

Deviations of the Equilibrium Order Parameter from Mean Field Theory in Superconducting Aluminum Films*

K. E. Gray and I. Schuller†

Argonne National Laboratory, Argonne, Illinois

(Received January 10, 1977)

Superconducting aluminum films show deviations from the mean field theory prediction of the temperature dependence of the equilibrium order parameter close to T_c . We show that these deviations can be explained by intrinsic variations in T_c from grain to grain. When the coherence length is larger than the grain size, the deviations will occur over a much smaller temperature interval than the intrinsic variations because of the proximity effect.

1. INTRODUCTION

Mean field theory (MFT) seems to describe superconductivity as well as or better than other systems undergoing a second-order phase transition. Therefore it is of interest to examine carefully any deviations from MFT in superconductors to better understand the limits of its validity. The most fundamental concept in MFT is the order parameter. In superconductivity the conduction electrons are ordered into bound pairs, called Cooper pairs, at the Fermi energy. The order parameter—the fractional number of conduction electrons bound in Cooper pairs—has been shown by Gor'kov¹ to be equivalent to the equilibrium energy gap in the excitation spectrum near the transition temperature T_c . We therefore expect the temperature dependence of the energy gap to follow the MFT dependence for the order parameter, i.e., $(T_c - T)^{1/2}$ close to T_c , which coincides with the prediction of the microscopic theory.²

There are a variety of methods of measuring the energy gap in superconductors, but one of the simplest and most accurate is by electron

*Work performed under the auspices of the U.S. Energy Research and Development Administration.

†Present address: Department of Physics, UCLA, Los Angeles, California.

tunneling. This method is especially good close to T_c where the gap is small. Previous tunneling measurements³⁻⁵ of the temperature dependence of the gap in thin films have shown reasonably good agreement with the BCS theory², except for deviations close to T_c . In one experiment,³ these are crucial since they occur over the temperature range of the measured divergence of the relaxation time of the order parameter, and make comparison with theory difficult.

On the other hand, the magnetization of small superconducting particles is proportional to the square of the order parameter. Such magnetization measurements⁶ are consistent with MFT, and in small particles show a predictable deviation near T_c due to fluctuations. It would seem reasonable to look to fluctuations as an explanation of the deviations in the tunneling measurements, since the most careful measurements near T_c were done in aluminum films with grain sizes comparable to the particle sizes used in the magnetization study. However, the important difference, which makes such a comparison of dubious merit, is that the grains in the films of the tunnel junctions are electrically continuous, whereas in the magnetization measurements the fine particles were electrically isolated (by an oxide layer and a minimal area of contact). The magnetization measurements therefore satisfy the zero-dimensional criterion of isolated particles smaller than a coherence length. However, in the thin films, the order parameters in the individual grains are correlated with each other by the proximity effect over a distance of the superconducting coherence length. In addition, it can be shown that fluctuation effects in two-dimensional thin films yield deviations which are much too small, so we must look elsewhere for an explanation of the tunneling experiments.

In an effort to explain this discrepancy in the tunneling measurements, and with the hope of improving the relaxation time measurements, we have undertaken a careful study of the temperature dependence of the gap near T_c in tunnel junctions. We prepare aluminum films with different grain sizes by introducing oxygen during evaporation.⁷ We find a simple model, without fluctuations, which explains the discrepancies with MFT in films, and gives an alternative explanation of the transition temperature widths in very dirty ($\rho \geq 10^3 - 10^4 \mu\Omega \text{ cm}$) granular aluminum films.⁷ We also find that in very clean films, the deviations from MFT are over a much smaller temperature region near T_c , allowing a definitive measurement of the order parameter relaxation time.⁸

2. EXPERIMENTAL

The aluminum films studied were prepared by electron beam evaporation onto glass microscope slides. Evaporation in a standard

diffusion-pumped vacuum system yields a moderately dirty film with about 400-Å-diameter grains. Dirty, small-grain films are produced by admitting oxygen into the chamber during evaporation. Previous work⁷ has shown that grain size, residual resistivity, and superconducting transition temperature are related in a regular, reproducible manner and depend on the oxygen content. Clean films are produced in a 24-in.-diameter vacuum system using a liquid-nitrogen-cooled titanium sublimation pump and ion pump. This provided a background pressure during evaporation of about 3×10^{-7} Torr, with a rate of 150–200 Å/sec. The electron mean free path in films made this way was size-limited even at 1 μm thickness, although films used in this study were about 1000 Å thick.

