In the region in question the film behaves like a classical superconductor with a penetration depth smaller than or, at best, comparable with the thickness of the film. Under these conditions a frozen-in radial magnetic field may become concentrated into certain small portions of the film and become much larger than the axial magnetic fields. Under the influence of the axial fields the radial field lines may cut through the film in an axial direction. There are some indications in the irregular hysteresis loops associated with the region under discussion [Figs. 1(c) and 1(d)] which point to a tendency of the trapped flux to escape when H_p passes through zero. However, experiments in which precautions were taken to compensate the horizontal component of the earth's magnetic field and in which the virgin branch of the hysteresis loop was studied [Fig. 1(d)] gave critical currents which were only about 30% above the values observed after the first breakdown of H_I.

We must therefore look for further causes for a concentration of the applied magnetic fields. With the geometry of short rings used by Mercereau,[1] such concentration can be expected to occur at the edges of the ring and may possibly account for his results. Perhaps in our geometry a similar field concentration is started off in pinholes or other defects we have noticed in our films.

Free Energy of Composite Wires in the Superconducting State

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PHENOMENOLOGY OF COMPOSITE STRUCTURES

Qualitative Effects

Widespread interest[1–7] has been aroused in the phenomena associated with superconductivity in composite superconducting normal metal films. The authors, in a recent note,[8] reported use of a new method (suggested by R. Garwin) to investigate superconductivity for filamentary specimens. The present work extends this technique and reports some qualitatively new observations which seem of fundamental interest.

Previous workers had already noted one primary effect, the depression of critical temperature, critical current, and critical field for a superconductor in contact with normal metal. The effect is a strong function of thickness of either element,[5] increasing with decreasing thickness of superconductor and increasing thickness of normal metal. Indeed, the superconductor has an apparent critical size, ~100 Å, below which it will not support superconductivity in contact with a normal metal. The depression in T_c is also found to be strongly dependent upon the characteristics of the normal metal,[7] being much larger for a paramagnetic element as compared to nonparamagnetic.

A second primary effect, the appearance of superconducting order in the normal metal has also been discussed in the authors' preliminary report.[8] In that report the effect was detected in Al well above its critical temperature by flux exclusion, while in an earlier article Smith *et al.*[4] report electron tunneling into Ag, demonstrating a superconducting energy gap when in contact with Pb.

Semiquantitative Theory of Composite Specimens

Although de Gennes[9] has suggested that the GL theory may not work for very thin films, it is of interest to examine this theory and, if possible, to apply

[1] E. F. Burton, J. O. Wilhelm, and A. D. Misener, Trans. Roy. Soc. Canada, Sec. III **28**, 65 (1934).
[2] A. D. Misener and J. O. Wilhelm, Trans. Roy. Soc. Canada, Sec. III **29**, 5 (1935).
[3] H. Meissner, Phys. Rev. **109**, 686 (1958), Report, Office of Naval Research, Contract NONR 248 (49), 1959; in *Eighth International Conference on Low Temperature Physics* (Butterworths Scientific Publications, Ltd., London, 1962).
[4] P. S. Smith, S. Shapiro, J. Miles, and J. Nicol, Phys. Rev. Letters **6**, 686 (1961); J. L. Miles and P. S. Smith, J. Appl. Phys. **34**, 2109 (1963).
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[6] A. C. Rose-Innes and B. Serin, Phys. Rev. Letters **7**, 278 (1961).
[7] W. Simmons and D. H. Douglas, Jr., Phys. Rev. Letters **9**, 153 (1962).
[8] D. P. Seraphim, F. M. d'Heurle, and W. R. Heller, Appl. Phys. Letters **1**, 93 (1962).
[9] P. G. de Gennes and E. Guyon (to be published).

it, because of its simple form. According to a theoretical formulation given first by Gorkov[10] one finds that κ_0, the bulk parameter introduced by GL, is multiplied by $X(\rho)$ a function which reduces to unity in bulk pure superconductors and to $f \cdot l/\xi_0$ in mean-free-path-limited superconductors. Here l is the mean free path, ξ_0 the coherence length of the pure material, and f a number near unity. An important extension of these ideas which seems to have approximate validity[11-13] is to regard the boundary of superconducting material as providing a mean free path limitation. It is really upon these partly empirical grounds that one can hope to apply the GL theory even to thin layers of superimposed metals.

