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 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.

[38] J. D. Livingston, General Electric Research Laboratory, Report No. 63-RL—3315M, 1963 (unpublished).

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–Landau[1] 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 superheating 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 films[4] 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 Moore[2] nearly 30 years ago, such materials will *always* exhibit irreversible properties because the state of a given volume element will depend upon

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

[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).

whether H is applied before or after the high-critical-field sponge is cooled below T_c. The specific-heat data of Mendelssohn and Moore[6] on Sn–4 at.% Bi (most likely a two-phase alloy[7]) represent an interesting example of such behavior.

In accounting for the high critical field of the sponge, Mendelssohn and Moore[2] hypothesized very thin meshes and invoked a new concept due to London,[8] viz., that magnetic stress relaxation associated with flux penetration in superconductors of thickness $d \ll \lambda$ would raise their transition fields H_d in approximate accord with

$$H_d(d \ll \lambda)/H_c \propto \lambda/d\,. \tag{1}$$

This expression is mainly of conceptual interest here, for we now know that in two-phase materials coherence effects will complicate this relationship. *Nevertheless, it should be emphasized that for such materials the transition field is a sensitive function of the dimension d of a sponge element, and the high-critical-field sponge is anchored to a given metallurgical phase.* Interesting examples of such systems have recently been studied by Cline *et al.*[9] and Seraphim *et al.*[10]

The second trend discernible in the early studies of "hard" superconductors anticipated many of the modern theoretical and experimental results on materials which we now recognize as "ideal" type II superconductors, and which, in contrast to the two-phase materials discussed above, are characterized by thermodynamic reversibility. Interesting theoretical concepts bearing on this trend were set forth in 1935 by London[8] and Gorter.[11] On the experimental side, Shubnikov *et al.*,[12] in 1937, studied the magnetization $M(H)$ curves of carefully prepared single-phase, single-crystal alloys in the systems Pb–Tl and Pb–In and speculated on the existence of a critical alloy composition (between 0.8 and 2.5 at.% Tl in Pb) which marks the boundary between type I and II behavior. Their $M(H)$ data show reasonable accord with the ideal type II curve shown schematically in Fig. 1. In fact, they remarked: "Such unusual magnetic properties of superconductors cannot be explained by hysteresis phenomena, inasmuch as it is just at high increasing and diminishing fields that the phenomenon is quite readily reversible and the hysteresis is quite low." Accordingly, with insight prophetic of developments to follow some 25 years later, Shubnikov *et al.* noted (1) that $\int MdH$ should represent the superconducting state condensation energy, (2) that even though the alloy upper critical field H_{c2} greatly exceeded the field H_c characteristic of a typical pure metal, the condensation energies for the two cases were comparable and depended upon T in the same way, and (3) that, therefore, the zero-field specific heat jump

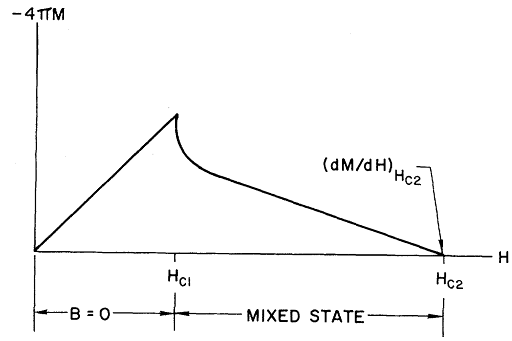

FIG. 1. Magnetization curve (schematic) for an ideal type II superconductor.

in an alloy superconductor should be comparable to that of a pure superconductor. In fact, Shubnikov *et al.* estimated a jump of $\sim$7% for Tl–33 at.% Pb. Unfortunately, such a jump was not detected in measurements[13] which had earlier demonstrated the absence of the order-of-magnitude-larger jump which would accompany complete flux exclusion up to H_{C2}.