After evaporation of the aluminum, the slide is removed from the chamber and exposed to air for about 15 min to provide an oxide insulator. Tin or lead is then evaporated to form the counter electrode of the tunnel junction. It is important to use a counter electrode with a much higher T_c than aluminum, so that the energy gap structure in the current-voltage curves of the tunnel junction remain sharp right up to T_c of the aluminum. In such a manner, structure as small as 0.5 μV can be measured. Using two identical superconductors or a normal metal to superconductor junction would limit the resolution such that the present experiment would be impossible.⁹

The I - V characteristics of the junctions were plotted on an x - y recorder, with the region near the voltage corresponding to the energy gap in the lead or tin expanded greatly. There is some ambiguity in the determination of the aluminum energy gap Δ from the curves, but we found that the different criteria^{4,10} only affected the slope of Δ^2 versus T in the MFT region. Within experimental error, the deviation from MFT occurred over the same temperature interval, since the disappearance of structure in the I - V curve due to superconductivity in the aluminum is unambiguous. Figure 1 shows Δ^2 versus temperature for three representative films. The MFT and BCS prediction is a straight line, which has been fitted to the data in the graph. Note that in a plot of Δ^2 the deviations from MFT appear much smaller than in a plot of the experimental data for Δ versus T . It should also be pointed out that covering the edges of the aluminum film of Fig. 1b with an insulator had no effect on the deviations shown. Also, in one of the clean films, the deviation of 1 mK was essentially unchanged upon application of a parallel magnetic field, which lowered T_c by 5 mK.

That the deviations were smaller for a much cleaner film (Fig. 1a) was not at all surprising. However, the film of Fig. 1c, whose mean free path is almost six times shorter and has much smaller grain size than that of Fig. 1b, shows deviations that are the same as or smaller than those of Fig. 1b. This crucial observation is hard to understand in terms of fluctuations.

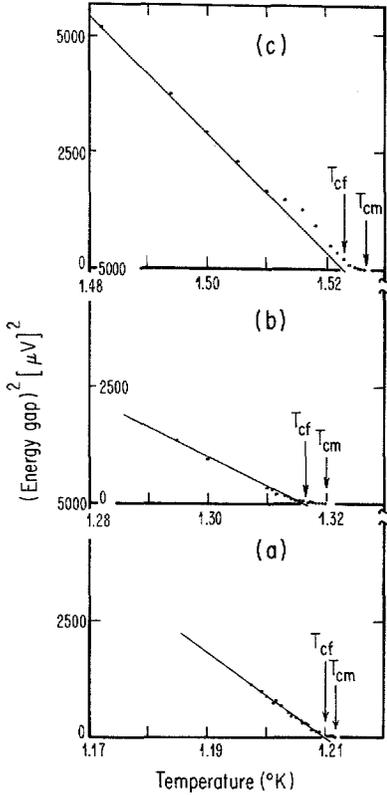


Fig. 1. A plot of Δ^2 versus temperature for three representative films: (a) clean, $\rho_N \sim 0.7 \mu\Omega \text{ cm}$; (b) average, $\rho_N \sim 1.7 \mu\Omega \text{ cm}$; (c) dirty, $\rho_N \sim 10 \mu\Omega \text{ cm}$. The extrapolations of the solid lines, which are the best fits to MFT, determine T_{cf} , and T_{cm} is the highest temperature for which structure in the $I-V$ curve due to superconductivity in the aluminum is found.

