not been studied in detail, we have studied transitions that are current-dependent even down to small current densities near 1 A/cm^2. This is in contrast to the case of the ultrathin films nucleated on SiO, Al$_2$O$_3$, or Ge, which are more strongly coupled and have higher critical currents. Actually, in these weakly coupled films on LiF or glass, $l_{\text{eff}}\sim0.1$ Å and the transmission coefficient is about 10^{-3}. Hence, the critical current density is about 10^4 A/cm^2 at 0°K. This explains why some of the transitions are fairly current sensitive, such as in Fig. 13. Another interesting feature of these transitions that should be mentioned is the annealing behavior. The irreversible nature of the temperature cycles is clear from Figs. 13 and 14. However, it is interesting to note that the annealing process can be seen to start near 7°K in Pb films, as can be seen from Fig. 13. The evidence for this is the sharp decrease in resistance as the temperature is increased (see also Fig. 14 path *B-C*). Of course, the higher *T* is raised the more significant is the annealing. It seems somewhat remarkable that observable atomic processes can occur near 7°K. It is conceivable that we are seeing movement in the surfaces of the Pb particles, and it seems reasonable that the activation energies for surface annealing are much smaller than for bulk motion.

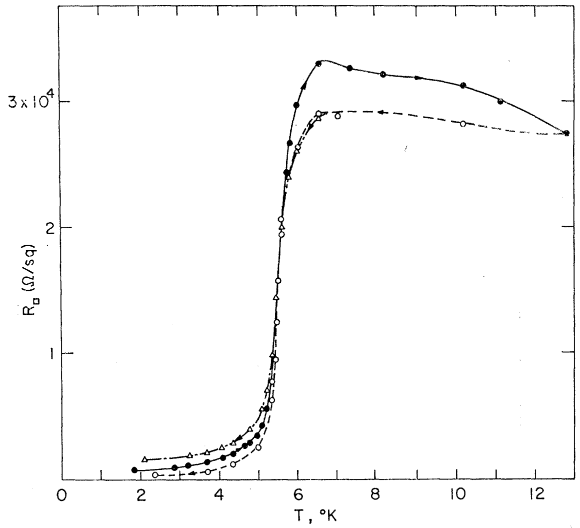

FIG. 13. Film resistance versus temperature for Pb deposited onto 20 Å of previously deposited LiF. Thickness of film is about 75 Å, width is about 0.45 mm. △—Initial decrease of temperature; measuring current is 4 μA. ●—Warming up; measuring current reduced to 0.1 μA; shows a change due to the decrease of current and then annealing starting near 7°K. ○—cooling down again; measuring current 0.1 μA. The AL theory predicts $\tau_0=\frac{1}{2}$, which gives a much broader transition than the curve shown here.

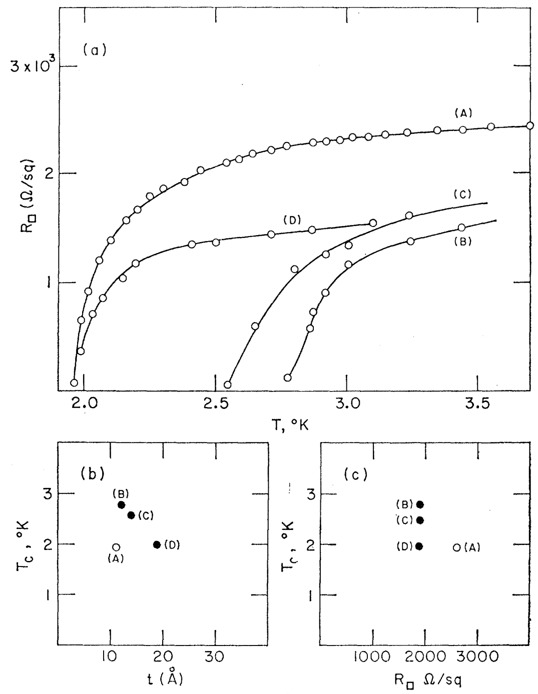

FIG. 12. Effect of Ge overlay on Pb film deposited on Ge: *A* film as deposited; *B, C, D*, effects of different amounts of Ge.

This annealing at such low temperatures means that our estimates of $R_\square$ may be somewhat low, since we cannot warm up significantly above the transition without reducing $R_\square$ by annealing.

