

of us who can recapture the mentality of a quarter of a century ago know that even the discovery of high current densities would have remained just another curiosity. The contemplation of the required technical effort in cryogenics and of all the ancillary

development would have appeared to us as outrageous folly. It needed radar, rockets, and atomic bombs to loosen up the stringency of prewar finance, which now must appear as an equal folly to the young scientific generation of the sixties.

HIGH FIELD SUPERCONDUCTIVITY

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Type II or London Superconductors

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I. INTRODUCTION

When a superconductor is placed in a magnetic field two competing processes take place. On the one hand, according to the London equation, which we may write

$$\nabla^2 H = H/\lambda_L^2, \quad (1)$$

the superconducting state attempts to exclude the magnetic field H from all but a thin penetration layer of thickness of the order of λ_L , the London penetration depth. On the other hand, in accordance with the concept of spatial coherence introduced by Pippard,¹ any local perturbation of the superconducting order parameter caused by the magnetic field spreads out to a distance of the order of ξ , the range of coherence, from the center of the disturbance.

It was recognized for some time² that Eq. (1) gave no indication of the existence of the positive interphase surface energy which is required in order to explain the Meissner effect, and it was left to Pippard³ to point out that a plane interphase boundary would indeed have a positive surface energy if ξ were greater than λ_L . Thus, the sign of $\xi - \lambda_L$ was destined to play a crucial role in determining the type of mag-

netic behavior shown by a superconductor. Following, with slight modification, an initiative due in particular to a number of Russian authors, it seems fitting to call type I superconductors, for which $\xi > \lambda_L$, Pippard superconductors, and type II superconductors, for which $\lambda_L > \xi$, London superconductors.

The reversible magnetic behavior of Pippard superconductors has been understood for some time and measurements on the structure of the intermediate state of such superconductors enabled their positive surface energy to be determined even before its origin was fully understood. For a Pippard superconductor lying in a field H_e the magnetization curve has the familiar triangular shape, all trace of superconductivity disappearing at the critical field H_e , defined by

$$F_n - F_s = - \int_0^\infty M dH_e = \frac{H_e^2}{8\pi}, \quad (2)$$

where M is the magnetization, and F_n and F_s are the free energies per unit volume of the normal and superconducting states, respectively. There are many indications, as yet mostly of a qualitative character, which suggest that flux trapping in Pippard superconductors is due to the pinning down of interphase boundaries by extended defects in the specimen.

As early as 1935, when it was known that many alloys did not conform to the Pippard or "ideal" type

¹ A. B. Pippard, Proc. Roy. Soc. (London) **A203**, 210 (1950).

² F. London, *Superfluids* (John Wiley & Sons, Inc., New York, 1950), Vol. I, pp. 125-130.

³ A. B. Pippard, Proc. Cambridge Phil. Soc. **47**, 617 (1951).

of behavior, Gorter⁴ and London⁵ suggested that a negative surface energy might account for their behavior. However, subsequent progress was slow and it is only through recent work that we have been led to recognize that a negative surface energy, resulting from the inequality $\xi < \lambda_L$, confers on what we propose to call London superconductors a new and different type of reversible magnetic behavior. In the short space of this article an attempt is made to summarize our understanding of this new type of reversible behavior and of the irreversible effects which can also be present.

II. THE LONDON PENETRATION DEPTH AND THE RANGE OF COHERENCE

This article, in its most abstract form, might simply summarize the solutions of the Ginzburg-Landau equations⁶

$$\frac{1}{2m} (-i\hbar\nabla - 2eA)^2\Psi + \alpha\Psi + \beta\Psi|\Psi|^2 = 0, \quad (3)$$

and

$$\nabla^2 A = \frac{4\pi e\hbar}{m} (\Psi^*\nabla\Psi - \Psi\nabla\Psi^*) + \frac{16\pi e^2}{m} |\Psi|^2 A, \quad (4)$$

(now known^{7,8} to follow from the BCS theory⁹ near the transition temperature if the carriers are ascribed a charge equal to twice that of the electron) when $\xi < \lambda_L$. In the first instance, we would be interested in solutions for a perfectly homogeneous superconductor, free of any extended defects, in which case α and β would simply depend on the composition, temperature, and uniform state of strain of the specimen. Having obtained a solution in this relatively simple case, as Abrikosov¹⁰ has done, one would then tackle the problem of the influence of extended defects. This might be attempted by letting α and β vary with position in the neighborhood of such defects.

However, rather than attempting an exact solution of Eqs. (3) and (4), it is helpful first of all to examine the significance of ξ and of λ_L and then to use the results of this investigation to construct and then compare two different models for the magnetic behavior of a London superconductor. Finally, we use

⁴ C. J. Gorter, *Physica* **2**, 449 (1935).

⁵ H. London, *Proc. Roy. Soc. (London)* **A152**, 650 (1935).

