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First-Order Transitions at H_{c1} and H_{c2} in Type-II Superconductors*

A. E. Jacobs
Department of Physics, University of Toronto, Toronto 181, Ontario, Canada
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From a consideration of several different definitions of the critical value of κ for type-II superconductivity at temperatures below T_c, it is proved that the initial flux penetration is not in the form of a singly quantized isolated vortex for pure to rather dirty materials with κ values near $1/\sqrt{2}$ at temperatures below T_c. It is predicted that the initial flux penetration in such materials is in the form of a vortex lattice with finite spacing; the transition at the field of first flux penetration would be first order in such materials, with a discontinuity in the magnetization and a latent heat. Recent experimental evidence supporting this prediction is discussed. A similar analysis leads to the prediction that the transition from the mixed state to the normal state is first order for very dirty materials ($l \lesssim \xi_0/50$) with κ values near $1/\sqrt{2}$, in qualitative agreement with the experimental results of Ehrat and Rinderer. Finally, it is shown by both qualitative and quantitative arguments that a negative normal-superconducting wall energy is only a sufficient condition for type-II superconductivity, and not a necessary one.

I. INTRODUCTION

The Ginzburg-Landau-Abrikosov-Gor'kov[1-3] (GLAG) theory of the properties of bulk superconductors in the presence of a magnetic field is now well established both theoretically[4] and experimentally.[5] If a magnetic field is applied to a type-I superconductor, the flux is completely excluded (except near the surface) for all values of the applied field H_a less than the thermodynamic critical field H_c; there is a first-order transition at $H_a = H_c$ from the Meissner state to the normal state as H_a is increased through H_c. For a type-II superconductor, flux exclusion from the bulk of the sample is complete for small values of H_a, but at $H_a = H_{c1} < H_c$ flux begins to penetrate. The initial flux penetration is in the form of an isolated vortex carrying one quantum of flux. It has been shown[6,7] that the interaction between isolated vortices is repulsive at $H_a = H_{c1}$ and hence the magnetization curve is continuous and the transition is of second order. Because the vortex-vortex interaction is exponentially weak at large distances, however, it is possible to accommodate many vortices in the sample at applied fields slightly larger than H_{c1} and the magnetization drops rapidly; the slope of the magnetization curve at $H_a = H_{c1} + 0$ is in fact predicted to be infinite. As H_a is increased beyond H_{c1}, the magnetization decreases in magnitude and goes linearly to zero at $H_a = H_{c2} > H_c$, at which point the sample becomes normal; like the transition at H_{c1}, the transition at H_{c2} is predicted by the GLAG theory to be second order—the magnetization is continuous and there is no latent heat. For applied fields between H_{c1} and H_{c2}, then, the flux penetration is incomplete, the microscopic magnetic field and the superconducting order parameter are functions of position, and the sample is said to be in the mixed state.

The quantity of the GLAG theory which determines if a given sample will show type-I or type-II behavior is κ, the ratio of the penetration depth to the Ginzburg-Landau (GL) coherence length; κ is defined more precisely below. In Sec. II we review the well-known reasons why the critical value of κ for type-II superconductivity is $1/\sqrt{2}$ in the GLAG theory; if κ is less than $1/\sqrt{2}$, the sample is type I, and if κ is greater than $1/\sqrt{2}$, it is type II.

The GLAG theory is, however, strictly valid only at $T = T_c$ and it is of interest to calculate κ_c, the critical value of κ for type-II superconductivity, at lower temperatures.[8] In Sec. III we use Tewordt's extension of the GLAG theory to lower temperatures to calculate the first-order correction in $1 - T/T_c$ to the GLAG result $\kappa_c = 1/\sqrt{2}$. We find, in contrast to the situation at $T = T_c$ where several different criteria give $\kappa_c = 1/\sqrt{2}$, that these same criteria give different results for κ_c at lower temperatures. For materials with $\kappa \approx 1/\sqrt{2}$ and large mean free paths, we show that the initial flux penetration at H_{c1} is not in the form of a singly quantized isolated vortex and predict that it is in the form of a vortex lattice with finite spacing; the transition at H_{c1} would then be first order, with a discontinuous magnetization curve and a nonzero latent heat. For materials with $\kappa \approx 1/\sqrt{2}$ and very short mean free paths, we predict that the transition at the upper critical field H_{c2} is first order, again with a discontinuous magnetization curve and a nonzero latent heat. Finally, we show on both qualitative (Sec. II) and quantitative (Sec. III) grounds that a negative value for the normal-superconducting wall energy σ_{NS} in a given superconductor at $H_a = H_c$ is only a sufficient condition for type-II superconductivity, and not a necessary one:

There is a range of parameter values such that $\sigma_{NS} > 0$, but the sample displays type-II behavior; on the other hand, when $\sigma_{NS} < 0$, there is no range of parameter values where the sample displays type-I behavior. Section III constitutes an expanded version of work presented in a previous publication.[9]

In Sec. IV, we discuss previous work related to first-order transitions at H_{c1} and H_{c2}; it appears that both have been observed. The prediction[9] and the observation of the first-order transition at H_{c1} were independent and essentially simultaneous. Previous theoretical work was speculative and has not been shown to be indicative of a first-order transition; previous experimental work was inconclusive. The observation[10] of the first-order transition at H_{c2} preceded Ref. 9; as a result, the theoretical work on the transition at the upper critical field presented in the previous[9] and the present articles should perhaps be regarded not as a prediction, but rather as an explanation or a verification. The author became aware of the work of Ehrat and Rinderer[10] only very recently.