F. Current Dependence of Transitions

The current dependence of the transitions in films on glass or previously deposited LiF, which are composed of weakly coupled grains, has been discussed above. In the ultrathin films discussed in the main section of the paper, the transitions are Ohmic for our small measuring currents. In general, we have run the

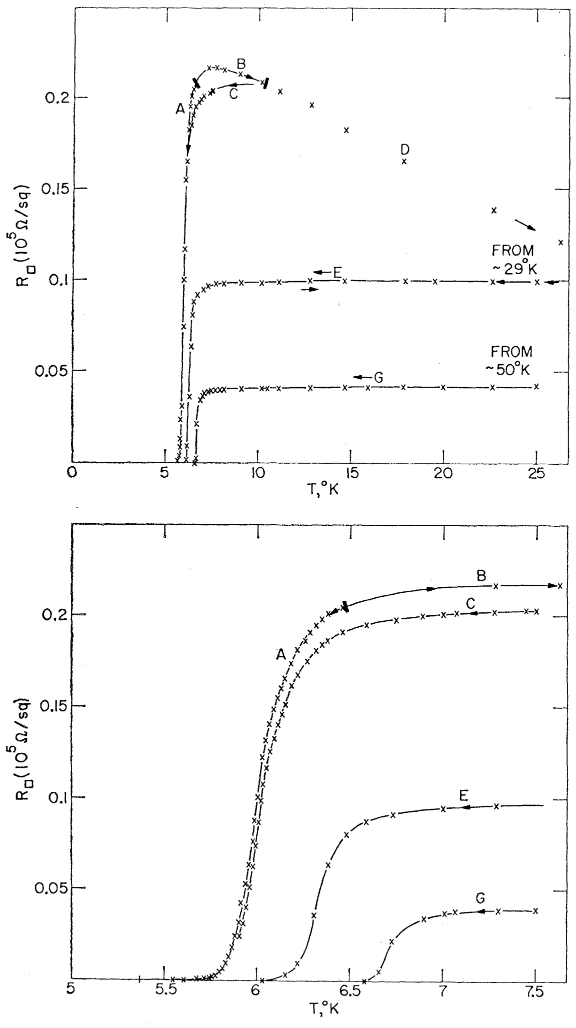

FIG. 14. Film resistance versus temperature for Pb deposited onto about 20 Å of previously deposited LiF. The effect of annealing to different temperatures is shown.

experiments on the thinner films with 3.5- to 1-μA measuring currents. These yield current densities normally around 200 A/cm^2 in the very thinnest films. This is many orders of magnitude smaller than the expected critical current densities, even close in to the transition temperature. Some experiments to investigate whether the transitions were current-independent are shown in Fig. 15. When the current changes from 3.5 to 0.35 μA, the resistive transition and T_c did not change within the experimental error. Upon raising the current to 35 μA, T_c shifted downwards a couple of hundredths of a degree. Hence, at our usual current of 3.5 μA we are measuring "true" transitions rather than critical current effects. Similar checks on other films gave similar results. Because of the high film resistance and the heating which occurs during the transition, we have found it difficult to make critical current measurements without providing enough heat to bring the film out of equilibrium with the thermometer.

IV. DISCUSSION

In Sec. III, we presented various observations on thin films. Now we would like to discuss the results and possible interpretations in more detail. The following factors which influence T_c will be considered in light of experiment: (a) the metal-insulator boundary; (b) changes in the phonon spectrum; (c) size quantization in small particles; (d) the appearance in the normal state of an energy gap and activated conduction; (e) fluctuations. We show that the last three effects are smaller than the observed changes in T_c, and that although phonon effects are very important for Al, they are not important for Pb. Thus, the first-mentioned effect probably dominates.

A. Substrate Effects

The most important influence on the critical temperature of thin Pb films seems to be the nature of the boundary region between the metal and the insulator. Clearly, the metal and substrate interact with each other, since we observe that the Pb nucleates differently on different substrates. Films which become continuous for only a few monolayers of deposition evidently interact more strongly with the substrate than those which only become continuous at about 75 Å. It seems reasonable to assume that electrons are lost from the film into the substrate in our ultrathin films. Glover[16] has already considered similar problems when discussing the effects of oxide coatings and charging.