⁶ V. L. Ginzburg and L. D. Landau, *Zh. Eksperim. i Teor. Fiz.* **20**, 1064 (1950); *V. L. Ginzburg, Nuovo Cimento* **2**, 1234 (1955).

⁷ L. P. Gor'kov, *Zh. Eksperim. i Teor. Fiz.* **36**, 1918 (1959) [English transl. *Soviet Phys.—JETP* **9**, 1364 (1959)].

⁸ L. P. Gor'kov, *Zh. Eksperim. i Teor. Fiz.* **37**, 1407 (1959) [English transl. *Soviet Phys.—JETP* **10**, 998 (1960)].

⁹ J. Bardeen, L. N. Cooper, and R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).

¹⁰ A. A. Abrikosov, *Zh. Eksperim. i Teor. Fiz.* **32**, 1442 (1957) [English transl. *Soviet Phys.—JETP* **5**, 1174 (1957)].

these two models to see what conclusions may be drawn from experiment concerning the structures predicted by Abrikosov and others for the mixed state.

Each of Eqs. (3) and (4) corresponds to one of the competing processes mentioned in the introduction. In a weak field the order parameter Ψ is spatially-independent and Eq. (4) then reduces to the London equation (1), yielding

$$\lambda_L^2 = m/16\pi e^2 |\Psi|^2.$$

In order to study ξ let us consider the one-dimensional simplification of Eq. (3) which results when Ψ and A are functions of the z coordinate only:

$$\frac{d^2\Psi}{dz^2} + \frac{2m|\alpha|}{\hbar^2} \left(1 - \frac{2e^2}{m|\alpha|} A^2\right) \Psi - \frac{2m\beta}{\hbar^2} \Psi^3 = 0. \quad (5)$$

If we add to Ψ a small perturbation $\delta\Psi$, then $\delta\Psi$ satisfies

$$\frac{d^2}{dz^2} (\delta\Psi) = \frac{4m\beta\Psi^2}{\hbar^2} \delta\Psi. \quad (6)$$

Solutions for $\delta\Psi$ are, therefore, of the form $\exp(-z/\xi)$, where we have introduced the range of coherence $\xi = \hbar/2\Psi(m\beta)^{1/2} = \lambda_L/\sqrt{2\kappa}$.

While recognizing that, through the relation⁶ $\kappa = (m/2e\hbar)(\beta/2\pi)^{1/2}$, κ may, like β , be considered to be a function of temperature, we shall devote most of our attention to temperatures near the critical temperature, where the variation of κ is small.

We notice that ξ is related to, but distinct from, ξ_0 , the original Pippard coherence length which appears in the kernels of various nonlocal integral relations. Both ξ and λ_L depend on the reduced temperature t , and on l , the electronic mean free path in the normal state.

For a pure superconductor ($l \gg \xi_0$), when t is not too small,⁹

$$\lambda_L = \lambda_{Lp}(0) \{2(1-t)\}^{-1/2}, \quad (7)$$

where $\lambda_{Lp}(0)$ is the weak field London penetration depth of the pure superconductor at 0°K. Furthermore, using the result⁷ $\kappa_{t=1} = 0.96 \lambda_{Lp}(0)/\xi_0$, we find

$$\xi = 0.52 \xi_0 (1-t)^{-1/2}. \quad (8)$$

For a very impure superconductor ($l \ll \xi_0$), when t is not too small, Gor'kov⁸ and Caroli *et al.*¹¹ find

$$\lambda_L = 0.62 \lambda_{Lp}(0) \{\xi_0/l(1-t)\}^{1/2} \quad (9)$$

and

$$\xi = 0.60 \{l\xi_0/(1-t)\}^{1/2} \quad (10)$$

¹¹ C. Caroli, P. G. de Gennes, and J. Matricon, *Phys. Kondens. Materie* **1**, 176 (1963).

(Caroli *et al.*¹¹ employ ξ_T where we use $\sqrt{2}\xi$). For all values of l/ξ_0 the ratio λ_L/ξ tends to a definite limit near $t = 1$; its value is given, to within a few per cent,¹² by

$$\frac{\lambda_L}{\xi} = 1.36 \lambda_{Lp}(0) \left\{ \frac{1}{\xi_0} + \frac{1}{1.32l} \right\}. \quad (11)$$

III. TWO SIMPLE MODELS

We now apply the above results to two simple models for the behavior of a homogeneous single crystal of a superconductor. In each case let us introduce into the specimen (of negligible demagnetizing coefficient) one or more narrow flux-carrying regions lying parallel to the external field H_e . Each flux-carrying region is thought of as consisting of a normal core, carrying a uniform field H_0 , embedded in a superconducting matrix in which the London equation (1) is obeyed. Since we have seen that Ψ cannot vary much over a distance less than ξ it is natural to require that no dimension of the core shall be less than ξ . We consider two types of core: (a) plane laminas of uniform thickness 2ξ , and (b) cylinders of radius ξ . In general, the models are not expected to be reliable unless $\xi \ll \lambda_L$.

