the case of the cylinder discussed here, the rotational invariance of the electron–electron interaction which produces the pair correlations responsible for superconductivity. For noninvariant interactions it is possible to construct a state with the properties of a superconductor for which the enclosed flux is not sharply quantized, which has a lower free energy than the related state with flux quantized. It would be interesting to attempt to construct such a superconductor.

Discussion 44

FERRELL: I'd like to make two brief comments. The first is that it seems to me that the relevance of the question of translational invariance and the presence of scattering centers is rather over-emphasized. In the talk we've heard it's been considered that the important thing is whether the translational invariance remains. I think that's the wrong symmetry principle. Anderson has shown that the correct symmetry principle underlying the BCS theory is time inversion. That symmetry of the Hamiltonian remains if you have nonmagnetic scattering centers. The question of whether we have just ordinary scattering center or not is quite irrelevant; it's hard to see how the presence of scattering centers would really change any physical properties of the film. The second comment is, if you look at these problems from the standpoint of the Gor'kov formalism there's always an underlying Gor'kov F function. When you start talking about pairing electrons in two different ways and throwing them in the pot together that must mean that the F function has structure. I wonder if you've looked at it from the standpoint of the Gor'kov formalism and to see how this structure would affect the energy.

COOPER: The first point is that we have explicitly constructed a state coupling pairs which are not time reversal invariant. This state has a lower free energy than the other state. The lack of invariance has nothing to do with impurity scattering but is related to the electron–electron interaction itself. The second point: if one translated this into the Gor'kov function then there would be a dependence on angle of the center of mass coordinates which usually doesn't exist. Then, presumably, one would get similar results.

One other comment. In the first talk there was a picture drawn in which Little pointed out that if one had occupation of pairs in a variety of states around $k = 0$, the question of flux quantization became obscured. Well, I think that diagram is a little misleading because if one has a cylindrical specimen then one can rigorously quantize the single particle states. The momenta of the states go as $2\pi/l$ and for a small specimen these are discretely spaced. We have explicitly placed pairs in these various angular momentum states, assumed a coupling due to the lack of rotational invariance of the electron–electron interaction, and determined the pairing which gives the lowest Gibbs function. The result is that in a sample like the one used in your experiment with Deaver, one would expect very strong flux quantization as is seen. It is really very difficult to get a specimen that is so noninvariant that one would get a breakdown of flux quantization, but maybe it can be achieved. Perhaps this is what happens in vanadium.

Direct Evidence for Quantized Vortices in a Thin Superconductor*

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Abrikosov[1] was first to suggest that quantized current vortices could exist in a simply connected superconductor. This idea formed the basis of his well-known theory of type II superconductors. More recently, Tinkham[2] has extended these ideas to the case of a thin superconducting film in a perpendicular field. His analysis explains reasonably well the critical field data of Morris and Tinkham[3] and Broom and Rhodinck,[4] and the more recent results of the penetration depth and critical field studies by Mercerau and Crane.[5] However, since these experiments measure the gross thermodynamic properties of a sample, they provide, at most, indirect evidence that quantized vortices actually exist in a superconductor.

In order to obtain more direct evidence for the existence of vortices, we have measured the properties of very narrow superconducting film strips

* Work supported in part by the National Science Foundation and by the United Aircraft Corporation.

† Union Carbide Predoctoral Fellow.

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[3] D. E. Morris and M. Tinkham, Phys. Rev. Letters **6**, 600 (1962).

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(approximately 1μ wide—see Fig. 1) at the transition temperature T_c. In this case the size of the vortices should be determined by the width of the strip rather than by the effects of physical inhomogenieties (holes, dislocations, etc.) in the film.

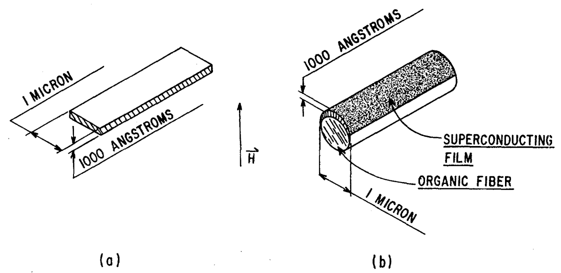

FIG. 1. (a) Ideal geometry of superconducting film strip with the approximate dimensions indicated. (b) Geometry of film strip used in experiment (approximate dimensions). The orientation of the strip in the magnetic field **H** is indicated.