The simplest, and probably the best, model for the effect on T_c of a different effective interaction between electrons in the surface layer was proposed by Cooper.[20] His result was that the usual formula for T_c applies, $T_c = 1.14\omega_D e^{-1/\lambda}$ with an average interaction strength $t\lambda = (t-a)\lambda_{\text{film}} + a\lambda_{\text{surface}}$, where a is the width of the

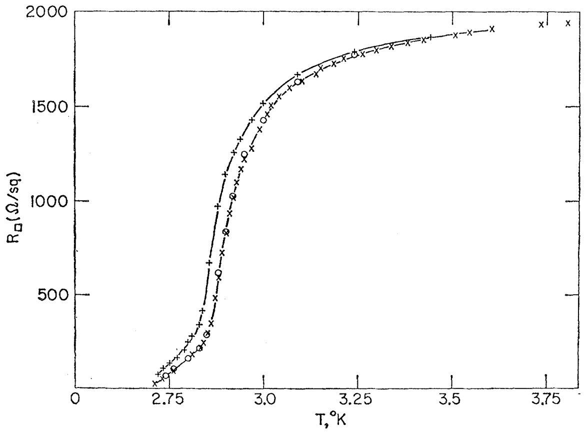

FIG. 15. Effect of measuring current for ~20 Å Pb film on SiO. × is 3.5 μA, ○ is 0.35 μA, and + is 35 μA.

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[20] L. N. Cooper, Phys. Rev. Letters **6**, 689 (1961); W. Silvert and L. N. Cooper, Phys. Rev. **141**, 336 (1966).

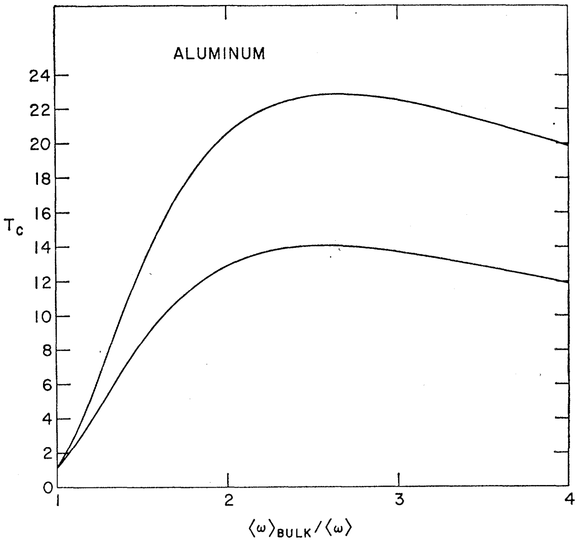

FIG. 16. Critical temperature of Al as a function of the lowering of the average phonon frequency according to the McMillan (upper curve) and Garland (lower curve) theories.

surface region ~10 Å. If $\lambda_{\mathrm{film}}=\lambda_{\mathrm{bulk}}>\lambda_{\mathrm{surface}}$, T_c will decrease as $\delta\tau=(T_{c0}-T_c)/T_{c0}\approx a/t$. In general, λ_{film} need not equal λ_{bulk}, but we will see in Sec. IV B that this is probably a good approximation for Pb. Then, $\lambda_{\mathrm{surface}}$ is probably less than λ_{film}, roughly by the ratio of the density of states which is lower near the surface $[\lambda=N(O)V]$.

Slight variations on this theme have been proposed by Shapoval[21] and by Naugle and Glover.[22] Shapoval, having the case of Al primarily in mind, assumed that the density of states in the film was increasing, giving an increase in T_c. We think that the increase of T_c observed in Al is primarily due to a change in the average phonon frequency and not to changes in the density of states, and that if disordered Al films of different thicknesses were prepared to maximize the phonon effect, then a decrease of T_c from its maximum value proportional to a/t would be observed.

Naugle and Glover have, in fact, performed such experiments on amorphous Bi and Ga and have obtained such a result. However, although they mentioned the interpretation we presented above, they preferred a slightly different one. They invoked de Gennes's[23] derivation of the boundary condition between a metal and an insulator and said that the resulting spatial change in the order parameter would give $\delta\tau\sim a/t$ also. Actually, the origin of the changed boundary condition is exactly the same as the change in $N(O)V$. Furthermore, de Gennes's derivation was for a very thick metal. When t decreases to the order of his extrapolation length $b\sim\xi_0 l/a$, the derivation ceases to be valid and the effect of spatial variation in the order parameter becomes negligible compared to the Cooper mechanism.