II. CRITICAL VALUE OF κ AT $T = T_c$

From the discussion in Sec. I, it is clear that the requirements

$$H_{c1} < H_c \tag{1}$$

and

$$H_{c2} > H_c \tag{2}$$

must both be satisfied for a type-II superconductor; the initial flux penetration (the transition from the Meissner state to the mixed state) must take place at a field less than H_c and the completion of the flux penetration (the transition from the mixed state to the normal state) must take place at a field greater than H_c. In the GLAG theory, the values of H_{c1}/H_c and H_{c2}/H_c are completely determined by specifying a single mean-free-path-dependent parameter κ which is to be calculated from[3]

$$\kappa = \kappa_{\text{pure}}\, 7\zeta(3)/8S_{21}\,, \tag{3}$$

where

$$\kappa_{\text{pure}} = 4\gamma[\tfrac{14}{3}\zeta(3)]^{-1/2}\lambda_L(0)/\pi\xi(0)$$
$$= 0.96\lambda_L(0)/\xi(0)\,, \tag{4}$$

$$S_{ij} = \sum_{n=0}^{\infty}(2n+1)^{-i}(2n+1+\alpha)^{-j}\,, \tag{5}$$

$$\alpha = \pi\xi(0)/2\gamma l = 0.882\xi(0)/l\,, \tag{6}$$

$\xi(0)$ is the BCS coherence length at zero temperature $[\xi(0) = \hbar v_F/\pi\Delta(0)]$, $\lambda_L(0)$ is the London penetration depth at zero temperature, ζ is the Riemann ζ function, γ is Euler's constant ($\gamma = 1.781$), and l is the electronic mean free path. When κ is less than $1/\sqrt{2}$, the material is type I, and when κ is greater than $1/\sqrt{2}$, it is type II; there are at least four different reasons why the critical value of κ is $1/\sqrt{2}$ and we now review them.

(a) Near $H_a = H_{c2}$ the flux penetration is almost complete; the superconducting order parameter is small and the microscopic magnetic field is almost constant and almost equal to the applied field. On linearizing the first GL equation for the order parameter and substituting $\vec{A} = \vec{H}_a x\hat{y}$, one finds[2] that the largest value of H_a for which bounded solutions of the linearized equation exist is $H_a = H_{c2}$, where

$$H_{c2} = \sqrt{2}\,\kappa H_c\,. \tag{7}$$

Thus the inequality (2) is satisfied only when $\kappa > 1/\sqrt{2}$.

(b) The requirement that bounded solutions exist is necessary for a second-order transition but is not sufficient; one must also demand that the superconducting solutions have lower free energy than the normal-state solutions. A somewhat involved calculation[2,4] gives the result (valid near $H_a = H_{c2}$)

$$G_{\text{mixed}}(H_a) - G_{\text{normal}}(H_a) = \frac{-1}{8\pi}\frac{(H_a - H_{c2})^2}{(2\kappa^2 - 1)\beta_A}\,, \tag{8}$$

where β_A depends only on the structure of the vortex lattice; the magnetization near H_{c2} is given by

$$-4\pi M = (H_{c2} - H_a)/(2\kappa^2 - 1)\beta_A\,. \tag{9}$$

Equation (8) shows that the superconducting state has lower free energy than the normal state when $\kappa > 1/\sqrt{2}$.

(c) The third reason for $\kappa_c = 1/\sqrt{2}$ is that if the initial flux penetration is assumed to be in the form of an isolated vortex, then the lower critical field H_{c1} obeys the inequality (1) only when $\kappa > 1/\sqrt{2}$. It has been shown analytically that $H_{c1} = H_c$ for $\kappa = 1/\sqrt{2}$, independent of p, the number of flux quanta carried by the isolated vortex.[11] For $\kappa > 1/\sqrt{2}$, H_{c1} is calculated by inserting numerical solutions of the cylindrically symmetric GL equations into the GL free-energy expression and demanding that the Gibbs free energy of the sample containing a single vortex be equal to the Gibbs free energy of the sample in the Meissner state. The calculations for $p = 1$ and $p = 2$ have been carried out by Harden and Arp[12] and by Matricon,[13] respectively. Since H_{c1}/H_c for $p = 1$ is less than H_{c1}/H_c for $p = 2$ when $\kappa > 1/\sqrt{2}$, the initial flux penetration is in the form of a singly quantized isolated vortex rather than a doubly quantized isolated vortex. Since the free energy of an array of vortices is greater than that of an isolated vortex at $H_a = H_{c1}$, one concludes that the interaction between vortices is repulsive, that the transition at H_{c1} is of second order, and that the initial flux penetration is in the form of a singly quantized isolated vortex.