3. DISCUSSION

The essence of our model to explain these results is that the deviations in the order parameter from MFT can be explained by an inhomogeneous local transition temperature $T_{cf}(r)$ which is *static*, i.e., not fluctuating. We further propose that $T_{cf}(r)$ has a distribution in the range $T_{cf} \pm \Delta T_{cf}$, where T_{cf} is the average value and the width ΔT_{cf} is $T_{cm} - T_{cf}$. The maximum temperature for which a gap is measured is T_{cm} (see Fig. 1). In spite of the fact that each grain may have its own intrinsic transition temperature T_{ci} , we assume that $T_{cf}(r)$ can only vary on the scale of the coherence length ξ because of the proximity effect. The individual grains will have different T_{ci} because the size, strains, and impurity content (mostly oxygen) will vary from grain to grain. If there are many grains N in the coherence volume ξ^3 , then the width of the distribution of local transition temperature ΔT_{cf} is narrower than the width of intrinsic transition temperature ΔT_{ci} by a factor

$N^{1/2}$. This factor is strictly true for a Gaussian distribution and we assume it is approximately valid for our model.

To test this model, we need to know ΔT_{ci} and N , since ΔT_{cf} is known from the tunneling measurements. It would be difficult to measure ΔT_{ci} directly, but we can make a rather coarse estimate. For dirty aluminum films, but with normal resistivity ρ_N less than about $10^{-2} \Omega \text{ cm}$, T_{cf} is always greater than the clean, bulk transition temperature $T_{cb} = 1.18 \text{ K}$. We therefore use T_{cb} as the lower limit of the intrinsic transition temperature T_{ci} . Since the average of T_{ci} must be the same as the average for the film T_{cf} , we can write $\Delta T_{ci} \approx T_{cf} - T_{cb}$. The number of grains in a coherence volume can be estimated from the average grain size and the coherence length. The average grain size as a function of normal resistivity has been measured previously⁷ using transmission electron microscopy, but determination of the coherence length ξ is not so straightforward. Although ξ is defined at all temperatures by $\xi^2 = \hbar^2/2m^*|\alpha|$, where α is the coefficient of the quadratic term in the Ginzburg–Landau free energy expression, it diverges at T_c . Now, T_{ci} varies from grain to grain, so that at a given temperature in the range of ΔT_{ci} some of the grains will have very large ξ . However, if the grain size is much smaller than ξ , these would have a small effect on the spatial variation of the order parameter anyway. Hence the spatial variation of $T_{cf}(r)$ will depend instead on the large number of grains with $\xi \sim \xi(0)$. Therefore we use the zero-temperature Ginzburg–Landau coherence length $\xi(0) \sim 0.84(\xi_0 l)^{1/2}$, where ξ_0 is the BCS coherence length. The electron mean free path l can be inferred from the normal-state resistivity (for $\rho_N \geq 10^{-3} \Omega \text{ cm}$, this may not be useful, because thick oxide layers on the surface of the grains may dictate a different conductivity mechanism, e.g., tunneling between grains).

We are now in a position to put the model to the test of our experimental results. In Table I, we show various measured and calculated parameters for our films as well as films studied elsewhere.^{7,11} For the dirtiest films ($\rho_N \geq 45 \mu\Omega \text{ cm}$), we assume ΔT_{cf} to be the resistive transition width measured in Ref. 7. We show the measured resistivity ρ_N and the calculated electron mean free path l obtained from $\rho_N l = 1.2 \times 10^{-11} \Omega \text{ cm}^2$, which is valid for polycrystalline aluminum films.¹² The coherence length $\xi(0)$ is determined using l and $\xi_0 = 16,000 \text{ \AA}$. The average grain size $\langle D \rangle$ comes from Ref. 7. The number of grains per coherence volume N is given by $[\xi(0)/\langle D \rangle]^3$. It is then a simple matter to multiply the measured ΔT_{cf} by $N^{1/2}$ to obtain a calculated value for ΔT_{ci} to compare with the measured $T_{cf} - T_{cb}$. This comparison in the last two columns shows the good agreement of the experimental results with the model.

It is interesting that the greatest reduction of transition width occurs precisely at the resistivity corresponding to the minimum in flux pinning

TABLE I
Comparison of Experimental Parameters for Aluminum Films

Film	ρ_N , $\mu\Omega$ cm	l , \AA	$\xi(0)$, \AA	$\langle D \rangle$, \AA	N	ΔT_{cf} , mK	$\sqrt{N} \Delta T_{cf}$, mK	$T_{cf} - T_{cb}$, mK
Ref. 7	10^4	0.12	37	30	1.8	350	470	800
Ref. 7	10^3	1.2	120	30	60	120	940	980
Ref. 7	100	12	370	40	750	50	1350	950
Ref. 7	45	27	550	50	1331	40	1440	900
Ref. 11	18	60	840	55	3700	10	610	600
This work, Fig. 1c	9.6	125	1200	70	5000	4	280	350
This work, Fig. 1b	1.7	710	2820	400	343	5	93	135
This work, Fig. 1a	0.7	1800	—	—	—	2	—	30

measured by Ekin.¹³ The maximum number of grains in a coherence volume leads to minimum pinning because in that case the structural defects (grain boundaries) look most homogeneous to a flux core of radius ξ .