Characteristic type II calorimetric data were obtained shortly thereafter by Keesom and Desirant.[14] In 1941 they reported results for Siemens Ta (impure by modern standards) in magnetic fields up to 3 kG and noted the inapplicability of thermodynamics based on complete flux exclusion. Smoothed curves of their data are presented in Fig. 2(a). Although these data lack modern precision, they can be shown to be semiquantitatively consistent with second-order phase transition theory for a type II superconductor with $\kappa \sim 2.5$. As noted by Keesom and Desirant,

[6] K. Mendelssohn, Proc. Roy. Soc. (London) **A152**, 34 (1935).
[7] That the nominal Sn–4 at.% Bi alloy studied in Ref. 6 may have consisted of two phases is implied by the $\sim$0.3°K depression of T_c below that observed by W. F. Love [Phys. Rev. **92**, 238 (1953)] for a quench-stabilized, single-phase alloy of the same nominal composition.
[8] H. London, Proc. Roy. Soc. (London) **A152**, 650 (1935).
[9] H. E. Cline, R. M. Rose, and J. Wulff, J. Appl. Phys. **34**, 1771 (1963).
[10] D. P. Seraphim, F. M. d'Heurle, and W. R. Heller, Appl. Phys. Letters **1**, 93 (1962).
[11] C. J. Gorter, Physica **2**, 449 (1935).
[12] L. V. Shubnikov, V. I. Khotkevich, Yu. D. Shepelev, and Yu. N. Riabinin, Zh. Eksperim. i Teor. Fiz. **7**, 221 (1937).
[13] K. Mendelssohn and J. R. Moore, Proc. Roy. Soc. (London) **A151**, 334 (1935). This negative result may not have been a consequence of detection sensitivity alone, for even today the metallurgical structure in the vicinity of this alloy composition remains uncertain [see M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958), p. 1113 ff.].
[14] W. H. Keesom and M. Desirant, Physica **8**, 273 (1941).

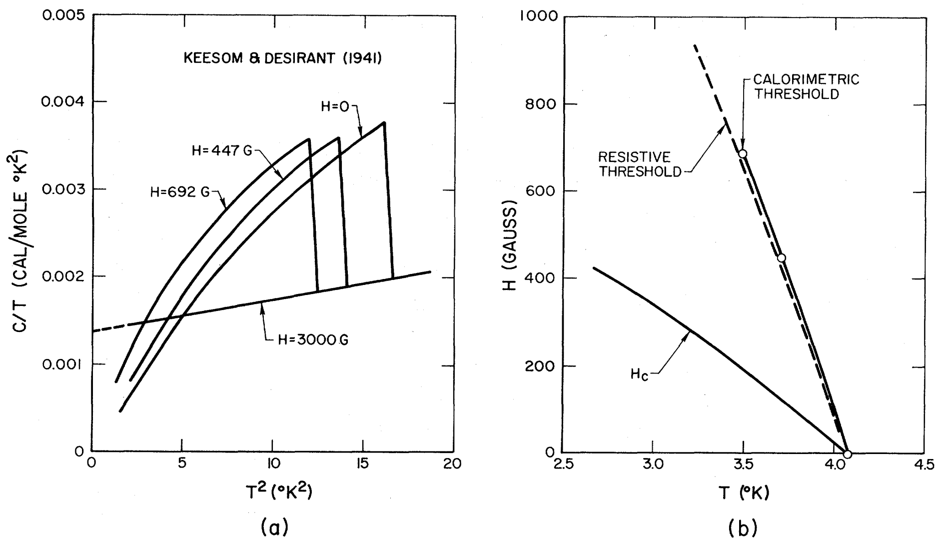

FIG. 2. (a) Early data (1941) of Keesom and Desirant (Ref. 14) for the specific heat C of impure Ta in various magnetic fields. These smoothed curves represent a fair approach to ideal type II behavior. (b) Comparison of resistive (Mendelssohn and Moore, Ref. 15) and calorimetric threshold curves (normalized at T_c) for Siemens Ta of the same era. The thermodynamic critical field H_c was calculated from calorimetric values of T_c and γ.

their calorimetric threshold field curve and the resistive threshold field curve of Mendelssohn and Moore[15] (also for Siemens Ta) exhibited nearly equal slopes [see Fig. 2(b)]. This appears to be the first evidence that the resistive threshold in a type II superconductor is associated with a bulk, nonfilamentary transition. Although this correlation could have been construed as a fortuitous consequence of metallurgical variability, such an explanation now appears unlikely.[16]

Thus, by 1941, the magnetic and calorimetric character of type II superconductors had been probed, and, in fact, the thermodynamic consequences of reversibility had been recognized by Shubnikov *et al.*[12] That this salient point was not generally recognized might be a consequence of several factors. Extensive data on two-phase sponge superconductors and on nonideal type II superconductors tended to obscure the more meager ideal type II data. Also, progress was probably inhibited by World War II and by the fact that the work of Shubnikov *et al.* was published in Russian.