(d) In their paper on the phenomenological theory of superconductivity, GL[1] considered the problem of a superconductor in an applied field $H_a = H_c$ and calculated σ_{NS}, the energy of formation of a normal-superconducting wall. They showed analytically that $\sigma_{NS} > 0$ for $\kappa \ll 1$ and that $\sigma_{NS} < 0$ for $\kappa \gg 1$ and numerically that $\sigma_{NS} = 0$ for $\kappa = 1/\sqrt{2}$; an analytic proof that $\sigma_{NS} = 0$ for $\kappa = 1/\sqrt{2}$ has recently been given.[11] These results suggest that it is energetically favorable for superconductors with $\kappa > 1/\sqrt{2}$ to split up into normal and superconducting regions so that the flux penetrates thermogeneously. Clearly $\sigma_{NS} < 0$ is a sufficient condition for type-II superconductivity but it is not obviously a necessary one; this qualitative comment is justified quantitatively in Sec. III.

In conclusion, then, for $\kappa > 1/\sqrt{2}$ the GLAG theory predicts a second-order transition at H_{c1} from the Meissner state to the mixed state with a singly quantized isolated vortex and a second-order transition at H_{c2} from the mixed state to the normal state; for $\kappa < 1/\sqrt{2}$, there is a first-order transition at H_c from the Meissner state to the normal state. The GLAG theory is strictly valid only at $T = T_c$ but it is generally believed that its predictions are only quantitatively and not qualitatively modified at lower temperatures; in Sec. III it is shown that for superconductors with $\kappa \approx 1/\sqrt{2}$, qualitatively different results are obtained.

III. CRITICAL VALUE OF κ FOR $T < T_c$

The GLAG theory discussed in Sec. II is a highly idealized model of inhomogeneous superconductors; it is restricted to temperatures very close to T_c and it neglects many "real metal" effects. There has been considerable activity aimed at extending and modifying the theory to describe real metals at all temperatures; progress in this direction has recently been reviewed.[4] In this article, however, we will consider only the simplest model at temperatures just below T_c; more precisely, we treat only the first-order correction (in $1 - T/T_c$) to the GLAG theory.

The first exact calculation for general mean free paths of a property of interest in the theory of the mixed state at temperatures below T_c was Tewordt's calculation[14] of H_{c2}. This work was followed by the calculation of the correction term to the GL free energy[15] (obtained from Tewordt's earlier work[16]), the derivation of the differential equations for the corrections to the solutions of the GL equations for the isolated vortex geometry,[15] the calculation of H_{c1}/H_c as a function of κ and α for $p = 1$,[15] and the calculation of the slope of the magnetization curve near H_{c2}.[17] This author[18] has recently obtained the correction term to the GL free energy as an explicit function of the microscopic magnetic field, the order parameter, and the superfluid velocity for all geometries, and has derived the differential equations for the corrections to the solutions of the GL equations for all geometries. In the important cases of the mixed state in type-II superconductors and the normal-superconducting-wall problem, it was possible to express the correction to the GL free energy solely in terms of the solutions of the GL equations; for these two important geometries, then, in some calculations one can avoid the heavy numerical work associated with solving the differential equations referred to above. This formulation has been used[18] to calculate H_{c1}/H_c for isolated vortices with $p = 1$ (where agreement with the results of Neumann and Tewordt[15] was found) and $p = 2$, and to calculate σ_{NS}.

In the GLAG theory, the critical value of κ is $\kappa_c = 1/\sqrt{2}$; in this section, we address ourselves to the question of how κ_c is changed as the temperature is decreased from $T = T_c$. The procedure is the same as that used in Sec. II to show that $\kappa_c = 1/\sqrt{2}$ at $T = T_c$.