In the following analysis we use the Abrikosov–Tinkham theory to determine the free energy versus magnetic field behavior of a thin superconducting strip at $T \sim T_c$ in a perpendicular magnetic field. At[6] $T \sim T_c$ the kinetic energy density of a vortex in a thin superconductor in a perpendicular magnetic field H is given by

$$T(r) = \frac{\omega(r)}{2\Lambda_0}\left(\frac{n\varphi_0 - \pi r^2 H}{2\pi rc}\right)^2 + O(r)\,, \quad (1)$$

where $\omega = n_s/n_s^0$ is the order parameter of the Ginzburg–Landau theory, $\Lambda_0 = m/n_s^0 e^2$ is the London parameter evaluated at 0°K, $\varphi_0 = hc/2e = 2.07 \times 10^{-7}$ G-cm² is the flux quantum for pairs, n is an integer, and r is the distance from the center of the vortex. $O(r)$ represents field-independent terms, n_s is the "number of superconducting electrons," and n_s^0 is the same quantity evaluated at 0°K. Equation (1) follows directly from London's theory if allowance is made for a spatially varying order parameter $\omega(r)$. After Tinkham,[2] we choose for the trial function,

$$\omega(r) = \omega_0(r/R)^\alpha\,, \quad (2)$$

where R is the over-all radius of the vortex and ω_0 is the value of $\omega(r)$ at the edge of the vortex. In order to obtain the total kinetic energy per unit volume KE/V of a circular vortex of over-all radius R, we integrate Eq. (1) over the volume element $2\pi r dr$. We obtain

$$\frac{\mathrm{KE}}{\mathrm{V}} = \frac{\omega_0 H}{4\pi c^2 \Lambda_0}\left(\frac{-2n\varphi_0}{\alpha+2} + \frac{\pi R^2 H}{\alpha+4}\right) + O(R)\,. \quad (3)$$

Minimizing this with respect to H, we obtain in addition to a minimum at $H = 0$, minima at the following values of H,

$$H_{\min} = \frac{n\varphi_0}{\pi R^2}\left(\frac{\alpha+4}{\alpha+2}\right). \quad (4)$$

In order to evaluate α one must consider all of the contributions to the free energy[2] which include, in addition to the kinetic energy term [Eq. (3)], the "gradient of the order parameter term" and the "condensation energy term" of the Ginzburg–Landau theory. Minimizing the total free energy with respect to α one obtains minima corresponding to $\alpha \sim 1.3$ for $n = 1$, $\alpha \sim 2.1$ for $n = 2$, etc. However, the free energy is very insensitive to the choice of α. Because of this and the crudity of the trial function [Eq. (2)], the above result could easily be shifted in a real superconducting film which has physical inhomogenieties.

We compare now the result in Eq. (4) to that for a multiply connected superconductor such as a ring or hollow cylinder of radius R_a and vanishingly small wall thickness. Then $\omega(r)$ in Eq. (1) is constant and $r \rightarrow R_a$. The free energy then has minima at $n\varphi_0/\pi R_a^2$. This has been observed in the experiments by Little and Parks[7] in which the transition temperatures of very small hollow superconducting cylinders were found to be periodic in the magnetic flux through the cylinder with a period φ_0. In the simply connected thin film case, according to Eq. (4), the first minimum which corresponds to $n = 1$ and $\alpha = 1.3$, occurs at $1.6\ \varphi_0/\pi R^2$, 60% higher than in the multiply connected case for $R = R_a$. Therefore, in a very narrow film strip of width $2R_f$, near T_c, where we expect the vortices to be limited in size by the width of the strip, minima in the free energy versus magnetic field should occur at

$$H_{1.6} = 1.6\ \varphi_0/\pi R_f^2 \quad (5)$$

corresponding to vortices of radius R_f. In order to determine the variation of the free energy with the magnetic field, we measured the reduced resistivities r/r_N of film strips in the intermediate state as a function of the applied, perpendicular field H. As discussed previously by Little and Parks,[7] a decrease in r/r_N corresponds to an increase in T_c. This, in turn, corresponds to a decrease in the free energy of the superconducting state.[8]

[6] At $T \sim T_c$ the penetration depth is extremely long and, therefore, the magnetic field is uniform in the film and equal to the applied magnetic field.

[7] W. A. Little and R. D. Parks, Phys. Rev. Letters **9**, 9 (1962); in *Proceedings of the Eighth International Congress on Low Temperature Physics, London, 1962* (Butterworths Scientific Publications, Ltd., London, to be published).