Douglass,[14] in accounting for the reduction of critical field and temperature of superposed metal films, was led to suggest that one could apply the GL equations and that the free energy function for the normal metal component be taken as positive. Consistent with a second-order transition at zero field, one may go further and assume that both normal and superconducting metals possess free energy functions which are expansions in the square of the order parameter, with coefficients analytic in the temperature variable. In doing this, it is of value to make a more specific assumption, than did Douglass, concerning the form of the free energy function. Using Bardeen's definition[15] of the order parameter, the GL equations then become

$$\frac{-\hbar^2}{2m^*}\left(\nabla - \frac{ie^*\mathbf{A}(\mathbf{r})}{hc}\right)^2\Psi \mp \alpha_{S,N}\Psi + \beta_{S,N}|\Psi|^2\Psi = 0\,,$$

and

$$-\nabla^2\mathbf{A} = \frac{4\pi\mu}{c}\left[-\frac{ine^*\hbar}{4m^*}(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*)\right] + \frac{2\pi\mu e^{*2}n}{m^*c}\mathbf{A}|\Psi|^2\,.$$

In a preliminary effort it is convenient to deal with one-dimensional problems. Reducing these equations in the usual way, we get for superconducting material:

$$\frac{\hbar^2}{2m^*}\Psi'' + \left(\alpha_S - \frac{A^2}{\Phi^2}\right)\Psi - \beta_S\Psi^3 = 0\,,$$
$$A'' = \epsilon_S A|\Psi|^2\,;$$

For normal material:

$$\frac{\hbar^2}{2m^*}\Psi'' + \left(-\alpha_N - \frac{A^2}{\Phi^2}\right)\Psi - \beta_N\Psi^3 = 0\,,$$
$$A'' = \epsilon_N A|\Psi|^2\,.$$

Here Φ is the quantum unit of flux and α_S, α_N, β_S, β_N, ϵ_S, ϵ_N, follow from the previous equations. Following the usual procedures, assuming the continuity of Ψ, Ψ', A, and A' across the interface, and as previously, simplifying to a thickness consistent with constant order, the order parameter can be obtained as

$$\Psi^2 = \frac{d_S\gamma_S - d_N\gamma_N}{d_S\delta_S + d_N\delta_N}\,,$$

at zero magnetic field.

Solving these equations provides the moment,

$$\mathbf{M} = -\frac{1}{2\pi}He\,(d_N + d_S) + \frac{1}{2\pi}B_N \sinh\Psi^2\epsilon_N(d_N + d_S) + C_N\cosh\Psi^2\epsilon_N(d_N + d_S)\,,$$

in which C_N and B_N are functions of $\epsilon_S\Psi^2$, $\epsilon_N\Psi^2$, d_S, d_N, and applied field.

Much can be deduced with precision from GL if one chooses to work with zero magnetic field. Rewriting provides

$$\Psi'' - \gamma_S\Psi + \delta_S\Psi^3 = 0 \text{ (super)}\,,$$
$$\Psi'' + \gamma_N\Psi + \delta_N\Psi^3 = 0 \text{ (normal)}\,.$$

The solutions of these are elliptic functions. The importance of the GL critical value of κ[16] is now seen through the value of the parameter $\delta_S/2\gamma_S$ at which one passes from sine-like to hyperbolic-like solutions. If we start with a maximum value of the order parameter at the center of the superconducting film (no normal film present) and look for solutions which decrease but do not become negative, there are none which have zero slope at positive values of x, if $\kappa < 1/\sqrt{2}$. With normal material present there is no need for a zero slope, we need merely ask for continuous connection with an hyperbolic-like solution in the normal material whose slope may go to zero at finite or infinite distances. If γ_N and δ_N are small, it may happen that the lowest energy solution will still be one of constant order in both materials. For large magnitudes of γ_N and δ_N the energy will be minimized by a small value of the order parameter at $x = 0$ together with a smooth decrease of order proceeding into the "normal" component.