(a) The generalization of Eq. (7) to lower temperatures is

$$H_{c2} = \sqrt{2}\,\kappa_1 H_c\,; \tag{10}$$

κ_1 has been calculated by Tewordt[14,17] to be

$$\kappa_1 = \kappa[1 + (1-t)(\phi - \eta_c + \eta_k - \eta_{4d} - 6\eta_{4c})]\,, \tag{11}$$

where $t = T/T_c$ and ϕ and the various η's are defined in Refs. 15 and 18. As in the GLAG theory, H_{c2} is the largest value of the applied field for which bounded solutions of the linearized equation for the order parameter exist. Unlike the situation at $T = T_c$ where the mean free path dependence of quantities such as H_{c2} appears only in the quantity κ, at lower temperatures one obtains an explicit dependence on the mean free path. If we expand κ_c as

$$\kappa_c = \frac{1}{\sqrt{2}} - (1-t)\left.\frac{d\kappa_c}{dt}\right|_{t=1} + O(1-t)^2\,, \tag{12}$$

and calculate κ_c from $H_{c2} = H_c$, we find

$$\left.\frac{d\kappa_{c1}}{dt}\right|_{t=1} = \frac{\phi - \eta_c + \eta_k - \eta_{4d} - 6\eta_{4c}}{\sqrt{2}} \tag{13}$$

from our first definition of κ_c.

(b) The generalizations of Eqs. (8) and (9) to lower temperatures are

$$G_{\text{mixed}}(H_a) - G_{\text{normal}}(H_a) = \frac{-1}{8\pi}\frac{(H_a - H_{c2})^2}{(2\kappa_2^2 - 1)\beta_A} \tag{14}$$

and

$$-4\pi M = (H_{c2} - H_c)/(2\kappa_2^2 - 1)\beta_A\,; \tag{15}$$

we have used the Neumann-Tewordt definition for κ_2.[17] The expression for κ_2 near $T = T_c$ is[17]

$$\kappa_2 = \kappa\{1 + (1-t)[\phi - 2\eta_c + \tfrac{3}{2}\eta_k + \tfrac{1}{4}\eta_w - 2\eta_{4d} + (\tfrac{1}{2}\kappa^{-2} - 12)\eta_{4c}]\}\,, \tag{16}$$

where η_w is defined in Refs. 15 and 18. As our second definition of κ_c we define κ_{c2} as that value of κ for which the slope of the magnetization curve at H_{c2} is infinite or, equivalently, as the lowest value of κ for which the free energy of the superconducting solutions of the linearized equation is less than the free energy of the normal state; we find

$$\left.\frac{d\kappa_{c2}}{dt}\right|_{t=1} = \frac{\phi - 2\eta_c + \frac{3}{2}\eta_k + \frac{1}{4}\eta_w - 2\eta_{4d} - 11\eta_{4c}}{\sqrt{2}} . \quad (17)$$

(c) Neumann and Tewordt have expressed their result for H_{c1}/H_c for $p = 1$ as

$$H_{c1}/H_c = (H_{c1}/H_c)\big|_{t=1}[1 + (1-t)\delta_1(\kappa, \alpha)] ; \quad (18)$$

δ_1 has been tabulated as a function of κ and α.[15,18] As the third definition of κ_c we use $H_{c1} = H_c$ for $p = 1$ and find

$$\left.\frac{d\kappa_{c3}}{dt}\right|_{t=1} = \frac{\delta_1(1\sqrt{2}, \alpha)}{K_1} , \quad (19)$$

where

$$K_1 = \left.\frac{d}{d\kappa}\frac{H_{c1}}{H_c}\right|_{p=1} \quad \text{at } t = 1, \ \kappa = 1\sqrt{2} ; \quad (20)$$

the result of a separate calculation is $K_1 = -0.8628$.

The quantity H_{c1}/H_c for $p = 2$ has been calculated in Ref. 18 and the results expressed as

$$H_{c1}/H_c = (H_{c1}/H_c)\big|_{t=1}[1 + (1-t)\delta_2(\kappa, \alpha)] ; \quad (21)$$

δ_2 has been tabulated.[18] As the fourth definition of κ_c we use $H_{c1} = H_c$ for $p = 2$ and find

$$\left.\frac{d\kappa_{c4}}{dt}\right|_{t=1} = \frac{\delta_2(1/\sqrt{2}, \alpha)}{K_2} \quad (22)$$

where

$$K_2 = \left.\frac{d}{d\kappa}\frac{H_{c1}}{H_c}\right|_{p=2} \quad \text{at } t = 1, \ \kappa = 1/\sqrt{2} ; \quad (23)$$

the numerical value is $K_2 = -0.6469$.

(d) The normal-superconducting wall energy σ_{NS} has been calculated as a function of α for $\kappa = 1\sqrt{2}$ in Ref. 18, the results being given in the form

$$4\pi\sigma_{NS}/H_c^2\lambda = g_0(\kappa) + (1-t)g_1(\kappa, \alpha). \quad (24)$$

As the fifth definition of κ_c we take $\sigma_{NS} = 0$; the result is

$$\left.\frac{d\kappa_{c5}}{dt}\right|_{t=1} = \frac{g_1(1/\sqrt{2}, \alpha)}{K_\sigma} , \quad (25)$$

where

$$K_\sigma = \left.\frac{d}{d\kappa}g_0(\kappa)\right|_{\kappa=1/\sqrt{2}} = -1.0965 . \quad (26)$$