[8] Since the free energy of the normal state is independent of the magnetic flux, a decrease in the free energy of the superconducting state corresponds also to an increase in the free energy difference between the normal and superconducting states, which determines T_c.

The superconducting film strips were prepared in the following way. An organic fiber of the order of 1μ in diameter was prepared from GE 7031 varnish and mounted over a hole on a Pyrex glass slide. Then, spectroscopically pure Sn was evaporated onto one side of the fiber and the slide at a pressure of 10^{-6} to 10^{-5} mm Hg.[9] A film strip prepared in this way is illustrated in Fig. 1(b). This is an approximation to the "ideal" geometry shown in Fig. 1(a). The effect of the curved surface of the actual geometry [Fig. 1(b)] will be to increase slightly the magnitude of the kinetic energy of the vortices [Eq. (1)], since the current loops will be larger than in the flat film case, for vortices enclosing the same number of flux quanta. However, the complex geometry will not shift $H_{\min}$ (the location of the free energy minima), which depends only upon the projected area of the vortex in the direction of the magnetic field. Therefore, R_f [in Eq. (5)] corresponds to the radius of the fiber in Fig. 1(b).

The film thickness of the strips was measured with an accuracy of ±20 Å by the Tolansky interference method. The diameters of the fibers were determined by interpreting the diffraction pattern in a conventional optical microscope. The diameter of one fiber was determined by electron microscopy and this measurement was used to calibrate the above technique. In the resistive transition region of the strip (a region up to 0.01°K in width just below T_c for bulk Sn) both dc and ac measurements of the resistivity of the strip were made. A 100-cps phase-sensitive, lock-in wheatstone bridge was used for the ac measurements. The ac and dc measurements gave identical results and in both cases current densities of the order of 10^4 A/cm^2 were used.

The results for a Sn film strip 1.5μ wide and for one 4.9μ wide are shown in Fig. 2, where r/r_N versus H curves are shown for various temperatures in the intermediate state. The curves exhibit the predicted minima corresponding to vortices containing one flux quantum. In the 1.5-μ strip the first minimum occurs at a value of the magnetic field very close to, but slightly lower than the predicted value, $H = H_{1.6}$. In the 4.9-μ strip the minima occur at values of the field much higher than the predicted ones, which indicates that the vortices are smaller than the width of the strip. This may be an intrinsic effect, or alternatively, may be due to the effects of physical inhomogenieties in the films. Additional experiments in which we will attempt to improve the film quality by using different superconductors should clarify this question. The second dip in the lower temperature curves corresponds, probably, to some or all of the vortices remaining approximately the same size, and n switching from 1 to 2 as the magnetic field is increased.

