

The Magnetic Behavior of Superconductors of Negative Surface Energy

Abstract: Abrikosov and the author have separately suggested that a new type of reversible magnetic behavior is to be expected in superconductors whose coherence length is small compared with their penetration depth. The treatments of these two authors are shown to lead to similar results for pure metals and to only slightly different results for alloys. The experimental evidence in favor of a new type of reversible magnetic behavior in superconductors is discussed.

1. Introduction

While the ideal magnetic behavior of a superconductor, characterized by its reversibility and by the disappearance of the magnetization M at the critical field H_c , is well understood, the frequently observed departures from this simple behavior have remained, in many respects, puzzling. However, in the light of comparatively recent measurements, it seems necessary to distinguish between two types of contribution to departures from ideal behavior:

- 1) There may be hysteresis, with flux being trapped in the superconductor when an external field greater than H_c is reduced to zero.
- 2) The field required for the complete suppression of the superconducting state may be much larger than the initial penetration field; this effect is quite distinct from that attributable to a nonzero demagnetizing coefficient.

The magnetization curves of certain specimens of rhenium and ruthenium¹ are extreme examples of behavior of type (1); while there is considerable hysteresis, the magnetization is suppressed over quite a narrow range of values of the external field. The measurements of Calverley and Rose-Innes² on a mixed single crystal of composition $Ta_{36}Nb_{64}$ show behavior of type (2) clearly, and by itself for the first time; while hysteresis is absent, the field required to suppress the superconducting state completely is more than ten times larger than the initial penetration field.

The impression that these two kinds of behavior are quite distinct is confirmed when one considers the rather scant experimental evidence concerning their respective origins. On the one hand, while flux trapping is not yet well understood, its relative absence in extremely well-annealed specimens, even of single-phase alloys,^{2,3} and its enhancement by cold working

(e.g., in tin⁴ or rhenium¹) or by fast neutron bombardment,⁵ support the idea that it is due to the presence of *extended* flaws in the specimen.⁶ Within these flaws the surface energy of a boundary separating a normal and a superconducting region probably assumes a value different from that characteristic of the flawless superconductor. On the other hand, the work of Abrikosov,⁷ based on the Ginzburg-Landau theory,⁸ and a somewhat similar treatment due to the author,⁹ both suggest that a superconductor with a *negative but spatially independent* surface energy should exhibit a new type of reversible magnetic behavior which we may identify with type (2) above. In this paper we shall compare the work of Abrikosov with that of the author and then review the evidence in favor of this new type of magnetic behavior of superconductors.

2. Abrikosov's theory

It is inherent in the Ginzburg-Landau theory that superconductors may be divided into two groups¹⁰ according to the value of the dimensionless parameter κ ; for superconductors of the first group ($\kappa < 1/\sqrt{2}$) the total surface energy of a normal-superconducting boundary is positive and the specimen exhibits ideal magnetic behavior, but for those of the second group ($\kappa > 1/\sqrt{2}$) a negative surface energy⁸ and quite different magnetic behavior⁷ are expected. This prediction is of particular interest since Gor'kov^{11,12} showed that, when the coherence length in the superconducting state is small compared with λ_L , the London penetration depth in small fields, then the Bardeen, Cooper and Schrieffer theory¹³ leads to the local Ginzburg-Landau equations if κ is given by:

$$\kappa = 2\sqrt{2}eH_c\lambda_L^2/\hbar, \quad (1)$$

e being the electronic charge. Throughout this paper we use electromagnetic units.