In the cleanest film we do not know the grain size nor can we easily obtain the coherence length from the electron mean free path, since it is limited by surface scattering in the thin film. Of greater consequence is the use of $T_{cf} - T_{cb}$ for an estimate of ΔT_{ci} . In the dirtier films, T_{cf} is sufficiently far from T_{cb} so that uncertainties in what to use for T_{cb} are less important. In the cleanest film T_{cf} is close to T_{cb} and it is not clear that the bulk T_{cb} is the correct limit. We feel that in this case the distribution ΔT_{ci} is approximately the same as the measured ΔT_{cf} .

We would like to point out that our model can also explain the premature drop in the order parameter relaxation rate measured¹¹ in aluminum films *above* T_c . These measurements follow the mean field behavior sufficiently far above T_c , extrapolating to a transition temperature which we would call T_{cf} . But as T_{cf} is approached from above, the rate drops to zero prematurely at T_{cm} . On the other hand, the Josephson critical current I_c through these junctions¹⁴ behaves like the energy gap. Sufficiently far *below* T_c , I_c follows the theoretical prediction using the same T_{cf} for the transition temperature. However, close to T_{cf} , I_c is too large and goes to zero only at T_{cm} . Our model, which postulates a static inhomogeneous transition temperature, qualitatively explains these results without invoking fluctuations.

Others^{15,16} have proposed a similar model to explain the relaxation time¹¹ *above* T_c . However, it is apparently necessary¹⁶ to choose adjustable parameters to fit the data of Ref. 11. Unfortunately, the values of transition temperature range (~ 0.15 K) and correlation length for frozen disorder

($\sim 500 \text{ \AA}$) chosen in Ref. 16 do not agree with our experimentally measured parameters $T_{cf} - T_{cb}$ and $\langle D \rangle$ for the film of Ref. 11 (see Table I).

In conclusion, we have proposed a model which explains the experimental results semiquantitatively and invokes only the most fundamental concepts of superconductivity. As a consequence, the deviations from the predicted temperature dependence of the equilibrium energy gap are not in contradiction with mean field theory.

REFERENCES

1. L. P. Gor'kov, *Sov. Phys.—JETP* **36**, 1364 (1959).
2. J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).
3. I. Schuller and K. E. Gray, *Phys. Rev. Lett.* **36**, 429 (1976).
4. D. H. Douglass, Jr., and R. Meservey, *Phys. Rev.* **135**, A19 (1964).
5. K. E. Gray, unpublished.
6. R. A. Buhrman and W. P. Halperin, *Phys. Rev. Lett.* **30**, 692 (1973).
7. G. Deutscher, H. Fenichel, M. Gershenson, E. Grünbaum, and Z. Ovadyahu, *J. Low Temp. Phys.* **10**, 231 (1973).
8. I. Schuller and K. E. Gray, to be published.
9. B. L. Blackford and R. M. March, *Can. J. Phys.* **46**, 141 (1968).
10. J. C. Keister, L. S. Straus, and W. D. Gregory, *J. Appl. Phys.* **42**, 642 (1971).
11. J. T. Anderson, R. V. Carlson, and A. M. Goldman, *J. Low Temp. Phys.* **8**, 29 (1972); R. V. Carlson, Thesis, Univ. of Minnesota (1975), unpublished.
12. F. R. Fickett, *Cryogenics* **11**, 349 (1971).
13. J. W. Ekin, *Phys. Rev. B* **12**, 2676 (1975).
14. A. M. Goldman, private communication.
15. J. C. Hayward and E. Simánek, *Phys. Lett.* **A53**, 55 (1975).
16. S. Cremer and E. Simánek, *Phys. Rev. B* **14**, 1927 (1976).