The Lamina Model

This model, originally considered by the author,¹³ is worth recalling, especially when one remembers that in the intermediate state of Pippard superconductors the flux is known to penetrate in lamina regions. The flux carried per unit width of an isolated lamina is, for $\xi \ll \lambda_L$,

$$\phi_l = 2H_0\lambda_L. \quad (12)$$

Since the laminas are thought of as being wide compared with any dimension characteristic of the superconducting state, we need not consider the possibility of the flux being quantized.

Taking the zero of energy to be that of the superconducting state in zero field, the Helmholtz free energy per unit area of an isolated lamina is

$$f_l = (1/4\pi) \{ \xi H_c^2 + \lambda_L H_0^2 \}, \quad (13)$$

where the first term on the right-hand side represents the configurational surface energy required to create the normal core³ and the second term comes from the energy density $\{H^2 + (\lambda_L \text{curl } H)^2\}/8\pi$ in the superconducting matrix. Writing $g_l = f_l - \phi_l H_e/4\pi$ for the Gibbs free energy per unit area we find, after mini-

mizing g_l with respect to H_0 , $H_0 = H_e$ and

$$g_l = (1/4\pi) \{ \xi H_c^2 - \lambda_L H_e^2 \}. \quad (14)$$

The initial penetration field, at which it becomes energetically favorable to introduce normal laminas, given by the condition $g_l = 0$, is

$$H_{c1} = (\xi/\lambda_L)^{1/2} H_c. \quad (15)$$

It may be shown that two parallel laminas, separated by a distance z , repel each with a pressure proportional to $\exp(-z/\lambda_L)$. Thus, when H_e exceeds H_{c1} only very slightly, the laminas, which are widely spaced, repel each other very weakly, so that a very slight further increase in H_e increases the flux inside the specimen rapidly. Once the distance between the laminas becomes comparable with λ_L , the flux penetrates more and more slowly with increasing field. In order to consider the behavior in fields large compared with H_{c1} one should take account of the effect of the field on the order parameter inside the superconducting matrix. Van Beelen and Gorter¹⁴ have recently proposed an empirical modification of the original lamina model which does this. They find that Eq. (15) remains practically unchanged and that a second-order transition to the normal state takes place at an upper transition field given by

$$H_{c2} \approx (\lambda_L/\xi) H_c. \quad (16)$$

The Flux Line Model

Friedel *et al.*¹⁵ have pointed out that, when $\xi \ll \lambda_L$, Abrikosov's flux lines can be pictured, in weak fields, as cylindrical cores of normal metal of radius ξ embedded in a superconducting matrix. The field in the superconductor at a distance r from the center of the core is then

$$H = H_0 \frac{K h_0(r/\lambda_L)}{K h_0(\xi/\lambda_L)}, \quad (17)$$

where $K h_n(x)$ is a modified Bessel function of the second kind. For the moment we assume without proof that just one quantum of flux $\phi_0 = h/2e$ is associated with an isolated flux line. Then, taking into account the contribution to ϕ_0 coming from the core ($\pi \xi^2 H_0$), Eq. (17) becomes

$$\begin{aligned} H &= \frac{\phi_0}{\pi \xi^2} \frac{K h_0(r/\lambda_L)}{K h_0(\xi/\lambda_L)}, \\ &\approx \frac{\phi_0}{4\lambda_L^2} K h_0 \left(\frac{r}{\lambda_L} \right) \quad \text{when } \xi \ll \lambda_L. \end{aligned} \quad (18)$$

¹⁴ C. J. Gorter, Rev. Mod. Phys. **36**, 27 (1964).

¹⁵ J. Friedel, P. G. de Gennes, and J. Matricon, App. Phys. Letters **2**, 119 (1963).

¹² B. B. Goodman, IBM J. Res. Develop. **6**, 63 (1962).

¹³ B. B. Goodman, Phys. Rev. Letters **6**, 597 (1961).

The Helmholtz free energy per unit length of flux line, made up of contributions $(H_c^2 + H_0^2)/8\pi$ per unit volume of normal core and $\{H^2 + (\lambda_L \text{curl } H)^2\} \times (8\pi)^{-1}$ per unit volume of superconducting matrix, is given by

$$f_{fl} = \pi\xi^2 \frac{H_c^2}{8\pi} + \frac{\phi_0^2}{8\pi^2\xi^2} \frac{Kh_0(\xi/\lambda_L)}{Kh_2(\xi/\lambda_L)}. \quad (19)$$

As before, the lower critical field is obtained by putting the Gibbs free energy per unit length of flux line, $g_{fl} = f_{fl} - \phi_0 H_c/4\pi$, equal to zero.