A glance at Fig. 6 reveals that, although the data generally approximates a/t with $a\approx 8$ Å, there is a good deal of scatter as might be expected due to differences in substrates and preparation conditions. The comparison of $\delta\tau$ with R in Fig. 5 shows less scatter, although we do not know why, with $\delta\tau\approx 5\times10^{-4}R_{\square}$. These numbers are in close agreement with previous work.[7]

B. Phonon Effects

Recently, McMillan[24] has presented a theory of T_c which says that the major change in T_c of various metals and alloys results from a change in the average phonon frequency $\langle\omega\rangle$. From his model, he predicted that metals with weak electron-phonon coupling and low T_c's, like Al, would show large increases in T_c on decreasing $\langle\omega\rangle$, whereas strong couplers, like Pb, would show small increases until the coupling constant $\lambda=N(O)\mathscr{I}^2/M\langle\omega^2\rangle$ reaches a value of around 2. His prediction is in qualitative agreement with experiment, although the high T_c's he predicted are never reached experimentally. For example, for Al his theory predicts a maximum T_c of ~23°K, whereas the maximum observed value is ~6°K, and for Pb his theory gives a maximum T_c of $\sim 9\frac{1}{2}$°K, whereas in the films T_c does not increase at all. Garland[25] has proposed a modifi-

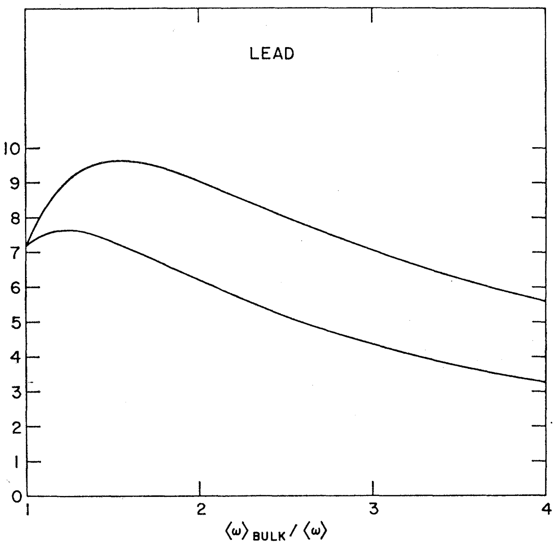

FIG. 17. Predictions of the same theories as Fig. 16 for Pb.

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[21] E. A. Shapoval, Zh. Eksperim. i Teor. Fiz. Pis'ma v Redaktsiyu **5**, 57 (1967) [English transl.: Soviet Phys.—JETP Letters **5**, 45 (1967)].

[22] D. G. Naugle and R. E. Glover, Phys. Letters **28A**, 611 (1969).

[23] P. G. de Gennes, *Superconductivity of Metals and Alloys* (W. A. Benjamin, Inc., New York, 1966), p. 229.

[24] W. L. McMillan, Phys. Rev. **167**, 331 (1968).

[25] J. W. Garland, K. H. Bennemann, and F. M. Mueller, Phys. Rev. Letters **21**, 1315 (1968). The actual formula we plot is given in Ref. 25. We set ω_0 in the formula equal to the Debye frequency for definiteness, since this choice gives good agreement with Ref. 23 for bulk Ni and with the values of the factor A given in the present reference.

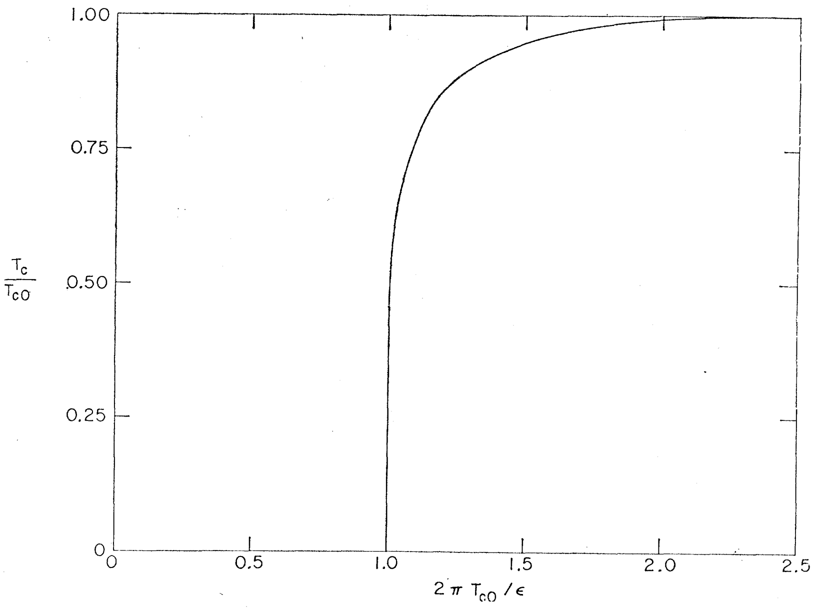

FIG. 18. Transition temperature of a small particle as a function of level spacing ϵ as calculated from Eqs. (2) and (3).