Equations (13), (17), (19), (22), and (25) together with

$$\kappa_{ci} = \frac{1}{\sqrt{2}} - (1-t)\left.\frac{d\kappa_{ci}}{dt}\right|_{t=1} \quad (27)$$

give five independent estimates of the correction to $\kappa_c = 1/\sqrt{2}$ for temperatures below T_c. In Table I we give the numerical values of $d\kappa_{ci}/dt$ at $t = 1$ for these five criteria as functions of $\alpha = 0.882\xi(0)/l$. As in Ref. 9, we extrapolate our results for κ_{ci} near $T = T_c$ to $T = 0\,^\circ$K to get an order-of-magnitude estimate for the maximum size of the effects; the table then gives the values of $1/\sqrt{2} - \kappa_{ci}$ extrapolated to $T = 0\,^\circ$K. As a result of the extrapolation, the numerical values given below are only approximate. The table has five interesting features, which we now list.

(i) Unlike the situation at $T = T_c$, the five different criteria give different results for κ_c.

(ii) For $\alpha \lesssim 50$, κ_{c3} is greater than κ_{c4}. For example $\kappa_{c3} = 0.7725$ and $\kappa_{c4} = 0.7495$ for $\alpha = 0$; this means that a sample in the Meissner state with a κ value of 0.76 would be unstable with respect to flux penetration in the form of a doubly quantized isolated vortex at some applied field less than H_c but would be stable with respect to flux penetration in the form of a singly quantized isolated vortex for all applied fields less than H_c. Thus the initial flux penetration in such a sample is not in the form of a singly quantized isolated vortex. As will be discussed below, however, we do not suggest for any material that the initial flux penetration is in the form of a doubly quantized isolated vortex.

(iii) For $\alpha \lesssim 40$, we have the inequalities $\kappa_{c2} < \kappa_{c1} < \kappa_{c4}$; the case $\alpha = 0$ is typical and we discuss it in detail. For $\kappa < 0.4190$, there are no bounded solutions of the linearized order parameter equation for applied fields greater than H_c, the sample is stable with respect to flux penetration in the form of singly and doubly quantized isolated vortices for all fields less than H_c, and the normal-superconducting wall energy is positive; we conclude that the sample is type I. For $0.4190 < \kappa < 0.7495$, the bounded solu-

TABLE I. $d\kappa_c/d(T/T_c)$ at $T = T_c$ as a function of α for five different definitions of κ_c.

			$H_{c1} = H_c$		
α	$\kappa_1 = 1/\sqrt{2}$	$\kappa_2 = 1/\sqrt{2}$	$p = 1$	$p = 2$	$\sigma_{NS} = 0$
0	0.2881	0.7694	−0.0654	−0.0424	0.0191
0.2	0.2506	0.6456	−0.0393	−0.0205	0.0300
0.5	0.2131	0.5226	−0.0140	+0.0007	0.0403
1.0	0.1758	0.4012	+0.0104	+0.0212	0.0500
2.0	0.1394	0.2827	0.0341	0.0410	0.0593
4	0.1118	0.1920	0.0530	0.0568	0.0670
10	0.0922	0.1228	0.0697	0.0712	0.0751
20	0.0861	0.0976	0.0776	0.0782	0.0797
50	0.0834	0.0826	0.0840	0.0840	0.0839
100	0.0831	0.0779	0.0869	0.0866	0.0860
∞	0.0838	0.0740	0.0910	0.0906	0.0893

tions exist for applied fields greater than H_c and are stable with respect to the normal-state solutions; hence the sample is in the mixed state for a range of applied field values greater than H_c. For this range of κ values, however, H_{c1} is greater than H_c if the initial flux penetration is assumed to be in the form of a singly or doubly quantized isolated vortex. But, since the area under the magnetization curve gives the free-energy difference between the superconducting and normal states, the initial flux penetration must take place at an applied field less than H_c if the flux penetration is incomplete for a range of applied field values greater than H_c; hence the initial flux penetration is not in the form of a singly or doubly quantized isolated vortex. There are many possibilities for the form of the initial flux penetration but a lattice of singly quantized flux lines with finite spacing is the most likely; this interpretation requires that the state with an isolated vortex be unstable with respect to the formation of a vortex lattice of finite spacing. It should be possible to extend the theory of the interaction of vortices at $T = T_c$ [2,6,7] to temperatures less than T_c to see if the above conjecture is correct; work on this problem is in progress. If the above interpretation is correct, the transition at H_{c1} would be first order and there would be a nonzero latent heat. For $\kappa > 0.7725$, we have $H_{c1} < H_c$ for $p=1$ and $H_{c2} > H_c$; hence there is no contradiction. It is likely, however, that the conjectured first-order transition at H_{c1} extends to κ values somewhat greater than the largest value for which a contradiction is obtained. The contradiction between κ_c defined from $\kappa_1 = 1/\sqrt{2}$ and $H_{c1} = H_c$ for $p=1$ was first noticed by Tewordt.[19] See Added Note.