Let us now turn our attention to pure superconductors. Using Eqs. (7) and (8), together with the standard expressions $\xi_0 = \hbar v_F/\pi \Delta(0)$, where v_F is the Fermi velocity and $2\Delta(0)$ is the energy gap at 0°K, $H_c \approx 1.73(1-t)H_c(0)$, $H_c(0)^2/8\pi = N(0)\Delta(0)^2/2$, where $N(0)$ is the density of states at the Fermi surface for a single spin orientation, and $\lambda_{Lp}(0)^2 = 3/8\pi v_F^2 N(0)e^2$, we find that $H_c(0) = 6^{1/2}\phi_0/2\pi^2\lambda_{Lp}(0)\xi_0$, and hence that

$$\frac{H_{c1}}{H_c} = 0.13 \left(\frac{\xi}{\lambda_L}\right) + 2.0 \left(\frac{\lambda_L}{\xi}\right) \frac{Kh_0(\xi/\lambda_L)}{Kh_2(\xi/\lambda_L)}. \quad (20)$$

For impure superconductors Eqs. (9) and (10) lead to the same result, as expected.

Equation (20) is more convenient than Eq. (19), in particular, since it permits us to notice that for $\xi < \lambda_L$ the first term on the right-hand side is always appreciably smaller than the second. Since the second term varies as the square of the flux, it follows that it is not energetically favorable for two or more flux lines each containing a single quantum of flux to coalesce into a single flux line. Our choice of $\phi_0 = h/2e$ for an isolated flux line is therefore justified. For $\xi \ll \lambda_L$ Eq. (20) reduces to

$$\frac{H_{c1}}{H_c} = \frac{\xi}{\lambda_L} \left(1.0 \ln \frac{\lambda_L}{\xi} + 0.24\right). \quad (21)$$

It is obvious from Eq. (21) for $\xi \ll \lambda_L$, and can be shown also to follow from Eq. (20) when we merely have $\xi < \lambda_L$, that the flux line model predicts a lower value of H_{c1} than that given in Eq. (15) for the laminar model, so that the former has the lower free energy. Indeed, in retrospect, this seems to be a natural consequence of Eq. (19), which indicates that any pattern of flux penetration is unstable with respect to the formation of isolated flux lines each containing one quantum of flux.

In order to calculate the force of interaction between two flux lines, the simplification by Friedel *et al.*¹⁵ of Abrikosov's theory is again useful. When $\xi \ll \lambda_L$, the contribution to the Helmholtz free energy arising

from the simultaneous presence of two parallel flux lines, separated by a distance r , can be shown to be simply $\phi_0 H(r)/4\pi$, where $H(r)$, the field at the center of one flux line due to the other, is given by Eq. (18). From this result it follows that $F(r)$, the force of repulsion per unit length for two such flux lines, is given by

$$F(r) = -\frac{\partial}{\partial r} \frac{\phi_0 H(r)}{4\pi} = \phi_0 J(r) \approx \frac{\phi_0^2}{16\pi\lambda_L^3} Kh_1\left(\frac{r}{\lambda_L}\right), \quad (22)$$

where $J(r)$ is simply the contribution of one flux line to the current density at the center of the other. This is exactly the expression for a Lorentz force. For $r \gg \lambda_L$

$$F(r) \approx \frac{\phi_0^2}{(128\pi^3\lambda_L^5 r)^{1/2}} \exp\left(-\frac{r}{\lambda_L}\right). \quad (23)$$

The exponential decrease in this force for large r , somewhat similar in character to that found for the variation of the repulsive pressure between the laminas of the previous model, again leads to a rapid increase in the flux penetrating the specimen for H_c just larger than H_{c1} . Finally, although no simple extension of this model has yet been proposed which would allow for the variation of the order parameter in high magnetic fields, we may note that Abrikosov's theory, which does this, predicts a second-order transition to the normal state at a field H_{c2} given by

$$H_{c2} = \sqrt{2}\kappa H_c = (\lambda_L/\xi)H_c. \quad (24)$$

Bearing in mind the similarities and differences between the two models which have been discussed, we may draw the following conclusions from the experiments which have so far been performed. Several studies¹⁶⁻¹⁹ have all confirmed, as had first been suggested by the measurements of Shubnikov *et al.*,²⁰ that there exists a second kind of reversible magnetic behavior of superconductors which is characterized by (a) an initially rapid penetration of the specimen by the external field once the latter exceeds $H_{c1} < H_c$, and (b) the persistence of superconductivity up to an upper transition field $H_{c2} > H_c$. These are just the two features of the behavior which the two simple models lead us to expect when the surface

¹⁶ G. Bon Mardion, B. B. Goodman, and A. Lacaze, Phys. Letters 2, 321 (1962).

¹⁷ T. F. Stromberg and C. A. Swenson, Phys. Rev. Letters 9, 370 (1962).

¹⁸ J. D. Livingston, Phys. Rev. 129, 1943 (1963).

¹⁹ T. Kinsel, E. A. Lynton, and B. Serin, Phys. Letters 3, 30 (1962).