cation in McMillan's theory for films and amorphous structures to take into account the change in the distribution of frequency as well as $\langle\omega\rangle$. The results of his theory for Al and Pb together with that of McMillan are shown on Figs. 16 and 17. Garland's theory still predicts a maximum T_c for Al of $\sim$15°K, which is too large, and an increase in T_c of $\sim\frac{1}{2}$°K for Pb. The work of Chen, Chen, Leslie, and Smith[26] has shown that large changes in $\langle\omega\rangle$, of the order of a factor of 2, do, indeed, occur in amorphous materials, and the results appear to be in good agreement with Garland's theory. From the figure, we can see that, although the effects of changes in $\langle\omega\rangle$ in Al are very large, for Pb changes in $\langle\omega\rangle$ probably change T_c by less than 1°K. The decrease of T_c due to substrate effects probably results from a decrease in $N(O)\mathcal{I}^2$ which McMillan found to be approximately constant for bulk polyvalent nontransition metals, but which need not be constant in general.

C. Size Quantization in Small Particles

In the initial stages of growth, metal films are thought to consist of isolated particles with gaps or barriers between them. At least nucleation studies of films which become continuous only when fairly thick show such a behavior. Therefore, one might think that a nearly isolated particle structure might affect T_c. Anderson has already indicated that superconductivity should not be possible if the number of electrons were $\sim10^3$, so that the energy level spacing ϵ becomes as large as the superconducting energy gap $\Delta(T=0)$. He further expected that particles with $\sim10^4$–10^5 electrons should begin to be affected. In this section, we will calculate explicitly the effect on the BCS equation of the finite level spacing in particles.

The BCS equation for T_c may be written as

$$1=\pi T_c\Omega^{-1}\sum_{\omega,k}^{\omega_D} V(\omega^2+\xi_k^2)^{-1},$$

where ξ_k is the energy level of the kth pair state measured from the Fermi level, $\omega=(2m+1)\pi T_c$, Ω is the particle volume, and V is the effective BCS electron-electron interaction which vanishes for $\omega>\omega_D$. We assume a uniform level spacing near the Fermi level E_F with spin degeneracy: $\epsilon=1/N(O)\Omega=4E_F/3N\ll\omega_D$. Considering the most favorable case of an even number of particles so the pairing may be complete, the Fermi level falls half-way between the last occupied and the first empty level at $T=0$, so ξ_k has the form $\frac{1}{2}(2n+1)\epsilon$. It is convenient to perform the sum in the BCS equation over the variables with the smaller spacing. If $\epsilon<2\pi T$, we sum first over ξ_k and obtain

$$[N(O)V]^{-1}=\pi T_c\sum_{\omega}\omega^{-1}\tanh(\pi\omega/\epsilon). \qquad (1)$$

The difference between this equation and the usual BCS result is the factor $\tanh(\pi\omega/\epsilon)$, which goes to unity when the level spacing goes to zero. Writing $N(O)V$ in terms of the bulk critical temperatures T_{c0} we get

$$\ln(T_c/T_{c0})=\sum_{m\geq 0}\left(\frac{2}{2m+1}\right)\times\left\{\tanh\left[\left(\frac{\pi}{2}\right)\frac{(2m+1)2\pi T_c}{\epsilon}\right]-1\right\}. \qquad (2)$$

The sum over m converges rapidly, and it usually

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[26] T. T. Chen, J. T. Chen, J. D. Leslie, and H. J. T. Smith, Phys. Rev. Letters 22, 526 (1969).

suffices to evaluate only the first term. In the opposite limit $2\pi T_c < \epsilon$, we perform the sum over ω first:

$$\ln \epsilon/2\pi T_c = \sum_{n\geq 0} \left(\frac{2}{2n+1}\right)\left[\tanh\left(\frac{\pi}{2}\frac{(2n+1)\epsilon}{2\pi T}\right)-1\right]. \quad (3)$$

This result follows directly from the symmetry in the sums over m and n with $2\pi T_c$ and ϵ interchanged. The detailed dependence of T_c on ϵ is shown in Fig. 18. The drop in T_c is exponential in ϵ with superconductivity vanishing at $\epsilon = 2\pi T_{c0}$. From this relation, we estimate the critical diameter for the disappearance of superconductivity in an isolated particle of Pb to be about 22 Å, containing about 750 electrons, in agreement with Anderson's[27] estimate. Of course, as has been pointed out by Kubo,[28] the use of Fermi statistics valid for an infinite system is not justified when $\epsilon < 2\pi T_c$, and one should worry mostly about the character of the first excited state. Such considerations will not essentially change our result: the value of the critical size, and the very rapid drop in T_c, such that particles with even twice the critical number of electrons have essentially $T_c = T_{c0}$.