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Abrikosov's theory of the magnetic behavior of superconductors of the second group⁷ predicts the existence of two transition fields. For an external field $H < H_{c1}$ the specimen shows a perfect Meissner effect, while for $H > H_{c2}$ it is entirely in the normal state. For intermediate fields there exists a mixed state characterized by an array of filaments of flux threading the specimen. Abrikosov's asymptotic expressions for the free energy of such a superconductor, assuming a square array of flux filaments, (a) for H just greater than H_{c1} and (b) for H just less than H_{c2} , may be used to obtain, by interpolation, a smooth curve representing the free energy of the superconductor for all intermediate values of the field. Graphical differentiation of such curves, for several values of κ , leads to the magnetization curves shown in Fig. 1. Clearly these magnetization curves satisfy the thermodynamic condition

$$\int_0^\infty M dH = -H_{c2}/8\pi, \quad (2)$$

where, as for superconductors of the first group, $H_{c2}/8\pi$ is the difference in free energies per unit volume between the normal state and the superconducting state in zero field.

Strictly, in a narrow range of fields just above H_{c1} , a triangular array of filaments is predicted to have a slightly lower free energy than a square array, but since this consideration only slightly modifies the magnetization curves in Fig. 1 we have ignored it. Abrikosov's⁷ equation (36) which relates $h_1 = H_{c1}/H_c$ to $h_2 = H_{c2}/H_c = \sqrt{2}\kappa$, and which is only valid in the limit of large h_2 , is represented by the continuous curve, Fig. 2. For values of h_2 which are not large we have followed Abrikosov in assuming that the true

behavior is better represented by a curve, such as the broken one shown, passing through the point $h_1 = h_2 = 1$.

In Section 4 we shall compare experimental values of h_2 with those derived from values of κ estimated by one of the following methods:

1) In pure metals, for which we shall henceforth use the symbol κ_0 , three methods are available:¹⁴

(a) At temperatures sufficiently close to T_c , λ_L in Eq. (1) is large compared with the coherence length and then coincides with the measured penetration depth λ .
(b) One may derive $\lambda_L(0)$, the London penetration depth at absolute zero, from measurements of the anomalous skin effect^{15,16} and use the BCS relation,¹³ valid near T_c :

$$\lambda_L(t) = \lambda_L(0)\{2(1-t)\}^{-1/2}, \quad (3)$$

($t = T/T_c$). This procedure is analogous to using Gor'kov's¹¹ relation:

$$\kappa_0 = 2a\pi\sqrt{6/7\zeta(3)}\lambda_L(0)/\xi_0 \quad (4)$$

$$= 0.96\lambda_L(0)/\xi_0,$$

where $\xi_0 = a\hbar v/kT_c$ is the coherence length in the pure superconductor, $a = 0.18$ and v is the mean Fermi velocity.

(c) If $\kappa_0 < 1/\sqrt{2}$ then, near T_c , the limiting field to which the superconductor will supercool, is $\sqrt{2}\kappa_0 H_c$.

2) In alloys κ may be deduced from methods 1(a) and 1(c) above; however it is more useful to note Gor'kov's¹² prediction that the occurrence of electron scattering leads to a value of κ which is related to that of the pure metal by $\kappa = \kappa_0/\chi(\rho)$. Here $\rho = \hbar/8\pi^2 kT_c \sigma \lambda_L^2(0) = \xi_0/2\pi a l = 0.884\xi_0/l$, σ is the conductivity of the alloy in the normal state and l is the electronic mean free path; the function $\chi(\rho)$ tends

Figure 1 Magnetization curves of a superconductor, according to Abrikosov.