²⁰ L. W. Shubnikov, W. I. Kotkevich, J. D. Shepelev, and J. N. Riabinin, Zh. Eksperim. i Teor. Fiz. 7, 221 (1937).

energy becomes negative. For $H_{c1} < H_e < H_{c2}$ a London superconductor is said to be in the mixed state. Apart from the possibility that, if the mixed state exists as an array of flux lines, it may change symmetry at some value of H_e , the properties of the mixed state vary continuously as a function of H_e , and nothing in particular happens at the point $H_e = H_c$. The second-order nature of the transition at H_{c2} , observed by all the authors mentioned,¹⁶⁻²⁰ merely reflects the continuous reduction of the order parameter to zero, brought about by the magnetic field.

Any attempt to decide experimentally between a laminar and a flux line structure for the mixed state must therefore, at present, rely on a more quantitative comparison between theory and experiment, and so we shall now examine more closely Abrikosov's solution of the Ginzburg-Landau equations.

IV. ABRIKOSOV'S THEORY

Abrikosov¹⁰ has obtained two limiting solutions of the Ginzburg-Landau equations. In the low field limit it is found that the flux should penetrate the specimen in single quantum flux lines which qualitatively have the properties discussed in the previous section. In particular, when $\lambda_L \gg \xi$, Abrikosov finds

$$\frac{H_{c1}}{H_c} = \frac{\xi}{\lambda_L} \left[\ln \left(\frac{\lambda_L}{\xi} \right) - 0.27 \right], \quad (25)$$

which is very close to the result [Eq. (21)] obtained from simpler considerations. In Fig. 1 the chain curve represents Eq. (25). Harden and Arp²¹ have obtained numerical solutions of the Ginzburg-Landau equations for the minimum external field necessary to introduce a single quantum flux line for values of $H_{c2}/H_c = \lambda_L/\xi$ which are not large compared with unity. In Fig. 1 the continuous curve which passes through their points tends towards Abrikosov's relation for $H_{c2}/H_c \gg 1$, as it should.

If the normal nuclei which are the most easily formed on increasing H_e from zero are single flux lines, even when $\xi > \lambda_L$, then here Harden and Arp's curve represents an upper limit to the magnetic superheating field of a Pippard superconductor. Thus, in Fig. 1, the upper case letters indicate the regions of stability of the superconducting, mixed, and normal states, respectively, while the lower case letters indicate the regions where a state may be obtained in the metastable condition.

²¹ V. L. Harden and V. Arp, *Cryogenics* **3**, 105 (1963).

In Fig. 2 the relationship between H_{c2}/H_c and H_{c1}/H_c predicted by Abrikosov¹⁰ and Harden and Arp²¹ for the flux line structure of the mixed state is compared with the measurements of several authors.^{16,17,19,20,22-26} For a laminar structure of the mixed state we would have, according to Eqs. (15) and (16), $H_{c1}/H_c \approx (H_c/H_{c2})^{1/2}$. Unfortunately for $H_{c2}/H_c < 20$ these two relations between H_{c2}/H_c and H_{c1}/H_c differ by little more than the experimental error of up to 20% in the measured values of these quantities, so that those measurements do not allow us to choose between the two structures. Furthermore, for the only superconductor with a larger value of H_{c2}/H_c on which measurements have been made, V_3Ga ,^{22,23,26} the good agreement with the behavior expected for a flux line structure of the mixed state is subject to the reservation that here H_{c2} may be so large as to be influenced by the spin susceptibility of the normal state.²⁷

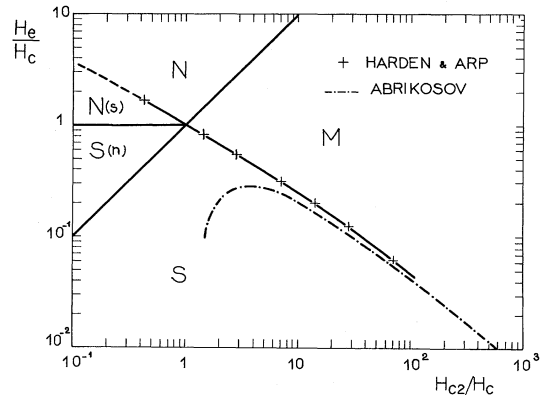


FIG. 1. Reduced magnetic phase diagram for reversibly behaved superconductors of zero demagnetizing coefficient, showing the regions of stability of the superconducting, mixed and normal states. The stable phase is indicated by an upper case letter and the metastable phase by a lower case letter in parentheses.

The upper transition field found by Abrikosov, given by Eq. (24), follows directly from the Ginzburg-Landau theory.⁶ Therefore, the excellent quantitative agreement that Berlincourt and Hake,²⁸ in particular, have found between the experimental values of H_{c2}/H_c and those predicted from

²² P. S. Swartz, *Phys. Rev. Letters* **9**, 448 (1962).

²³ F. J. Morin, J. P. Maita, H. J. Williams, R. C. Sherwood, J. H. Wernick, and J. E. Kunzler, *Phys. Rev. Letters* **8**, 275 (1962).

²⁴ W. DeSorbo, *Phys. Rev.* **130**, 2177 (1963).