Definitive recognition of type II superconductivity waited some 10 years for the theoretical developments of the Ginzburg–Landau theory,[1] and the negative-surface-energy ideas of Pippard.[17] Then, in 1952, Abrikosov[18] and Zavaritskii[19] identified alloy superconductivity with the case $\kappa > 1/\sqrt{2}$ of the Ginzburg–Landau theory. The classic paper of Abrikosov[20] on type II superconductors appeared five years later and set forth a comprehensive model with κ as a parameter.

Gor'kov's subsequent derivation[21] of an expression for κ in terms of T_c and measurable bulk electronic parameters of the normal state placed the theory on a more explicit basis. In addition, Gor'kov[22] suggested that type II behavior might not be confined solely to alloys, for, by virtue of large penetration depth and short intrinsic coherence length, a defect-free, chemically pure elemental superconductor might be characterized by $\kappa > 1/\sqrt{2}$. It should be emphasized at this juncture that the high upper critical field of the ideal type II superconductor follows from the spatially uniform negative surface energy, as determined by uniform *bulk* electronic parameters, rather than, as in the sponge superconductor, from the *size* of inhomogeneities.

The significance of the work of Abrikosov and Gor'kov was not generally recognized until after Goodman[23] applied a simplified negative-surface-energy theory to the quasireversible $M(H)$ data of

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[15] K. Mendelssohn and J. R. Moore, Phil. Mag. **21**, 532 (1936).

[16] A similar correlation between calorimetric and resistive values for $(dH_{c2}/dT)_{T_c}$ was noted by G. T. Armstrong [J. Am. Chem. Soc. **71**, 3583 (1949)] in comparing his calorimetric data on NbN with the resistive transition data of G. Aschermann, E. Friederich, E. Justi, and J. Kramer [Physik. Z. **42**, 349 (1941)].

[17] A. B. Pippard, Proc. Cambridge Phil. Soc. **47**, 617 (1951).

[18] A. A. Abrikosov, Dokl. Akad. Nauk SSSR **86**, 489 (1952).

[19] N. V. Zavaritskii, Dokl. Akad. Nauk SSSR **86**, 501 (1952).

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

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

[22] L. P. Gor'Kov, Zh. Eksperim. i Teor. Fiz. **37**, 835 (1960) [English transl.: Soviet Phys.—JETP **10**, 593 (1960)].

[23] B. B. Goodman, IBM J. Res. Develop. **6**, 63 (1962); Phys. Rev. Letters **6**, 597 (1961).

Calverley and Rose-Innes[24] on Nb–Ta alloys and further suggested that the very high upper critical fields newly discovered by Kunzler *et al.*[25] might be associated with type II behavior. Evidence in support of this view was provided shortly thereafter by Berlincourt and Hake[26] in studies of the upper critical fields of very-high-field nonideal type II superconductors. In addition, several features of the Abrikosov $M(H)$ curve were verified by Bon Mardion *et al.*,[27] Kinsel *et al.*,[28] and Livingston[29] in studies of ideal lower-field materials. In the next section the corroborative evidence will be reviewed in more detail, aspects which remain to be tested will be noted, and areas where experiment has outrun theory will be indicated.

III. RECENT DEVELOPMENTS

A. Properties of Bulk Specimens

According to Abrikosov[20] the magnetization curve for a bulk type II superconductor (see Fig. 1) is characterized by complete flux exclusion from $H = 0$ up to the lower critical field H_{c1}. Above H_{c1} flux gradually penetrates, forming throughout the sample a "mixed state" comprised of a lattice of quantized, flux-enclosing supercurrent vortices. It is this magnetic stress relaxation mechanism which allows superconductivity to survive in high magnetic fields. We may note that the "mixed state" is a bulk superconducting state in the sense that the position-dependent superconducting state energy gap is finite everywhere except along a (zero-volume) line at the center of each vortex. The transition to the normal state is of the second order and takes place at a field given by