Markowitz[29] has considered an electrostatic fluctuation effect which he said would affect even particles as large as several hundred Å. However, he neglected screening. Although one should definitely consider the effects of change fluctuation in small weakly interacting particles, we think that the phase fluctuations he considered will not effect T_c appreciably, since any superconducting charge fluctuations are easily cancelled by normal electrons near T_c. Caroli and Maki[30] have shown that fluctuations in the order parameter are not coupled to charge fluctuations in the limit of vanishing order parameter. We would expect superconductivity to be unaffected purely by the finite size in the 50 Å particles of Giaver and Zeller[31] which contain about 10 times the critical number of electrons, in agreement with their observations.

Parmenter[32] has also considered the influence of finite size on superconductivity. In contrast to our results, he obtained an enhancement of T_c. Like Shapoval, he was looking for a mechanism for the increase of T_c observed in Al. We believe his result is a consequence of his assumption that energy levels exactly at the Fermi surface can contribute to the interaction. If we had summed over even-integer level spacings instead of odd-integer spacing, the $\tanh(\pi\omega/\epsilon)$ in our modified BCS equation would have been replaced by $\coth(\pi\omega/\epsilon)$, leading to spurious enhancement effect. Actually, an energy level falls at ϵ_F, for equal level spacing, only for a particle with an odd number of electrons, and the odd electron does not participate in pairing. Furthermore, the Fermi level concept is no no longer valid when $\epsilon \sim 2\pi T_c$, and the statistics and excitation levels of a system with a small number of particles must be considered. The changes in statistics are not important in deciding if superconductivity exists at $T=0$. Since there are no excitations of the system, we may set the right-hand side of Eq. (3) equal to zero. The actual level distribution will be important, but, since the left-hand side of Eq. (3) comes from a sum over many levels, we again expect a vanishing of superconductivity when the average level spacing $\epsilon \approx 2\pi T_{c0}$. Actually, the odd system will be less favorable than the even one because of the unpaired spin of the extra electron which can cause spin scattering.

If the energy level spacings of finite size particles were affecting the T_c of our Pb films, one should see an exponential dependence of the normal-state conductivity on t with an activation energy of about $\sim 2\pi T_{c0} = 45°\text{K}$. Actually, the maximum activation energy observed is about 2°, which would imply a level spacing so small as to have no effect on T_c. Further, we estimate from the resistance that the transmission coefficient between particles is about ~0.1, so that the probability of an electron going into one of the six neighboring particles is of the order unity; the particles are not at all isolated. In Sec. IV D, we will investigate what effect the observed normal-state activation energy might have on T_c for a well-connected system.

D. Normal-State Activation Energy

The normal-state conductivity in our ultrathin films was observed not to be constant, but to depend exponentially on T with an activation energy A with a maximum value of ~2° when superconductivity disappears. In this section, we evaluate, in the spirit of Sec. IV C, what effect A of this order has on T_c. We start with the same BCS equation, but let the spectrum of ξ be continuous except for a gap of width $2A$ around E_F. For simplicity, we assume a constant density of states $N(O)$ outside the gap:

$$1 = \pi T_c N(O) V \int_A^\infty d\xi \sum_\omega^{\omega_D} \frac{1}{\omega^2+\xi^2+\Delta^2}. \quad (4)$$

To obtain T_c, we let $\Delta \rightarrow 0$.

If $A < \pi T_c$, we do the integration before the sum:

$$\ln\frac{T_{c0}}{T_c} = \frac{4}{\pi}\sum_{n\geq 0}\frac{1}{2n+1}\tan^{-1}\frac{A}{(2n+1)\pi T_c} \approx \frac{A}{2T_c}. \quad (5)$$

For small changes in T_c,

$$T_{c0} - T_c \approx \tfrac{1}{2}A.$$

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[27] P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959).

[28] R. Kubo, J. Phys. Soc. Japan **17**, 975 (1962); Solid State Phys. **1**, 61 (1968).

[29] D. Markowitz, J. Appl. Phys. 3, 199 (1967).

[30] C. Caroli and K. Maki, Phys. Rev. **159**, 306 (1967).

[31] I. Giaver and H. R. Zeller, Phys. Rev. Letters **20**, 1504 (1968).