²⁵ A. Calverley and A. C. Rose-Innes, *Proc. Roy. Soc. (London)* **A255**, 267 (1960).

²⁶ B. B. Goodman, *Phys. Letters* **1**, 215 (1962).

²⁷ A. M. Clogston, *Phys. Rev. Letters* **9**, 266 (1962).

²⁸ T. G. Berlincourt and R. R. Hake, *Phys. Rev.* **131**, 140 (1963).

Gor'kov's^{8,12} result

$$\kappa = \kappa_0 + 0.167 N(0)^{1/2} \rho_0 \quad (26)$$

(where ρ_0 is the resistivity in the normal state) does not constitute an experimental verification of the existence of flux lines in the mixed state. Equations (24) and (26) would apply equally well to the one-dimensional solutions of the Ginzburg-Landau equations which Marcus has presented.²⁹

Near H_{c2} Abrikosov predicts that the flux lines will arrange themselves in a square lattice. The side of this square lattice, which tends to $2\pi^{1/2}\xi$ when H_e tends to H_{c2} , is of the same order of magnitude as the spacing between the laminas at $H_e = H_{c2}$ in the laminar model.

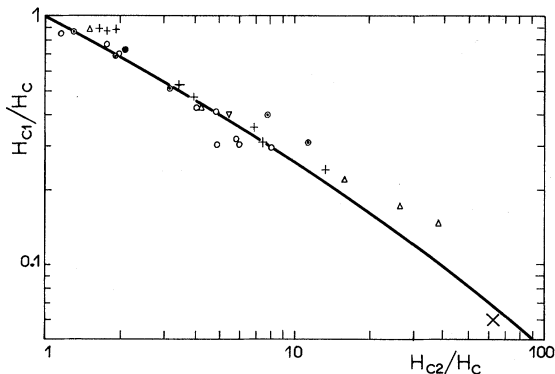


FIG. 2. Comparison of the relation between H_{c2}/H_c and H_{c1}/H_c predicted by Abrikosov (Ref. 10) and Harden and Arp (Ref. 21) (continuous curve) with experiment: ∇ Ta and alloys (Ref. 24), Δ V and alloys (Ref. 24), $+$ Nb and alloys (Refs. 17, 24, 25), \circ Pb-Tl alloys (Ref. 20), \odot Pb-Tl alloys (Ref. 16), \bullet In-Bi alloy (Ref. 19), \times V_3Ga (Refs. 22, 23, 26).

We conclude that although the theoretical arguments which indicate that the mixed state has a flux line structure rather than a laminar structure are extremely persuasive, there has not yet been performed an experiment which succeeds in distinguishing unambiguously between the two possibilities. The nearest approach, so far, to a verification of the flux line structure is probably provided by the agreement between the values of κ derived from different aspects of the magnetization curves of an In-Bi alloy studied by Kinsel *et al.*¹⁹

V. IRREVERSIBLE EFFECTS

So far we have been concerned principally with the properties of the mixed state in thermodynamic equilibrium, when each flux carrying region (which, from now on, we assume to be a single quantum flux line)

is in equilibrium under the influence of the repulsive forces due to its neighbors and, if it is near the surface of the specimen, the repulsive force due to the penetration of the external field into the interior of the specimen in accordance with Eq. (1).

In the presence of extended lattice defects we may expect small local fluctuations in the values of α and β in the Ginzburg-Landau equations to cause the free energy of a flux line to fluctuate with position, thus giving rise to potential barriers of various amplitudes near the lattice defects. Anderson,³⁰ by assuming that the fluctuations in α and β were of the order of a fraction of a percent, has derived a relation between the Lorentz force $\mathbf{J} \wedge \phi_0$, due to a current density \mathbf{J} in the neighborhood of the flux line, and the rate of thermally activated creep of flux lines or bundles of flux lines across the potential barriers.

The film shown by DeSorbo in Toronto at the 7th International Conference on Low Temperature Physics³¹ illustrated rather well the process of flux penetration in an irreversibly behaved specimen of niobium, a superconductor which we now know to be of the London type.¹⁷ Nothing resembling the intermediate state was seen, and the mixed state, having a structure which is too fine to be resolved by optical techniques, appeared as a continuously variable flux density. As the field surrounding a virgin specimen was gradually increased, the mixed state ate its way into the superconducting interior of the specimen, the existence of a fairly sharp front separating the two states corresponding to the rapid increase in flux penetration at a field H_{c1} in reversibly behaved specimens. The apparent pinning down of the boundary between the superconducting and the mixed states, at certain points where the flux lines must have been particularly firmly held, was evident from the fact that this boundary was concave outwards.