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

where H_c is defined by

$$\int_0^{H_{c2}} M dH \equiv \frac{H_c^2}{8\pi}\,. \tag{3}$$

The theory also yields the expressions

$$(dM/dH)_{H_{c2}} = [1.18(4\pi)(2\kappa^2 - 1)]^{-1} \tag{4}$$

and

$$H_{c1}(\kappa \gg 1) = (H_c/\sqrt{2}\,\kappa)(\ln \kappa + 0.08)\,. \tag{5}$$

In tests of his theory, Abrikosov used the data of Shubnikov *et al.*[12] He deduced H_c values from Eq. (3) and used these values along with Eq. (2) and experimental H_{c2} values to deduce κ values. This permitted calculation of $(dM/dH)_{H_{c2}}$ according to Eq. (4), and H_{c1} according to Eq. (5). Agreement with experiment was excellent in the former case. In the latter case, the condition $\kappa \gg 1$ was not fulfilled and discrepancies arose, but these have since been resolved by extension of the theory to small κ.[23,30]

The recent magnetization studies of Bon Mardion *et al.*[27] and Kinsel *et al.*[28] on homogeneous low-melting-point alloys ($\kappa \lesssim 10$) yielded still better internal consistency among the quantities H_c, κ, H_{c2}, $(dM/dH)_{H_{c2}}$, and H_{c1}. Also, in several instances the approach to reversibility was better than achieved in the early studies of Shubnikov *et al.* The closest approach to reversibility yet reported appears to be that observed by Stromberg and Swenson[31] in studies of type II behavior in very high purity Nb [$\rho(300°\mathrm{K})/\rho(4.2°\mathrm{K}) = 1900$] for which $\kappa \sim 1.1$. These data also illustrate the approximate nature of Abrikosov's theory for small-κ materials in that the $M(H)$ curves exhibited significant departures from predicted values of H_{c1} and $(dM/dH)_{H_{c2}}$. In fact, Abrikosov indicated that the transition at H_{c1} could be either first or second order, depending upon the magnitude of κ, and further that a predicted change in the symmetry of the vortex lattice just above H_{c1} could lead to another small (first-order) transition.

As already mentioned, Gor'kov's explicit expressions[21] obviate the necessity of treating κ as an adjustable parameter. For a pure crystal (with electronic mean free path much greater than the BCS coherence length) he obtained a relation which may be written[32]

$$\kappa_0 = 1.61 \times 10^{24}(T_c\gamma^{3/2}/n^{4/3})(S_f/S)^2\,, \tag{6}$$

where γ is the electronic specific heat coefficient in erg cm^{-3} deg^{-2}, n is the number of "valence" electrons per unit volume, S is the free area of the Fermi surface, and S_f is the area of the Fermi surface for a free electron gas of density n. For an impure sample, Gor'kov obtained a more complicated expression, which Goodman[23] has approximated as

$$\kappa = \kappa_0 + \kappa_l = \kappa_0 + 7.53 \times 10^3 \rho_n \gamma^{1/2}\,, \tag{7}$$

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

[25] J. E. Kunzler, E. Buehler, F. S. L. Hsu, and J. H. Wernick, Phys. Rev. Letters **6**, 89 (1961); see also J. E. Kunzler, Rev. Mod. Phys. **33**, 501 (1961).

[26] T. G. Berlincourt and R. R. Hake, Bull. Am. Phys. Soc. **7**, 408 (1962); Phys. Rev. Letters **9**, 293 (1962); Phys. Rev. **131**, 140 (1963).

[27] G. Bon Mardion, B. B. Goodman, and A. Lacaze, Phys. Letters **2**, 321 (1962).

[28] T. Kinsel, E. A. Lynton, and B. Serin, Phys. Letters **3**, 30 (1962).

[29] J. D. Livingston, Phys. Rev. **129**, 1943 (1963).

[30] J. L. Harden and V. Arp, Cryogenics **3**, 105 (1963).

[31] T. F. Stromberg and C. A. Swenson, Phys. Rev. Letters **9**, 370 (1962).