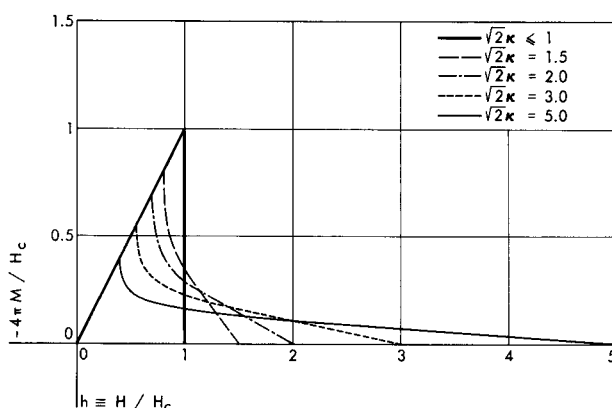
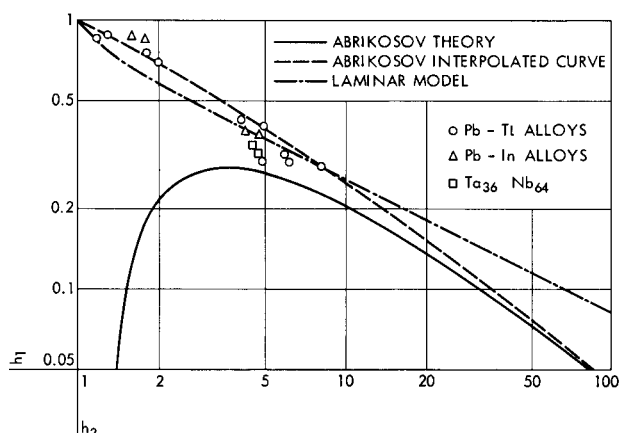


Figure 2 Relation between the two reduced transition fields for Abrikosov's theory and for the laminar model. Experimental points obtained by fitting magnetization curves to Abrikosov's theory.



to unity for $\rho \rightarrow 0$ and to $\pi^2/7\zeta(3)\rho$ for $\rho \rightarrow \infty$. If we define $\xi_G = \xi_0\chi(\rho)$ as the coherence length of the alloy, so that Eq. (4) is now extended to relate κ and ξ_G , then the latter quantity is given, to better than 6%, by the expression:

$$\xi_G^{-1} = \xi_0^{-1} + (\alpha'l)^{-1}, \quad (5)$$

where $\alpha' = 2\pi^3/7\zeta(3) = 1.32$. It is striking to note that the coherence length of an alloy originally introduced by Pippard, ξ_P , is given by an almost identical expression, α' being merely replaced by $\alpha \approx 0.8$.¹⁵

To within the accuracy of Eq. (5) one may then write

$$\begin{aligned} \kappa &= \kappa_0 + (e\gamma^{1/2}/\sigma k\pi^3)\sqrt{21\zeta(3)/2\pi} \\ &= \kappa_0 + 7.5 \times 10^{-6}\gamma^{1/2}/\sigma, \end{aligned} \quad (6)$$

where γ is the coefficient of the electronic specific heat per unit volume in the normal state. Unlike Gor'kov's Eq. (25) this equation is not restricted to alloys with $\rho \gg 1$.

3. The author's laminar model

Although suggestions^{17,18} concerning the role of a negative surface energy in superconducting alloys were made many years ago, it was not until recently that a very simple quantitative treatment based directly on this concept was put forward.⁹ Essentially this model supposes that in a magnetic field H a superconductor may split up into alternate normal and superconducting laminae lying parallel to the field. In addition to the magnetic free energy of the system, which, at an isolated boundary, may be thought of as giving rise to a surface energy $-\lambda H^2/8\pi$, there is assumed to exist a positive "configurational" surface energy of magnitude $\Delta'H_c^2/8\pi$. Pippard^{19,20} has suggested that Δ' should be of the order of ξ_P ; both ξ_P and λ may be estimated from his nonlocal theory.¹⁵

While for $q (= \Delta'/\lambda) > 1$ the model leads to ordinary "ideal" superconducting behavior, for $q < 1$ the magnetic behavior is quite different, a mixed laminar structure being stable between the two transition fields $h_1 = q^{1/2}$ and h_2 ; the upper transition field is given by $q = h_2 + (1 - h_2^2)\tanh^{-1}(1/h_2)$, $\approx 2/3h_2$ for $h_2 \gg 1$. The magnetization curves based on this model⁹ are clearly quite similar to those in Fig. 1. Since Eq. (2) must always be obeyed, it is therefore hardly surprising that the relation between h_1 and h_2 predicted by this model, represented by the chain curve in Fig. 2, is similar to that found by Abrikosov. The failure of the laminar model to predict a second-order transition from the mixed to the normal state arises from the fact that λ is assumed to be field-independent.