Occasionally this boundary moved too rapidly for the eye to be able to follow it, exhibiting what is now called a flux jump. Kim *et al.*³² have suggested that flux jumps are favored if the thermal energy released by the movement of bundles of flux lines is conducted away more slowly than the electromagnetic energy released by local heating is converted into heat, thus giving rise to an inherently unstable process which may ultimately render large parts of the specimen normal. Now both the removal of heat from a locally overheated region and the influx of electromagnetic energy through the normal conducting wake of a flux

³⁰ P. W. Anderson, Phys. Rev. Letters 9, 309 (1962).

³¹ W. DeSorbo and W. A. Healy, General Electric Research Laboratory, Report No. 61-RL-2743M, 1961 (unpublished).

³² Y. B. Kim, C. F. Hempstead, and A. R. Strnad, Phys. Rev. 129, 528 (1963).

²⁹ P. M. Marcus, Rev. Mod. Phys. 36, 294 (1964).

jump are governed by the diffusion equation, so that flux jumping should be favored if D_{th} , the thermal diffusivity, is small compared with the electromagnetic diffusivity of the normal state, D_{em} . If, as in many alloys, the thermal conductivity and specific heat are principally due to the conduction electrons, we have (neglecting differences in these properties between the normal and mixed states)

$$D_{th} = L_0/\gamma\rho_0, \quad (27)$$

where L_0 is the constant of the Wiedemann–Franz law and γ is the coefficient of the electronic specific heat per unit volume. Furthermore,

$$D_{em} = \rho_0/4\pi. \quad (28)$$

Using Gor'kov's result [Eq. (26)] for the case of a very impure alloy ($\kappa \gg \kappa_0$) we find

$$D_{th}/D_{em} = 0.17/\kappa^2, \quad (29)$$

so that we may expect flux jumping to be favored by large values of κ . Equation (29) would, of course, need modification for alloys in which the lattice plays a large role in the thermal properties, and it is interesting to note that flux jumping does not seem to have been observed in lead alloys, where the role of the lattice is indeed important.

The suggestion that flux jumping is due to a kind of instability which can occur when $D_{th} < D_{em}$ finds support in the effect of copper cladding on the niobium–zirconium wire used in superconducting solenoids. The transitions to the normal state which, in solenoids, frequently take place at values of the current density smaller than the critical values measured on isolated short specimens, and which are thought to be connected with flux jumping,^{32a} are inhibited by copper cladding. Suppose that a niobium–zirconium wire of radius a and residual resistivity ρ_a is electroplated with a thickness b of copper, of residual resistivity ρ_b . Then very crudely we may consider that the composite wire has a mean resistivity ρ_c given by the usual expression for resistances in parallel:

$$\frac{(a+b)^2}{\rho_c} = \frac{a^2}{\rho_a} + \frac{(2a+b)b}{\rho_b}. \quad (30)$$

For the niobium–zirconium alloy itself, $\kappa \approx 40$ and²⁸ $\rho_a \approx 30 \mu\Omega\text{-cm}$; Eq. (29) yields $D_{th}/D_{em} \approx 10^{-4}$. Furthermore, neglecting both the difference between the specific heats of copper and niobium–zirconium and also the composite nature of the wire (so that in

^{32a} H. Riemersma, J. K. Hulm, and B. S. Chandrasekhar, to be published in the Proceedings of the 1963 Cryogenic Engineering Conference, Boulder, Colorado.

both respects we underestimate the influence of the copper), we may use Eqs. (27) and (28) to predict that the composite wire behaves as if it had a mean value of $D_{th}/D_{em} \approx 10^{-4}(\rho_a/\rho_c)^2$. On the basis of what has already been said, we may expect flux jumping to be inhibited once the latter quantity is large compared with unity, or, inserting the usual values, $2a = 0.010$ in. and $b = 0.0015$ in., into Eq. (30), when $\rho_b < 0.1 \mu\Omega\text{-cm}$. The residual resistivity of electrolytically deposited copper can, of course, be much lower than $0.1 \mu\Omega\text{-cm}$, so that the inhibiting effect of copper cladding lends support to the suggestion that we must have, at least approximately, $D_{th}/D_{em} < 1$ for flux jumping to be possible.

Finally, we must examine the claims of the other hypothesis put forward to explain the magnetic behavior of superconducting alloys, namely, that in certain alloys there exists a mesh or sponge of superconducting filaments whose critical field exceeds that of the matrix which fills the intervening space.³³ Undoubtedly in certain special cases, such as that of mercury in porous Vycor glass,³⁴ or perhaps in certain very special metallurgical systems, this hypothesis may be valid. The latter case might arise if there were present different phases each extending over distance sufficiently large compared with the coherence length for it to be possible to consider them distinct superconductors.

However, the filamentary model fails to give any indication of the existence of an initial penetration field less than H_c , and the irreversible behavior of all the more usual superconducting alloys can be explained, qualitatively at least, in terms of the suggestion, due to Gorter³⁵ and Anderson,³⁰ to the effect that the mixed state may be pinned down by extended lattice defects. The critical value $J_c(H)$ of the local current density necessary to overcome the pinning force provides³⁰ a more natural basis than the filamentary model for Bean's³⁶ earlier suggestion that the magnetic properties of an irreversibly behaved superconductor may be described in terms of the function $J_c(H)$. Furthermore, while a number of authors have interpreted their measurements in terms of superconducting filaments which were thought to be dislocations,²⁹ it has been shown, beyond doubt, in two cases^{36,37} to be quite unnecessary to invoke the latter. Thus, far from being essential

³³ K. Mendelssohn, Proc. Roy. Soc. (London) **A152**, 34 (1935).