[32] B. B. Goodman, Phys. Letters **1**, 215 (1962).

where ρ_n is the normal state resistivity in Ω-cm. In apparent accord with this equation Goodman[23] and Livingston[29] have found κ to be a linear function of ρ_n in Pb alloys for which constancy of κ_0 and γ is a reasonable assumption.

A more detailed adjustable-parameter-free prediction of magnetization curve features can be accomplished in terms of the measurable quantities γ, T_c, ρ_n, n, and S/S_f if we add to Eqs. (2) and (4)–(7) the relation

$$H_c \approx 2.42\,\gamma^{1/2}T_c[1-(T/T_c)^2]\,, \qquad (8)$$

which follows from the BCS relation[33] $\gamma T_c^2/H_0^2 \approx 0.17$ and the approximation $H_c \approx H_0[1-(T/T_c)^2]$, where $H_0 = H_c(T=0)$. Although data on S_f/S are usually unavailable, errors in estimating this quantity are of little importance for alloys in which $\kappa_l \gg \kappa_0$. In several such instances, reasonable agreement between theory and experiment has been found by Berlincourt and Hake,[26] Bon Mardion *et al.*,[27] and Kinsel *et al.*[28]

Several of the experimental results mentioned above involved relatively low-κ ($H_{c2} \lesssim 3$ kG) samples which exhibited nearly ideal reversible type II behavior and were hence incapable[34,35] of supporting large transport current densities. It could be argued that such measurements shed little light on the question of a choice between the sponge model [as typified by Eq. (1)] and the Ginzburg–Landau–Abrikosov–Gor'kov (GLAG) mechanism as the basis for high-field superconductivity in the very-high-critical-field, high-current-density samples of materials such as Nb_3Sn, V_3Ga, Zr–Nb, Ti–Nb, and Ti–V. However, in their studies of concentrated transition metal alloys having resistive transition fields as great as 145 kG, Berlincourt and Hake[26] noted a near independence of the low-current-density resistive critical field $H_r(J \lesssim 10\ \text{A/cm}^2)$ on degree of cold-working and relative orientations of field, current, and defect structure. This suggested that $H_r(J=10)$ was a function of the bulk parameters of the GLAG theory rather than the defect parameters of Eq. (1). Moreover, adjustable-parameter-free comparisons of $H_r(\text{J}=10)$ with H_{c2} of the GLAG theory revealed excellent accord for wide ranges of alloy composition. Discrepancies noted for certain compositions could be simply accounted for in terms of paramagnetic lowering of the normal-state free energy, a consideration ignored in the GLAG formulation. Such an effect was predicted independently by Chandrasekhar[36] and Clogston[37] in reference to the sponge model, but is equally applicable to the GLAG picture. Clogston's model, which appears to show the better accord with experiment, leads to a paramagnetic limit for the upper critical field given by

$$H_p \approx (\epsilon_0/\sqrt{2}\,\mu_B)[1-(T/T_c)^2] = 18\,400\,T_c[1-(T/T_c)^2]\,, \qquad (9)$$

where $2\epsilon_0$ is the energy gap at $T=0$, and μ_B is the Bohr magneton. It may be simply shown[26] that the experimental upper critical field should be less than the smaller of the GLAG and Clogston predictions. That this indeed appears to be the case is illustrated for the Ti–V system in Fig. 3.

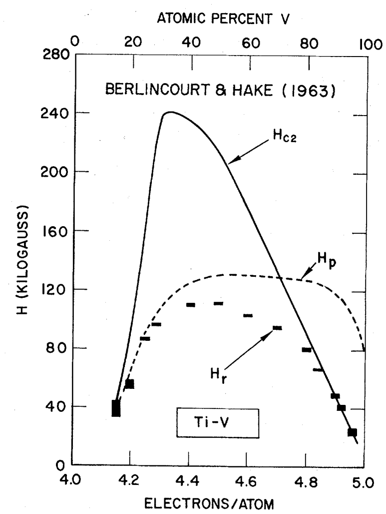

Fig. 3. $H_r(J = 10\ \text{A/cm}^2$, $T = 1.2°\text{K})$, $H_{c2}(T = 1.2°\text{K})$ [from Eqs. (6)-(8) and (10)], and $H_p(T = 1.2°\text{K})$ [from Eq. (9)] vs composition and electron concentration for Ti-V alloys (Berlincourt and Hake, Ref. 26). Excellent quantitative accord is obtained between H_r and H_{c2} for V-rich alloys. Elsewhere, limits appear to be imposed by paramagnetic depression of the normal state free energy as implied by the near agreement between H_r and H_p.