In attempting a more detailed comparison between the two models care must be exercised since, on the one hand the Ginzburg-Landau equations are only valid as long as the "density of superconducting electrons" may be considered small, i.e., at tempera-

tures close to T_c , while on the other hand Pippard's nonlocal theory is essentially concerned with the properties of ξ_P and λ at temperatures well below T_c . Nevertheless, just as Whitehead found for superconducting colloids,²¹ it seems probable that the shapes of the magnetization curves of superconductors of the second group do not change much as one passes from a temperature close to T_c to one small compared with T_c . Thus if the two models are physically equivalent, the values they predict for h_2 should be in fair agreement. For pure metals this is indeed so, since Abrikosov's theory leads to $h_2\xi_0/\lambda_L(0) = 1.35$, while according to the laminar model, for h_2 not too close to unity, the same quantity should equal $2/3$. However for alloys with $l \ll \xi_0$ the work of Abrikosov and Gor'kov suggests that h_2 should be equal to $1.02\lambda_L(0)/l$, while the laminar model predicts $h_2 = 0.93\lambda_L(0)\xi_0^{1/2}/l^{3/2}$. Thus the two models disagree in their dependence of h_2 on l ; Pippard²⁰ has suggested that according to the nonlocal theory, h_2 should be proportional to $l^{-1/2}$.

4. Comparison with experiment

(a) Tantalum-niobium alloys

The reversible magnetic behavior of an alloy of composition $\text{Ta}_{36}\text{Nb}_{64}$ has already been discussed briefly in terms of the laminar model,⁹ and we shall now extend this discussion somewhat. According to the nonlocal theory¹⁵:

$$\lambda(0) = \lambda_L(0)(\xi_0/\xi_P)^{1/2},$$

which, for $l \ll \xi_0$, becomes

$$\lambda(0) = (a\hbar/4\pi\alpha\sigma kT_c)^{1/2}. \quad (7)$$

Taking $a = 0.18$, $\alpha = 0.8$, $\sigma = 2.5 \times 10^{-4}$ emu and $T_c = 6.9^\circ\text{K}$ we find $\lambda(0) = 890$ A for this alloy*. The value $q = 0.16$ derived by fitting the experimental results to the laminar model therefore suggests that $\xi_P \approx 142$ A.

We may now note the particular interest afforded by the temperature variation of η , the permeability measured in a small alternating field, for two rather similar specimens, both of composition $\text{Ta}_{53}\text{Nb}_{47}$.² Since the results for the two specimens, reproduced in Fig. 3, are indistinguishable, and since the specimens had quite different flux trapping characteristics, it seems hard to believe that the width of the transitions was determined by anything susceptible to random variation, such as a slight inhomogeneity or a minority defect concentration in the specimen. Pippard²² has suggested that the breadth of the zero-field transition should be due to fluctuations in temperature of regions whose size is of the order of magnitude of the superconducting coherence length. The full curve in Fig. 3 represents Pippard's expression for the shape of the resistive transition (which we have assumed to be

*Previously⁹ $\lambda(0) = 800$ A was obtained by assuming $\alpha = 1$.

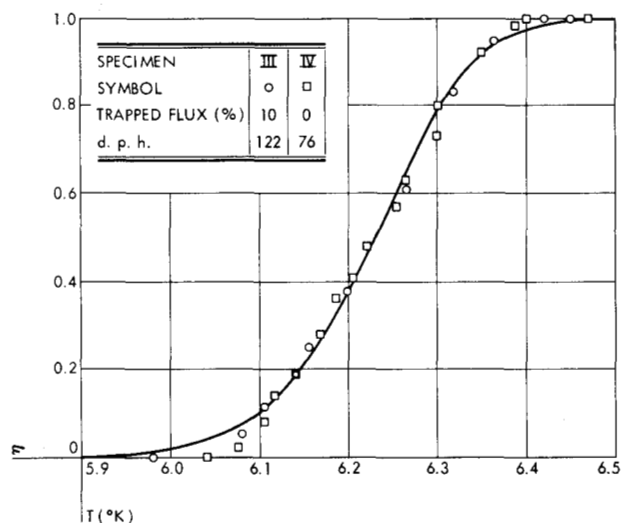


Figure 3 Temperature variation of the alternating field permeability of $Ta_{53}Nb_{47}$.