WEAK MAGNETIC FIELD SUSCEPTIBILITY AND MOMENT

Experiments have been designed to isolate the super filaments as much as possible to minimize the

[10] L. P. Gorkov, Zh. Eksperim. i Teor. Fiz. **36**, 1918 (1959); **37**, 833 (1959); **37**, 1407 (1959) [English transl.: Soviet Phys.—JETP **9**, 1364 (1959); **10**, 593 (1960); **10**, 998 (1960)].
[11] W. B. Ittner, Phys. Rev. **119**, 1591 (1960).
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[15] J. Bardeen, Rev. Mod. Phys. **34**, 667 (1962).
[16] A. A. Abrikosov, Zh. Eksperim. i Teor. Fiz. **32**, 1442 (1957) [English transl.: Soviet Phys.—JETP **5**, 1174 (1957)].

effect of multiple connections. The experimental results are reported directly as diamagnetic volume. Experiments have included (1) Pb and PbBi alloy filaments ~700 Å surrounded by a second superconductor Al well above its critical temperature and (2) Pb filaments ~700 Å surrounded by a nonsuperconducting noble metal Ag or Au. (See Ref. 8 for details of preparation.)

For case (1) orders of magnitude more than the volume of Pb or PbBi is diamagnetic while for case (2) less than the volume of Pb is diamagnetic. The data are plotted as a function of temperature in Fig. 1 with the ordinate identifying the diamagnetic volume divided by the total volume of Pb or PbBi which was calculated from the results of chemical analysis.

As previously discussed[8] the moment curves for Pb filaments in Al show two peaks depending upon the size of the filaments. Roughly, the two cases may

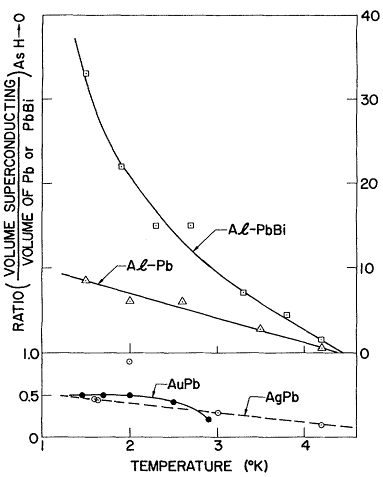

FIG. 1. Weak magnetic field susceptibility of composite wires. Filaments of Pb or PbBi are ~350 Å radius and shells are Al ~ 1400 Å surrounding Pb, Al ~ 300 Å surrounding PbBi, Ag and Au ~ 300 Å.

be characterized by (a) large d_S and (b) small d_S. In (a) the filaments can exist quite independently to exhibit characteristics typical of bulk properties and at the same time have effects on the normal matrix nearby. In (b) the usual bulk effects are absent, leaving just one moment peak typical of the composite.

The moment curves for Pb (15% Bi) filaments in aluminum are quite similar to those for Pb in Al in both ranges of size. For filaments ~700 Å [case (b)] Fig. 2 is typical. The moment peaks at very weak field and then decreases rapidly as the field is increased.

The moment curves for the Au matrix (see Fig. 3) are much like those for a soft superconductor with a sharp transition. In fact, a critical magnetic field (defined at one-half of the weak field susceptibility) has a slope near T_c of ~160 G/deg, typical of soft superconductors with critical temperatures in the same range. Extrapolation of the critical field to zero provides a T_c of 3.05°K.

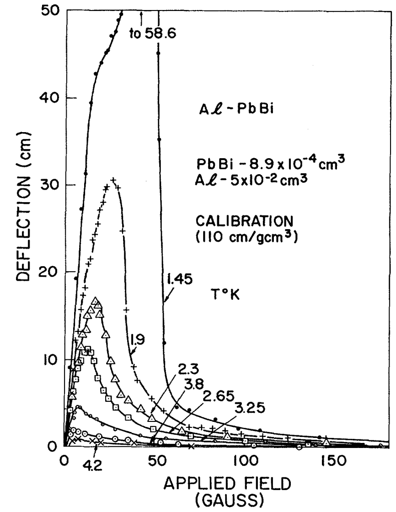

FIG. 2. Magnetic moment (calibration as shown) of Pb–Bi filaments in Al.