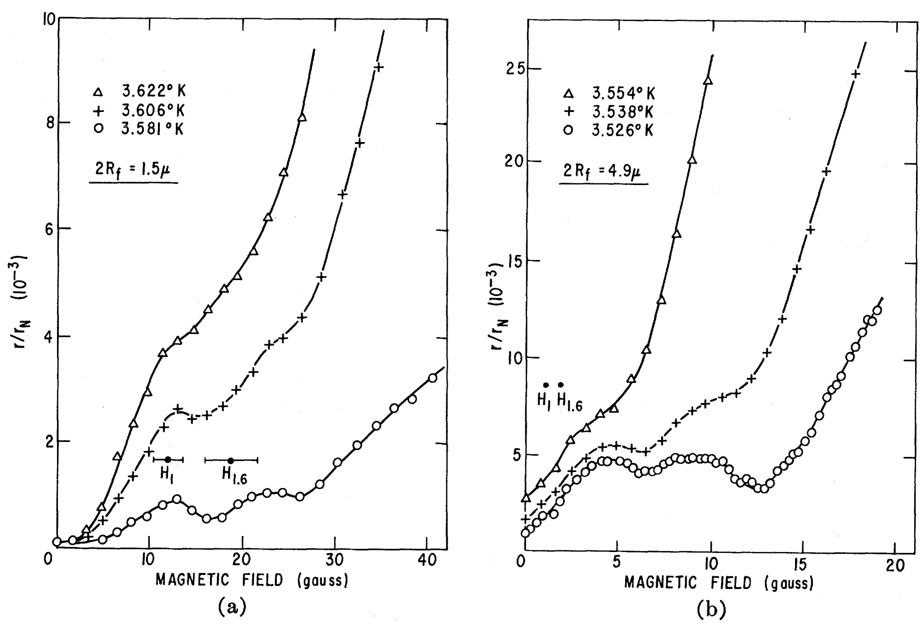

Fig. 2. (a) Reduced resistivity (r/r_N) versus H curves at various temperatures for a superconducting strip 1.5μ wide and 860 Å thick. H_1 is determined by $H_1 = \varphi_0/\pi R_f^2$ and $H_{1.6}$ by 1.6 $\varphi_0/\pi R_f^2$. The error on the values of H_1 and $H_{1.6}$ reflect the errors in the measurements of the diameters of the fibers, which for the smallest fibers is approximately ±7% of the diameter. This corresponds to errors in H_1 and $H_{1.6}$ of ±14%. (b) Similar series for a strip 4.9μ wide and 1480 Å thick.

In order to correlate the first dip in the r/r_N versus

[9] This is similar to the technique used by Little and Parks (Ref. 7) in preparing hollow superconducting cylinders of very small diameter.

H curves with the width of the strips, representative curves for four different samples are shown in Fig. 3. The shapes of the curves, in particular, the steepness of the r/r_N versus H background, depends upon the film thickness, the quality of the film, and the temperature in the intermediate state at which the

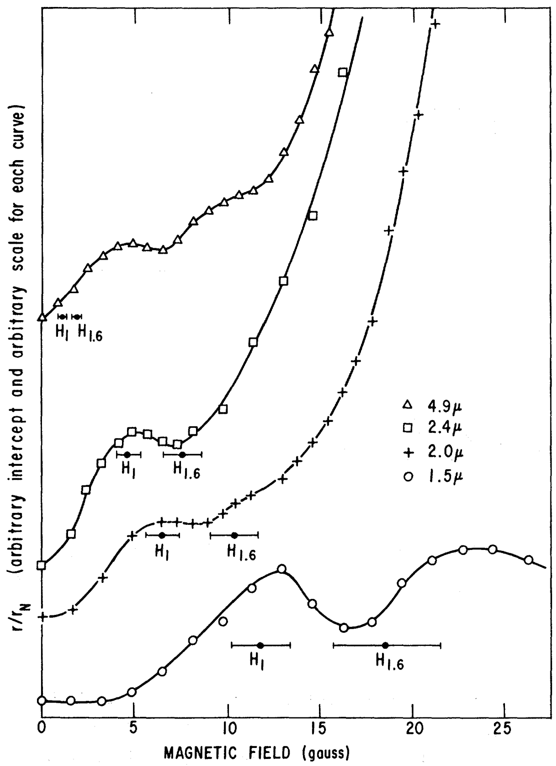

FIG. 3. Reduced resistivity curves for four superconducting strips of various widths. Since the curves for the various strips were obtained at different temperatures, the ordinate intercepts and scale are arbitrary, and different for each sample.

measurements were made. Therefore, only the qualitative nature of the curves, specifically, the location on the abscissa of the minima should be considered. For the very wide film (4.9μ) the results are anomalous as discussed above. However, for the 1.5-, 2.0-, and 2.4-μ strips the first minimum occurs very close to, but slightly lower, than the predicted value of the field $H_{\min} = H_{1.6}$. Possible explanations for the slight disagreement with the predicted values for the minima are the following. The order parameter within the vortex may vary more rapidly than $(r/R)^{1.3}$, which is the weak variational result using Tinkham's approximation. Certainly, closer agreement with the predictions might be considered fortuitous because of the crudity of the trial function used. A second explanation is that the vortices may not be circular but are distorted in such a way as to more completely fill the space of the strip. The true shapes of the vortices might be somewhere between that shown in Figs. 4(a) and 4(b). This would correspond to vortices with larger areas which would bring the experimental results into better agreement with the theoretical predictions.

In all of the films studied the resistive anomalies, which we have explained in terms of vortices in the film strips, were observed only at the lower end of the resistive transition at values of r/r_N of the order of 0.01 or less. Our qualitative explanation for this is the following. At the higher temperature end of the resistive transition we imagine that the intermediate states of the film consists of small "islands" of superconducting metal in a "sea" of normal metal.[10] This will have two detrimental effects. Firstly it is improbable that supercurrents of the order of the diameter of the strip—and therefore, vortices, can form until the "islands" are quite large and almost completely fill the space of the strip. Secondly, the size of the "islands" will be sensitive to the magnetic field. This will give rise to a monotonically varying r/r_N versus H background which obscures the presence of the vortices. This background will be steepest for the largest surface to volume ratio of the "islands," which corresponds to the higher temperature end of the resistive transition. Both of these effects become less important at the lower temperature end of the resistive transition.