³⁴ C. P. Bean, M. V. Doyle, and A. G. Pincus, Phys. Rev. Letters **9**, 93 (1962).

³⁵ C. J. Gorter, Phys. Letters **1**, 69 (1962); **2**, 26 (1962).

³⁶ C. P. Bean, Phys. Rev. Letters **8**, 250 (1962).

³⁷ B. Bonnin, J. Geneste, and B. B. Goodman, Compt. Rend. **256**, 3274 (1963).

for the persistence of superconductivity up to very high magnetic fields, dislocations must probably be regarded as just one of several possible kinds of extended lattice defect which may pin down the flux lines in the mixed state. In agreement with the results of two very recent experiments^{37,38} on similar

³⁸ J. D. Livingston, General Electric Research Laboratory, Report No. 63-RL-3315M, 1963 (unpublished).

alloys covering a range of compositions (and therefore of values of ξ/λ_L) and of concentration of extended defects, we may safely conclude that the sign of the surface energy plays an overwhelmingly more important role in determining the magnetic behavior of superconductors than was generally thought two years ago.

Type II Superconductivity

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I. INTRODUCTION

Two ideal types of thermodynamically reversible superconductors are now known to exist. They are distinguishable according to their respective values for the Ginzburg-Landau¹ parameter $\kappa \sim \lambda_L(0)/\xi$, where $\lambda_L(0)$ is the London penetration depth at $T = 0$, and ξ is the superconducting coherence length. Superconductors for which $\kappa < 1/\sqrt{2}$ are characterized by a positive interphase surface energy and are designated as type I. The case $\kappa > 1/\sqrt{2}$ corresponds to negative surface energy or type II superconductivity.

This paper reviews developments of three decades which have led to the identification, experimental characterization, and theoretical understanding of type II behavior. Recent advances are discussed with reference to magnetic, thermal, and tunneling experiments, and the implications of these findings relative to the nature of very-high-field superconductors are explored. Size effects are also briefly mentioned.

II. HISTORY

Early magnetic and thermal investigations led to broad classification of superconductors as either "soft" or "hard." The former, principally pure strain-free elemental superconductors, were characterized by (1) nearly complete flux exclusion (Meissner effect) below the bulk thermodynamic critical field H_c , (2) a first-order phase transition with associated latent heat in the presence of a magnetic field H , (3) near coincidence of the resistive transition with H_c , and (4), except for some supercooling and superheat-

ing effects, independence of final state on magnetic and thermal history. Such characteristics comprised rather precise classification criteria and justified the early recognition of such behavior as characteristic of a thermodynamically reversible system. Such "soft" materials may be readily identified as positive-surface-energy type I superconductors.

On the other hand, the so-called "hard" superconductor classification was quite imprecise. In fact, with the advantage of hindsight we may discern two distinct and divergent trends in the early experimental evidence on "hard" superconductors. The first trend may be identified with two-phase alloy compositions in systems such as Pb-Bi, Sn-Bi, and Sn-Cd. Such two-phase materials *always* exhibited highly irreversible magnetic and thermal properties, and flux penetration commenced at fields much less than that required to restore a detectable resistance.² Modern studies by Shiffman *et al.*³ demonstrate that coherence effects analogous to those encountered in superimposed metallic films⁴ are operative in such two-phase systems and may lead to a spatial variation of T_c (transition temperature) sufficient in some instances^{3,5} to obscure the characteristic superconducting specific-heat jump. Consisting of both high- and low-critical-field material, two-phase alloys are clear examples of the Mendelssohn sponge structure.² Indeed, as correctly noted by Mendelssohn and Moore² nearly 30 years ago, such materials will *always* exhibit irreversible properties because the state of a given volume element will depend upon

² K. Mendelssohn and J. R. Moore, *Nature* **135**, 826 (1935).

³ C. A. Shiffman, M. Garber, J. F. Cochran, E. Maxwell, and G. W. Pearsall, *Bull. Am. Phys. Soc.* **8**, 66 (1963).

⁴ For a discussion of superimposed film effects see E. A. Lynton, *Superconductivity* (Methuen and Company, Ltd., London, 1962), p. 139 ff.

⁵ L. V. Shubnikov and V. I. Khotkevich, *Physik. Z. Sowjetunion* **6**, 605 (1934).

¹ V. L. Ginzburg and L. D. Landau, *Zh. Eksperim. i Teor. Fiz.* **20**, 1064 (1950); V. L. Ginzburg, *Nuovo Cimento* **2**, 1234 (1955).