valid also for η) obtained by taking $T_c = 6.164^\circ K$, c_n (the specific heat per unit volume of the normal metal at T_c) $= 6.7 \times 10^4 \text{ erg cm}^{-3} \text{ deg}^{-1}$ (obtained by interpolation^{23,24}) and $\xi = 125 \text{ \AA}$. The small difference between the values of the coherence length for $Ta_{36}Nb_{64}$ and $Ta_{53}Nb_{47}$ could very well result from their somewhat different values of l .

Thus, except possibly for the nature of the transition at H_{c2} , the laminar model accounts reasonably well for what is so far known about these alloys. Nevertheless, the experimental points in Fig. 2, Reference 9, may be equally well represented by a very similar pair of curves, derived from Abrikosov's theory,⁷ if one takes $h_2 = 4.7$ and $H_c = 425$ oersteds at $6.0^\circ K$ and $h_2 = 4.5$ and $H_c = 890$ oersteds at $4.2^\circ K$. These values of h_2 may be compared with the prediction of Eq. (6). The slight supercooling found by Budnick²⁵ in pure tantalum suggests that for this metal $\kappa_0 \approx 0.6$; we shall use this value in Eq. (6). From the values of $H_c(T)$ given above we find $\gamma = 7000 \text{ erg cm}^{-3} \text{ deg}^{-2}$, which, together with $\sigma = 2.5 \times 10^{-4} \text{ emu}$,² leads to $h_2 = 4.4$, again in excellent agreement with experiment.

Since the behavior of the tantalum-niobium alloys does not therefore permit a clear choice to be made between Abrikosov's theory and the laminar model we shall now examine the behavior of two other alloy systems. Although neither has yet shown reversible magnetic behavior, there are indications in both cases of an initial penetration field less than H_c , as required for superconductors of the second group.

(b) Lead-thallium alloys

Magnetization curves of these alloys,²⁶ showing some hysteresis, have already been commented on by Abrikosov.⁷ Clearly, the experimental values of (h_1, h_2) plotted in Fig. 2 do not allow a choice to be

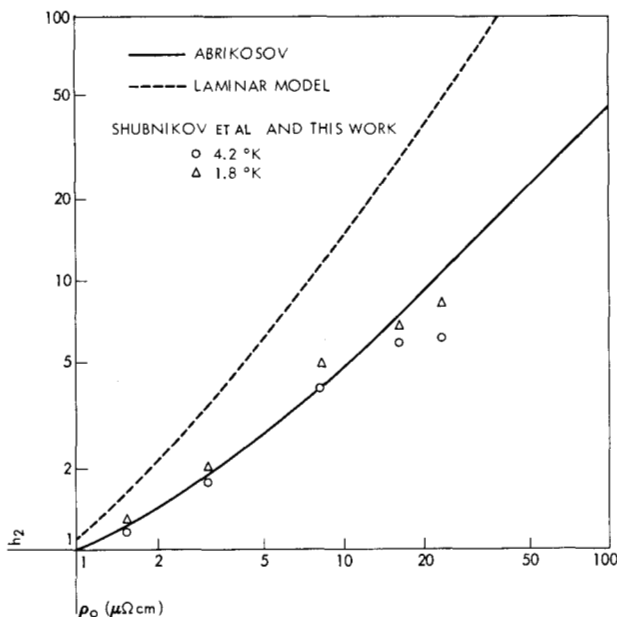
made between Abrikosov's theory and the laminar model. However, such a choice may be made by studying the behavior of h_2 as a function of ρ_0 , the residual resistivity. The laminar model, together with the non-local theory, leads to the broken curve in Fig. 4; it has been assumed that in the extreme anomalous limit the surface conductance Σ_∞ , and the angular frequency ω would continue to be related by $\omega^2 \Sigma_\infty^3 = 21 \text{ emu}$, as for pure lead.¹⁶ In order to study Abrikosov's theory we first need to know κ_0 for lead. The above value of $\omega^2 \Sigma_\infty^3$ leads, by procedure 1(b), to $\kappa_0 = 0.5$, while the results²⁷ $\lambda(0) = 390 \text{ \AA}$ and $(dH_c/dT)_{T_c} = -238 \text{ oersted deg}^{-1}$ lead²⁸ by procedure 1(a), to $\kappa_0 = 0.28$. By inserting the average value $\kappa_0 = 0.4$ into Eq. (6) and assuming that γ takes the same value as for pure lead,²⁸ viz., $1713 \text{ erg cm}^{-3} \text{ deg}^{-2}$ we obtain the continuous curve in Fig. 4. As expected, for small ρ_0 the two curves differ little, but for large ρ_0 their gradients tend, on a logarithmic plot, to $3/2$ and unity respectively.