Additional evidence in support of the GLAG mechanism as the basis for the high-field survival of superconductivity in nonideal, very-high-field superconductors is to be found in the magnetization studies of Hauser,[38] Swartz,[39] and DeSorbo.[40] Also pertinent are the calorimetric studies of Morin *et al.*,[41] who noted that in applied fields as great as 70 kG magnetically hysteretic V_3Ga underwent *reversible* specific heat jumps (similar to those of Fig. 2) of magnitude indicative of bulk transitions. These transitions coincided in H and T with the resistive

[33] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[34] J. W. Heaton and A. C. Rose-Innes, Appl. Phys. Letters **2**, 196 (1963).
[35] R. A. Kamper, Phys. Letters **5**, 9 (1963).
[36] B. S. Chandrasekhar, Appl. Phys. Letters **1**, 7 (1962).
[37] A. M. Clogston, Phys. Rev. Letters **9**, 266 (1962).
[38] J. J. Hauser, Phys. Rev. Letters **9**, 423 (1962).
[39] P. S. Swartz, Phys. Rev. Letters **9**, 448 (1962).
[40] W. DeSorbo, Phys. Rev. **130**, 2177 (1963).
[41] F. J. Morin, J. P. Maita, J. H. Williams, R. C. Sherwood, J. H. Wernick, and J. E. Kunzler, Phys. Rev. Letters **8**, 275 (1962).

transitions observed by Wernick *et al.*[42] for the same material. The bulk character of these specific-heat data was originally attributed to nearly complete filling of the sample volume with dislocation-centered, high-field superconducting filaments (i.e., to inhomogeneities) of the type reliant for their existence upon the mechanism inherent in Eq. (1). However, Goodman[33] pointed out that such results are equally compatible with the GLAG picture, and, by thermodynamic procedures, deduced reasonable type-II-like magnetization curves from the calorimetric data. A definitive choice between the defect and GLAG hypotheses is possible, because on the former the magnitude of the specific-heat jump should diminish with decreasing dislocation content. Recent measurements of a high-perfection reversible type II superconductor by Hake[43] have demonstrated that the high-field specific-heat jump is not reliant for its existence upon defects such as dislocations, and also that the magnitudes of the specific-heat jumps are in good *quantitative* accord with thermodynamic theory for second-order phase transitions of the GLAG type.[44] Hake has further shown that over a considerable range of T the high-field superconducting electronic specific heat follows an exponential form, reflecting a field-dependent "effective" energy gap, possibly representative of the spatially varying gap of the Abrikosov theory. Such an "effective" gap was also used by Dubeck *et al.*[45] in accounting for the magnetic field dependence of thermal conductivity in type II superconductors.

These results taken together add weight to the argument that the so-called "mixed state"[20] is, in fact, a *pure* superconducting state in the sense that the volume fraction of material with a finite energy gap is unity for all fields less than H_{c2}. Although this ideal high-field state by itself cannot support large transport current densities,[34,35] it nonetheless emerges as a choice superconducting medium into which relatively modest inhomogeneities may be introduced to stabilize transport currents by the mechanisms of Gorter[46] and Anderson.[47]

Implicit in Eqs. (2), (6), (7), and (8) is a temperature independence of the ratio H_{c2}/H_c. However, more detailed considerations of the theory have led to a variety of temperature dependencies[22,48,49] [all of which agree with Eq. (2) near T_c]. Experimental results[26,50,51] appear to range mainly between the Gor'kov[22] and Ginzburg[48] predictions, which are given, respectively, by