[32] R. H. Parmenter, Phys. Rev. **166**, 392 (1968).

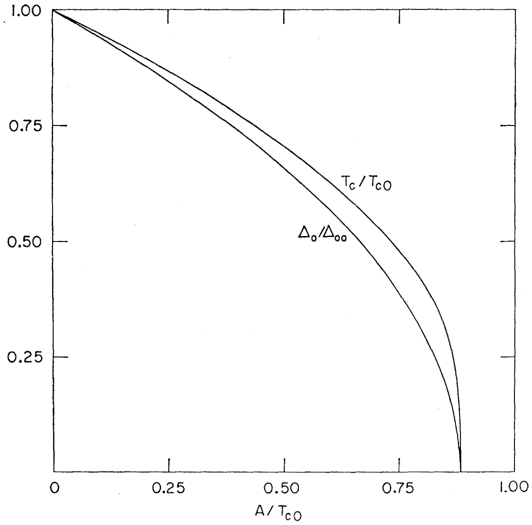

FIG. 19. Transition temperature and zero-temperature gap for a metal with a normal-state activation energy A as calculated from Eqs. (5)–(7).

For bigger changes in T_c, when $A>\pi T_c$, we do the frequency sum first:

$$\ln\frac{2A}{\Delta_0}=\int_A^{\omega_D}\frac{d\epsilon}{\epsilon}\left(\tanh\frac{\epsilon}{2T}-1\right)\approx\frac{2T_c}{A}e^{-A/T_c}. \qquad (6)$$

Superconductivity vanishes when $A=\frac{1}{2}\Delta_0=\pi T_{c0}/2\gamma=0.88T_{c0}$. The value of Δ at zero temperature is also easily obtained:

$$\frac{1}{N(O)V}=\int_A^{\omega_D}\frac{d\xi}{\xi^2+\Delta^2}=\ln\frac{2\omega_D}{A+(A^2+\Delta^2)^{1/2}},$$
$$\Delta_0=A+(A^2+\Delta^2)^{1/2}, \qquad (7)$$
$$\Delta^2=\Delta_0(\Delta_0-2A).$$

Δ goes to zero when T_c goes to zero at $A=\frac{1}{2}\Delta_0$. A plot of T_c and Δ as a function A is given in Fig. 19.

For our films, the maximum shift of T_c obtained from this effect is about 1°.

E. Fluctuations

The T_c measured from the Curie-Weiss-Aslamazov-Larkin asymptotic behavior of the resistance can be different from the T_{c0} in the absence of fluctuations by approximately $\tau_0 T_c$. We obtained this estimate previously[11] by comparing the fluctuation energy kT with the coupling energy $(h/e)J_c$ between different regions of area equal to the coherence length squared in the film thickness, or with the free energy in such regions. We now give a slightly more fundamental derivation of this result, which is equivalent to the others and is the basis of their validity. We calculate the free energy in the presence of fluctuations and single out a change in T_c. The free energy F as a function of the order parameter Δ is given for small Δ by

$$F(\Delta)=N(O)\{[\tau+(\xi q)^2]\Delta^2+\alpha\Delta^4\},$$

where $N(O)$ is the density of states, $\tau=(T-T_{c0})/T_{c0}$, ξ is the coherence length which for dirty materials is $(\pi D/8T)^{1/2}=0.85(\xi_0 l)^{1/2}$, D is the diffusion constant $\frac{1}{3}vl$, v is the Fermi velocity, l is the mean free path, ξ_0 is the BCS coherence length, iq is the derivative of Δ, and $2\alpha=1.05/(\pi T)^2$. If fluctuations are ignored, Δ is a constant Δ_0, whose value is found by minimizing $F(\Delta)$, $\Delta_0^2=-\tau/2\alpha$.

Following Rice,[33] we add a fluctuating component Δ_q to Δ_0 and expand to second order in Δ_q. First-order fluctuations vanish when the spatial average is taken:

$$F(\Delta_0,\Delta_q)=N(O)\{\tau\Delta_0^2+\alpha\Delta_0^4+[\tau+6\alpha\Delta_0^2+(\xi q)^2]\Delta_q^2\}.$$

We ignore phase fluctuations, since their effect cannot be interpreted as a simple shift in T_c. We form the partition function Z

$$Z=\prod_q\int_0^\infty d\Delta_q^2 e^{-\beta F},$$

$$Z=\prod_q\frac{1}{\beta N(O)}\frac{1}{\tau+6\alpha\Delta_0^2+(\xi q)^2}e^{-\beta F(\Delta_0)}.$$