In order to use the experimental values of h_2 already measured^{7,26} to test the two theories, the residual resistivities of alloys of the appropriate compositions have been measured. When plotted in Fig. 4 the results are seen to be in much better agreement with Abrikosov's theory than with the laminar model.

(c) γ -uranium-molybdenum alloys

Specific heat measurements²⁹ on alloys of this series containing about 25 at. % molybdenum may be used to estimate $H_c(T)$; at $1.2^\circ K$, for example, one finds 290 oersteds. However, even for a specimen showing considerable hysteresis, the initial penetration field at this

Figure 4 Upper reduced transition field as a function of residual resistivity, for lead-thallium alloys.



temperature was found to be only of the order of 100 oersteds.³⁰ Since hysteresis can only have the effect of increasing the initial penetration field above its true thermodynamic value, it seems clear that this alloy must be a superconductor of the second group with quite a small value of h_1 .

Existing information only permits its behavior to be compared with Abrikosov's theory. If, in Eq. (6), we neglect κ_0 and insert $\gamma = 12,500 \text{ erg cm}^{-3} \text{ deg}^{-2}$ (Ref. 29) and $\sigma = 1.3 \times 10^{-5} \text{ emu}$,^{30,31} we obtain $\kappa = 65$. Thus at 1.2°K we would expect $H_{c2} = 2.7 \times 10^4$ oersteds, which agrees, perhaps surprisingly well, with the observation that at this temperature the resistance is restored over the range of fields $(2.7 \pm 0.6) \times 10^4$ oersteds.³¹

5. Discussion

The close similarity between the predictions of Abrikosov and those of the author, together with their over-all agreement with the rather meager experimental evidence so far available, strongly suggests that a new type of reversible magnetic behavior is to be expected from superconductors in which the coherence length is

small compared with the penetration depth. There is some evidence that, of the two theories, that due to Abrikosov is to be preferred. A filamentary structure may therefore well exist in the mixed state, differing from previous suggestions,³² however, in that it arises even in the absence of extended defects and is then free to migrate as the external field is varied.

It is interesting to note that Abrikosov's theory and the author's model both predict a sudden fall in the magnetization of a superconductor of the second group when the external field just exceeds H_{c1} , contrary to what is observed in $\text{Ta}_{36}\text{Nb}_{64}$.² It may well be that the relevant feature missing in the two theories is that of local temperature fluctuations, such as undoubtedly contribute to the broadening of the zero-field transition.

Finally, it seems probable that a complete understanding of superconductors of the second group will eventually lead to an explanation of the differences of the patterns of trapped flux in "soft" and in "hard" superconductors.³³

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