The moment curves for the Ag matrix were roughly semicircular in shape with a broad maximum at approximately 200 G at all temperatures between 4.2° and 1.5°K. The data were complicated by paramagnetic moment which might have been contributed by

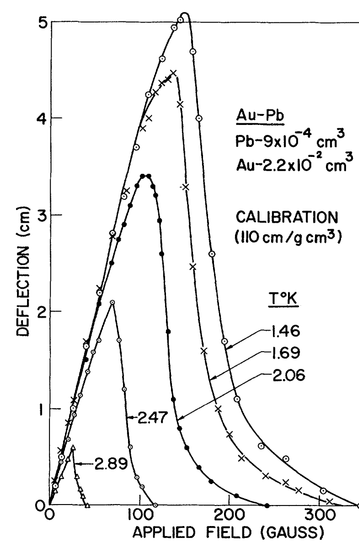

FIG. 3. Magnetic moment (calibration as shown).

the residual impurities in the Ag, 99.999% pure by the vendor's analysis.

The data discussed above are for specimens designed with filaments sizes of the order of 700 Å. As

Hilsch *et al.* suggest (for Cu–Sn), superconductivity disappears for the Ag–Pb and Al(PbBi) if the filaments are reduced by another factor of 10. However, this effect is not evident for the Au–Pb, possibly because of atomic migration during fabrication. To speed the processing, the specimens with filaments 700 Å were rolled (thickness decreased by 10) and immediately quenched in liquid nitrogen. Since no changes in the moment curves occurred for these specimens, it may be inferred that substantial atomic rearrangement toward larger filament sizes occurred in a brief period of handling at room temperature. Such an effect occurred for the ∼100-Å Pb filaments in Ag which, after standing at room temperature for several hours, provided a measurable moment again.

FREE ENERGIES OF THE COMPOSITES

The free energy difference ΔF between the normal and superconducting states of the composites was obtained by integration of the area under the moment curves. In Fig. 4 the results are presented as the ratio

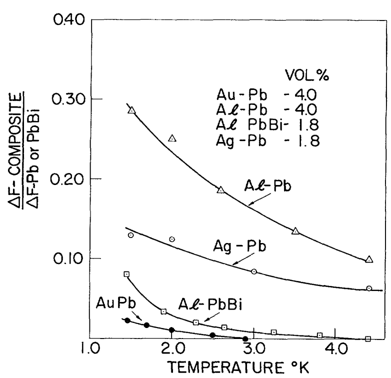

FIG. 4. Ratio of the free energy difference ΔF of the composite to the free energy difference of the volume of Pb or PbBi as noted in the figure.

of the free energy difference of the composite to the calculated free energy difference of the lead contained in the composite. In all cases, the ratio is less than one by one to three orders of magnitude. It is remarkable that although Au and Ag matrices are reasonably similar in susceptibility, there is much more depression of ΔF in Au than in Ag. The effect is even larger than that illustrated if allowance is made for the volume percent Pb which is a factor of 3 greater in the Au matrix as compared to the Pb in Ag. The differences between the Al–Pb and the Al–PbBi may be explained partly by the difference in volume percent and otherwise by the greater d_n (factor of 5) in the Pb–Bi.

DISCUSSION

(a) The free energy difference of superconducting Pb is strongly depressed by the "proximity" of a normal metal, be it Ag and Au or Al. (b) Superconductivity (as measured by susceptibility) expands substantially into Al above its critical temperature but is contracted into the lead by close proximity to Ag and Au at temperatures between 1.5° and 4.0°K. (c) The order parameter is extremely weak in the aluminum surrounding the lead, i.e., it is quenched by a weak magnetic field. (d) In agreement with previous work, the critical temperature is decreased by proximity. (e) Size effects are apparent but have not been measured quantitatively. The critical size of lead (supporting superconductivity) in proximity to a much larger quantity of Ag or Al is of the order of 100 Å.