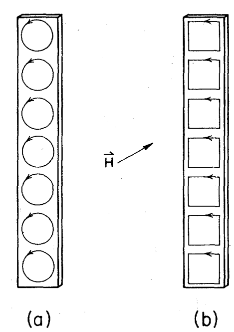

FIG. 4. (a) Circular vortices limited in size by the width of the strip. (b) Square vortices limited in size by the width of the strip.

We wish to thank B. Brandt for measuring the film thickness of the samples and M. Foster, P. G. de Gennes, and M. Tinkham for stimulating discussions.

[10] One expects that the size of the superconducting "islands" must be at least as large as the coherence length. The thin films studied here are type II superconductors and the coherence length ξ is determined from the relation $\xi = \frac{1}{3}(lv_F\hbar/E_g)^{\frac{1}{2}}$ where l is the mean free path, v_F the velocity of the electrons at the Fermi surface, and E_g the energy gap. (See P. G. de Gennes, these Proceedings.) Using this relation we obtain $\xi \sim 200$–400 Å for the films studied. Since this is much shorter than the width of the films, the "island" picture is feasible at least with respect to this consideration.

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MEISSNER: I wonder if you would get better agreement with the minima if you assume that the effective width of the film is smaller than the fiber diameters. The reason is that on the outside of the fibers the tin may have a tendency to bounce off so that you really don't get any film there.

R. PARKS, *University of Rochester:* We would get better agreement with the results if we assumed that the vortices were larger than the predicted value. Now there is a question of film quality at the very edge of the film and I don't know how we can really determine this.

FIELD AND CURRENT EFFECTS

CHAIRMAN: *J. Bardeen*

Magnetic Field and Phase Transition in Superconducting Thin Films*

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There has been a steady accumulation of literature both theoretical[1-3] and experimental[4,5] on the question of phase transition in a thin film superconductor (thickness $L \lesssim 10^{-5}$cm) allowing essentially complete penetration of equal magnetic field which runs parallel to the film surface. Theoretical calculations by Douglass[1] based on the Ginzburg–Landau–Gorkov (G–L–G) theory[6] are in good agreement with experimental measurements near $T \sim T_c$; Bardeen's microscopic calculations[3] are also in good agreement with experiments for this near critical temperature range. At lower temperatures down to zero, the theoretical situation is less clear. The (G–L–G) theory is essentially a London theory, $\xi_0 \ll \lambda_0$, where ξ_0 and λ_0 are the bulk coherence distance and penetration depth, respectively; since $\xi_0 = v_F/\pi\phi$, at $T = 0$, we have $\xi_0 \to \infty$ as $\phi \to 0$ (strong magnetic field near critical field H_c), and the London limit is not satisfied.

Mathur *et al.*[2] arrived recently at the conclusion that a second-order phase transition is expected at $T = 0$°K for thin films based on an earlier formulation which used Wentzel's theory of gauge invariance.[7] It appears that Mathur *et al.* took the London limit for bulk specimen parameters ξ_0 and λ_0 in their study; this is evidently not satisfactory for thin films where the appropriate limit is the Pippard nonlocal form when expressed in terms of bulk material parameters. Bardeen's microscopic theory,[3] on the other hand, predicts a first-order phase transition in thin films for reduced temperature $T/T_c \lesssim 0.3$.

We have adapted the results of a previous perturbation calculation[8] done for bulk matter at

* This work is supported by the U. S. Atomic Energy Commission, the U. S. Air Force office of Scientific Research, and the National Science Foundation.

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[6] V. L. Ginzburg and L. D. Landau, Zh. Eksperim. i Teor. Fiz. **20**, 1064 (1950); L. P. Gorkov, Zh. Eksperim. i Teor. Fiz. **36**, 1918 (1959) [English transl.: Soviet Physics—JETP **9**, 1364 (1959)].

[7] G. Wentzel, Phys. Rev. **111**, 1488 (1958). See also, K. K. Gupta and V. S. Mathur, *ibid.* **121**, 107 (1961).

[8] Y. Nambu and S. F. Tuan, Phys. Rev. **128**, 2622 (1962); *Proceedings of the Eighth International Conference on Low Temperature Physics, London, 1962* (Butterworths Scientific Publications, Ltd., London, to be published).