(iv) For $\alpha \gtrsim 50$, one finds the inequalities $\kappa_{c3} < \kappa_{c4} < \kappa_{c1} < \kappa_{c2}$; the first of these implies that the flux penetration is in the form of a singly quantized rather than a doubly quantized isolated vortex. The case $\alpha = \infty$ is typical and we discuss it in detail; then $\kappa_{c3} = 0.6161$, $\kappa_{c1} = 0.6233$, and $\kappa_{c2} = 0.6331$. For $\kappa < 0.6161$, we have type-I behavior. For $0.6161 < \kappa < 0.6233$, H_{c1} is less than H_c for $p=1$ and hence the flux exclusion is incomplete for a range of fields less than H_c; bounded solutions of the linearized order parameter equation do not, however, exist (and would not be stable if they did exist) for any applied field greater than H_c. The flux penetration must be incomplete for some range of fields greater than H_c, however, and we conclude that there is a first-order transition at H_{c2}. For $0.6233 < \kappa < 0.6331$, H_{c1} is less than H_c and the bounded solutions exist but they are unstable; if one considers the shape of the magnetization curve as κ is decreased through $\kappa = 0.6331$ by varying the κ of the pure superconductor, one is led by a continuity argument to the conclusion that the transition at H_{c2} is first order. Experimental difficulties make it unlikely that the predicted first-order transition can be observed in simple materials; it is difficult to make high-quality samples with the very short mean free paths required and the range of κ values for which the first-order transition occurs is quite small. Moreover, samples with slightly greater κ values would have quite steep magnetization curves, making it difficult to distinguish a first-order transition from a second-order transition. As we discuss in Sec. IV, however, the first-order transition at H_{c2} has been observed[10]; a "real metal" effect (strong coupling) makes the observation possible.

(v) An inspection of Table I shows that for every value of α there exists a range of κ values such that $\sigma_{NS} > 0$, but the sample shows type-II behavior because either $H_{c2} > H_c$ or $H_{c1} < H_c$. For $\alpha = 0$, for example, σ_{NS} is greater than zero for κ less than 0.6280 but bounded solutions of the linearized order parameter equation exist for $H_a > H_c$ and are stable with respect to the normal-state solutions when κ is greater than 0.4190. Thus $\sigma_{NS} < 0$ is a sufficient condition for type-II superconductivity, but not a necessary one, in agreement with the qualitative argument in Sec. II.

IV. REVIEW OF RELATED WORK

In his article on flux penetration in type-II superconductors, Abrikosov[2] noted that if the transition at H_{c1} were of first order, then one would expect to find an intermediate mixed state in samples with a nonzero demagnetizing coefficient D for some range of applied fields greater than $(1-D)H_{c1}$; an experiment to observe this state was suggested by Gayley,[20] but was not carried out. By the "intermediate mixed state" we mean that the sample is divided into flux-free regions in the Meissner state and flux-carrying regions consisting of an array of vortices (rather than a homogeneous normal region as in the intermediate state in type-I materials). As discussed above, however, the transition at H_{c1} is predicted by the GLAG theory to be of second order for all κ values greater than $1/\sqrt{2}$; when a sample of type-II material with nonzero demagnetizing coefficient is placed in a magnetic field greater than the field of first flux penetration, the GLAG theory predicts a uniform distribution of vortices. In 1966, magnetization measurements on pure Nb were thought to indicate a first-order transition at H_{c1},[21] but Serin[5] states that the data are consistent with the GLAG theory. Somewhat earlier, an approximate calculation[22] of the magnetization curve between H_{c1} and H_{c2} at $T = T_c$ gave a first-order transition at H_{c1}, but it was later found that this result was in error and that the transition was indeed of second order.[23]

The intermediate mixed state as defined above has, however, been observed in Pb-In alloys by

Träuble and Essmann[24] in contradiction to the predictions of the GLAG theory; these results have been interpreted in terms of an attractive interaction between vortices, and the conclusion has been drawn that such materials would have a first-order transition (with the accompanying discontinuity in the magnetization curve and latent heat) at $H_a = H_{c1}$ in samples with zero demagnetizing coefficient.[25] At about the same time, theoretical work[26] on the structure of an isolated vortex at low temperatures indicated that the order parameter and the magnetic field displayed damped oscillations far from the center of the vortex for small κ, and it was postulated that this behavior could result in an attractive interaction between vortices. The results of Ref. 26 have been critized by Cleary,[27] however, and the relevance of the work of Eilenberger and Büttner[26] to the possibility of a first-order transition at H_{c1} is not clear.