To find Δ_0, we minimize the free energy $F=T\ln Z$ with respect to Δ_0:

$$0=\beta N(O)(\tau+2\alpha\Delta_0^2)+\int\frac{d^nq}{(2\pi)^n}\frac{6\alpha}{\tau+6\alpha\Delta_0^2+(\xi q)^2}.$$

For a film of thickness $d<\xi/|\tau|^{1/2}$, the momentum element becomes

$$\frac{1}{d}\int\frac{d^2q}{(2\pi)^2}.$$

The correction to the critical temperature is obtained from the last term

$$\delta\tau=\frac{\delta T_c}{T_{c0}}=\frac{1}{N(O)Dd}\frac{4}{\pi^4}1.05\int\frac{d(\xi q)^2}{-2\tau+(\xi q)^2}.$$

The constants in front of the integral are just $2.1\tau_0$. Unfortunately, the integral is logarithmically divergent, so one must choose a cutoff for large ξq. A very reasonable choice, which gives a simple temperature-independent shift of T_c, is to take the values at which the two terms in the denominator are equal, which would have been the natural cutoff if the denominator had been raised to a higher power. With the cutoff, we obtain $\delta\tau=1.5\tau_0$.

If one does not accept this value for the cutoff, the maximum q at which one could use the expression would be $(\xi q)^2\approx 1$, since for large $(\xi q)^2$ this expression is not

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[33] T. M. Rice, Phys. Rev. **140**, A1889 (1965).

valid and higher powers of $(\xi q)^2$ must be included. (Unfortunately, the inclusion of these higher powers does not actually remove the divergence problem.) With this larger cutoff, one obtains

$$\delta\tau = 2.1\tau_0 \ln[(T_{c0}+2\delta T_c)/2\delta T_c].$$

Fortunately, for our purposes, the two estimates are about the same if the shift of T_c is significant. They are exactly the same if $\delta\tau=\frac{1}{2}$, which requires $\tau_0=\frac{1}{3}$ or $R_\square = 2.2\times10^4\ \Omega$. This value of the resistance is more than an order of magnitude larger than that where the $\delta\tau$ in our films is observed to be $\frac{1}{2}$. For our dirtiest films $R_\square \sim 3\times10^3\ \Omega$, $\tau_0 \sim 0.05$, and the two estimates give a shift of T_c due to fluctuations $\delta T_c = \frac{1}{2}°$ and $\delta T_c = 1°$.

V. CONCLUSION

We have measured the transition temperature for Pb films of varying thickness and found it to decrease substantially as the thickness decreases, vanishing for film thicknesses of the order of 10 Å. We have discussed various influences on T_c which may occur in very thin films and decided that the most important was interaction of the metal film with the substrate. Our understanding of the nature of these thin films is still rather qualitative. Further experiments, particularly tunneling experiments to extract the phonon spectrum and electron-phonon coupling strength, would add a great deal to our understanding.

ACKNOWLEDGMENTS

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Superconducting Surface Sheath of a Semi-Infinite Half-Space and its Instability due to Fluctuations*

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The surface sheath of a semi-infinite half-space for applied magnetic fields $H_0 \geq H_{c2}$ and Ginzburg-Landau κ values ≥ 0.707 was investigated with regard to its current-carrying capacity and stability. It is found that infinitesimally three-dimensional fluctuations of the order parameter and the vector potential make the surface sheath unstable and the total stable transport current zero.

I. INTRODUCTION

IN recent years, Abrikosov,[1] Park,[2] Christiansen,[3] and Christiansen and Smith[4] have calculated for certain specific cases the maximum transport current of the surface sheath of a semi-infinite half-space. Their calculations are based on the Ginzburg-Landau (GL) equations, and the maximum current (or critical current) is defined as that current at which solutions of the GL equations cease to exist. Experiments seem to indicate that these theoretical values are orders of magnitude too large.[5–10]

A different approach was taken in Ref. 11. In order to obtain reasonable agreement with experiments, the critical current J_c was defined as that current which raises the total energy of the superconducting specimen to that of the normal state.[11,12] Various experimenters[5–8] seem to get fair agreement with this definition of the critical current. The critical current, however, is theoretically size-dependent. For example, J_c is proportional to $R^{-1/2}$, where R is the radius of a long cylinder, and the critical current is that which circulates on the surface around the axis of a cylinder when the applied field H_0 is parallel to the axis of the cylinder. The $R^{-1/2}$ dependence has been questioned by a number of

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