At any temperature appreciably below the transition temperature of the sample, the diamagnetic material in Al–Pb or Al–PbBi composite is greater than the volume of Pb, whereas in the case of the Ag–Pb and Au–Pb composites it is less than the volume of Pb. This result could conceivably arise from differences in the metallurgical microstructure (i.e., multiply connected Pb) of the various composites, but we regard this possibility as unlikely. More likely, the experimental results imply a qualitative difference between the noble metals and aluminum and, furthermore, between Ag and Au with regard to their tendencies toward becoming superconducting.

Comparison of the experimental results to the version of GL given in the earlier section yields: (a) For Al the values of γ_N and δ_N are not very large. Thus, the order can spread large distances into the Al at the cost of reduction of the mean order parameter. (b) For Ag and Au the values of γ_N and δ_N are so large that the magnetic field even penetrates the Pb significantly. (c) For thin enough d_N and d_S the theory predicts practically complete field penetration. It appears from the present work that GL theory has at least qualitative support even in composite materials.

ACKNOWLEDGMENTS

We have greatly appreciated the assistance of A. C. Burgess in the experiments and discussions with P. M. Marcus, P. B. Miller, and M. F. Merriam.

Discussion 53

GAULÉ: I would like to remark that we also made lead aluminum films by coaxial extrusion. We get transition temperature slightly higher than that of lead, by about 0.2°K.

D. SERAPHIM, *I.B.M. Research Center:* I see. Well, it depends very greatly on the actual filament sizes.

GAULÉ: Yes, we have to check this. Maybe we had some rather thick filaments which were under some strain and this would explain the discrepancy in a very simple manner.

SERAPHIM: I did not refer here to our original results, which were reported in Journal of Applied Physics, that if the lead filaments were quite large, that is larger than the coherence length, you can see both effects. You can see the typical characteristics of lead in the specimen and also these new characteristics associated with the interaction depth into the aluminum.

GAULÉ: I agree.

PIPPARD: Were your magnetization curves reversible?

SERAPHIM: They are as reversible as these high field superconductors that are prepared in an ideal way. That is, there's a small amount of flux trapping in some, perhaps 10%, and in others none at all.

In answer to Pippard's question regarding the reversibility of the moment curves for composite normal-superconducting wires, regard the figure. Note that the trapped moment is just a small fraction of the total peak height. The filaments were widely spaced here. More trapping was evident in some earlier work where the filaments were more closely spaced. Generally, the fractional moment trapped (relative to peak height) increased with temperature. The AuPb was quite reversible in behavior.

DRUYVESTEYN: Have you done any resistance measurements?

SERAPHIM: Yes, we have done a few resistance measurements. We must make an estimate of kappa in these specimens, so it's very important to measure the mean free path as closely as we can.

DRUYVESTEYN: And you found the same transition points?

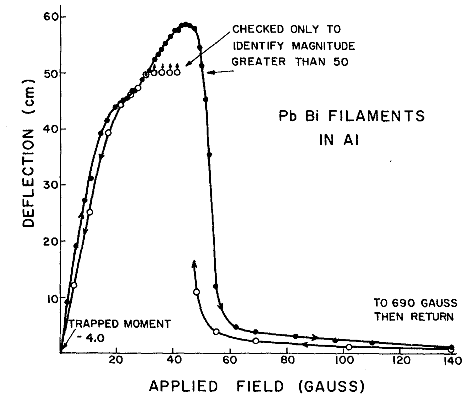

FIG. 9. Magnetization curve of PbBi filaments in aluminum.

SERAPHIM: Very closely.

CHANDRASEKHAR: Brief comment. As I understand it, the way you prepared these samples the superconductor is surrounded by the normal conducting metal and presumably they have considerable differential contraction between the two upon cooling down. Is this likely to influence your results?

SERAPHIM: I believe this would be a second order effect on top of that which we believe is just the interaction.