Another unusual phenomenon in superconductors with small values of κ is that of field reversal[28] in the penetration of a magnetic field into a superconductor. The effect has been considered in detail by Halbritter[29]; for pure materials at low temperatures, it is found that the magnetic field changes sign deep inside the superconductor when $\kappa \lesssim 1.6$. Further work is required to determine how (if at all) the work of Eilenberger and Büttner,[26] the phenomenon of field reversal, and the work of this paper are interconnected. See Added Note.

Further experimental results on the intermediate mixed state have been obtained and a brief review of this work, with references, has been given[30]; Krägeloh[31] has described more recent work and Seeger[32] has commented on the present situation. Both Krägeloh and Seeger state that a first-order transition at H_{c1} has been observed,[33] but give no details; these articles were published after the submission of the manuscript of Ref. 9. In related work, Aston, Dubeck, and Rothwarf[30] have observed linear regions in the magnetization curves of Pb–2-at.%-In and In–1.5-at.%-Bi samples with nonzero demagnetizing coefficient.

It appears then that the first-order transition at H_{c1} predicted in Ref. 9 has been observed. Further experiments would, however, be desirable to test the mean free path and temperature dependence of the effect. In samples with κ less than $1/\sqrt{2}$, the discontinuity (in units of H_c) in the magnetization curve should increase with increasing temperature until at some temperature less than T_c the sample displays type-I behavior. In samples with κ greater than $1/\sqrt{2}$, the discontinuity should decrease with increasing temperature until, at some temperature less than T_c, the sample displays the usual GLAG behavior; in Ref. 32, it is stated that the latter behavior has been observed.

On the theoretical side, the theory of the interaction of vortices[2,6,7] should be extended to temperatures less than T_c to verify the conjecture that the state with an isolated vortex is unstable with respect to formation of a vortex lattice (or, more crudely, to verify that the interaction of vortices can be attractive) for the applied fields and κ values of interest. To calculate the field of first flux penetration may require a theory of the mixed state with finite vortex spacing; perhaps the best way to do this is to extend the Wigner-Seitz method of Marcus[22] to lower temperatures. The attractive interaction between vortices required to explain the intermediate mixed state is very likely related to the attractive interaction between vortices for $\kappa < 1/\sqrt{2}$ found in the GLAG theory,[7] modified at lower temperatures where the critical value of κ is no longer $1/\sqrt{2}$ and additional terms in the free energy must be considered. There is no reason to expect this attractive interaction to have a significantly longer range than the repulsive interaction. See Added Note.

It is of interest to interpret the results of a recent calculation[34] of H_{c1}/H_c at $T = 0\,^\circ\mathrm{K}$ in the light of the results of Sec. III. In Ref. 34, it was assumed that κ_c calculated from $H_{c2} = H_c$ was identical with κ_c calculated from $H_{c1} = H_c$ for initial flux penetration in the form of an isolated vortex with $p = 1$. For pure superconductors at $0\,^\circ\mathrm{K}$, κ_c from $H_{c2} = H_c$ is 0.56, while κ_c from $H_{c1} = H_c$ is 0.74; to account for this difference, it was assumed that the variational functions used in the calculation of the free energy were not good representations for the exact order parameter and magnetic field. It is now clear that the assumption that the two κ_c's are identical is incorrect and the variational functions of Ref. 34 are probably very good; for $T = T_c$, H_{c1}/H_c calculated using these functions differs by less than 2% from the exact values for κ between $1/\sqrt{2}$ and 50. The conclusion "as the temperature is decreased from T_c, the reduced lower critical field $H_{c1}(T)/H_c(T)$ for a given value of κ first increases above the GL value and then decreases below it" must also be changed; there is no evidence that H_{c1}/H_c decreases below the GL value at low temperatures.

We now turn our attention to the transition at H_{c2}. As we have discussed, it is unlikely that the first-order transition can be observed in the simple materials for which Tewordt's extension of the GLAG theory is valid; the theory neglects strong coupling, Fermi-surface anisotropy, spin paramagnetism, spin-orbit coupling, anisotropic defect scattering, multiple bands, and perhaps other "real metal" effects. In work overlooked in our previous article[9] on this subject, Ehrat and Rinderer[10] have, however, observed (in a Pb–2-at.%-In alloy with $\kappa \approx 0.72$) a discontinuity in the magnetization, in increasing field at constant temperature, at H_{c2}, as well as a high, narrow peak in the specific heat, at constant field in increasing temperature, at the temperature at which the mixed-state–normal-state phase boundary is crossed. Because the latent heats calculated from the magnetic and calorimetric measurements agree to within 10%, we believe these observations to be bulk effects indicative of a first-order transition at H_{c2}; we do not believe the suggestion[35] that "a discontinuity in the magnetization in increasing field ··· can be due to a sharp difference in surface pinning at H_{c2}" to be applicable to the measurements of Ehrat and Rinderer. The first-order transition is observable in the relatively clean samples of Ehrat and Rinderer because of strong-coupling effects.[36] Fischer and Usadel[36] have used arguments similar to those used in Ref. 9 and Sec. III above to explain the results of Ehrat and Rinderer. Our arguments are, however, more complete in that, by showing that H_{c1} is less than H_c, we have proved the existence of the mixed state in the materials under consideration; since the effects of strong coupling on H_{c1} have not been calculated, the corresponding demonstration was not carried out by Fischer and Usadel, leaving open the possibility that the material is actually type I. The work of Fischer and Usadel[36] and this author[9] on the nature of the transition at H_{c2} was independent and essentially simultaneous.

Finally, we mention that first-order transitions at H_{c2} have been predicted by Sarma[37] for a uniform exchange field acting on the conduction-electron spins and by Maki[38] for a superconductor with large Pauli-spin paramagnetism relative to the spin-orbit coupling. The discussion of Maki's work by Fetter and Hohenberg[4] is similar to our argument for a first-order transition at H_{c2}. The work of Sarma and Maki is, however, unrelated to the results of Sec. III.

Added Note. The interaction between widely separated vortices at temperatures below T_c has been examined theoretically[39] and has been found to be attractive for κ near $1/\sqrt{2}$ and small to moderately large values of ξ_0/l, in agreement with our comments above; an extrapolation to $T = 0$ °K predicts, for example, an attractive interaction for $\kappa < 1.382$ and $\xi_0/l = 0$. The attractive interaction is just the attractive interaction found by Kramer[7] in the GLAG theory for $\kappa < 1/\sqrt{2}$, modified at lower temperatures. In Ref. 39 it is argued that the phenomenon of field reversal and the work of Eilenberger and Büttner are *not* related to an attractive interaction between vortices in type-II materials near T_c, although the situation at lower temperatures is not clear. A mechanism by which field reversal might lead to an attractive interaction at lower temperatures is suggested in Ref. 39.

In work published very recently, Kumpf[40] has reported observation of steep linear regions near H_{c1} in the magnetization curves of Pb-Tl alloys and, with reservations, in Nb single crystals; the demagnetizing factor in these experiments was 0.02 and there is little room for doubt that the transition is first order. Similar results were obtained earlier by Aston, Dubeck, and Rothwarf,[30] but in samples with a much larger demagnetizing factor (~0.45). Whether the observations of Ref. 21 were the first indication of a first-order transition at H_{c1} is a question which we do not attempt to answer here. Although a pure, simple metal with the same κ value as Nb (0.78)[21] should have a first-order transition at H_{c1} at sufficiently low temperatures, the neglect of real metal effects may be serious, and one cannot apply with confidence the theory developed above to such a material.

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Interaction of Vortices in Type-II Superconductors near $T = T_c$

A. E. Jacobs
Department of Physics, University of Toronto, Toronto 181, Ontario, Canada
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The theory of Müller-Hartmann and Kramer for the interaction of widely separated vortices is extended to temperatures immediately below T_c. The interaction is found to be attractive below T_c for type-II materials with $\kappa \approx 1/\sqrt{2}$ and not too small a mean free path, in agreement with experimental observations on such materials. The phenomenon of field reversal and the work of Eilenberger and Büttner are shown to be unrelated to an attractive interaction between vortices and the consequent first-order transition at the lower critical field, at least for temperatures near T_c; it is shown how field reversal, if it occurs in the mixed state, might result in an attractive interaction at lower temperatures.

I. INTRODUCTION

In the Ginzburg-Landau theory, the interaction between vortices, at the applied field at which flux penetrates in the form of an isolated vortex, has been shown to be repulsive[1,2] for $\kappa > 1/\sqrt{2}$ and attractive[2] for $\kappa < 1/\sqrt{2}$. Since the critical value of κ for type-II superconductivity is $1/\sqrt{2}$ in the Ginzburg-Landau theory, the interaction is repulsive for type-II superconductors. This is not conclusive evidence that the phase transition at the field of first flux penetration is of second order, but it is highly suggestive; a proof that the first flux penetration is in the form of a singly quantized isolated vortex requires a demonstration that the free energy for each and every possible form of flux penetration be greater than that of a singly quantized isolated vortex.

The Ginzburg-Landau theory is, however, strictly valid only at $T = T_c$, and the nature of the initial flux penetration at lower temperatures is an open question. Recently, both theoretical and experimental evidence has been obtained for a first-order transition at the field of first flux penetration, and hence for some materials ($\kappa \approx 1/\sqrt{2}$ and mean free path l not much smaller than ξ_0) the first flux penetration is not in the form of a singly quantized isolated vortex. The experimental evidence has been partially reviewed in a previous article.[3] The most direct evidence is the observation of a first-order transition by Krägeloh, Kumpf, and Seeger[4]; this work is unpublished at the time of writing, and Krägeloh[5] and Seeger[6] merely state that the first-order transition has been observed,