$$H_{c2} = [1.77 - 0.43(T/T_c)^2 + 0.07(T/T_c)^4]\kappa H_c \quad (10)$$

and

$$H_{c2} = 2\sqrt{2}\,\kappa H_c/[1 + (T/T_c)^2]\,. \quad (11)$$

Thus the deviations from a universal form appear to be much greater than in the case of $H_c(T)$. This is not unexpected, since differences may arise between large and small κ or between $\kappa_0 \gg \kappa_l$ and $\kappa_0 \ll \kappa_l$, and the paramagnetic limit [Eq. (9)] may lead to complications. On the other hand, the large spread in the data could merely reflect experimental uncertainties, especially since many of the data apply to nonideal samples studied by resistive techniques in pulsed magnetic fields. For a number of reasons, specific-heat measurements are superior to magnetization measurements which are, in turn, superior to resistive measurements as a means for determining $H_{c2}(T)$. In any event, two aspects of $H_{c2}(T)$ are worthy of further comment. First, none of the observed curves appears to display the large $(dH_{c2}/dT)_{T=0}$ predicted by Shapoval.[49] Second, as experimentally demonstrated by Wipf,[52] a superconductor which exhibits type I behavior at high temperatures may undergo a transition to type II behavior at lower temperatures. This will occur if κ is less than $1/\sqrt{2}$ but large enough to lead in equations such as (10) and (11) to a coefficient of H_c which is greater than unity at some temperature below T_c.

B. Properties of Thin Specimens

From the foregoing, it is apparent that bulk type II superconductors have been rather extensively investigated and are reasonably well characterized by theory. The picture is less complete for thin samples. The universal relation plotted in Fig. 4 represents Abrikosov's early (1952) prediction[18] for the thickness and temperature dependence of the upper critical field for a plate or film of thickness d

[42] J. H. Wernick, F. J. Morin, F. S. L. Hsu, D. Dorsi, J. P. Maita, and J. E. Kunzler, *High Magnetic Fields* (Tech. Press, Cambridge, Massachusetts, and John Wiley & Sons, Inc., New York, 1962), p. 609.

[43] R. R. Hake, Bull. Am. Phys. Soc. **8**, 475 (1963); Rev. Mod. Phys. **36**, 124 (1964).

[44] For a discussion of complications observed in calorimetric studies of a type II superconductor characterized by a much smaller κ, see T. McConville and B. Serin, Rev. Mod. Phys. **36**, 112 (1964).

[45] L. Dubeck, P. Lindenfeld, E. A. Lynton, and H. Rohrer, Phys. Rev. Letters **10**, 98 (1963).

[46] C. J. Gorter, Phys. Letters **2**, 26 (1962).

[47] P. W. Anderson, Phys. Rev. Letters **9**, 309 (1962).

[48] V. L. Ginzburg, Zh. Eksperim. i Teor. Fiz. **30**, 593 (1956) [English transl.: Soviet Phys.—JETP **3**, 621 (1956)].

[49] E. A. Shapoval, Zh. Eksperim. i Teor. Fiz. **41**, 877 (1961) [English transl.: Soviet Phys.—JETP **14**, 628 (1962)].

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in a longitudinal field. Implicit in this theory are the relations

$$\kappa(T) = [(\sqrt{8})e/\hbar c]H_c\lambda^2 \qquad (12)$$

(which is modernized here to include the double electronic charge), $H_c = H_0\,[1-(T/T_c)^2]$, and $\lambda = \lambda(T=0)[1-(T/T_c)^4]^{-\frac{1}{2}}$ where λ is the low-field penetration depth. Thus $\kappa(T)$ is a temperature-

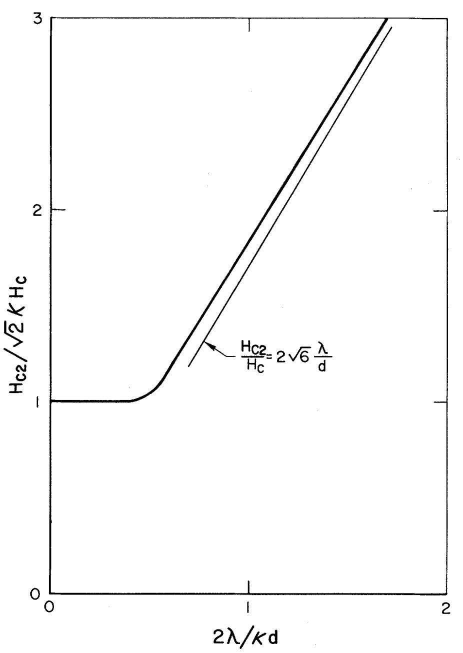

FIG. 4. Abrikosov's predicted universal dependence of H_{c2} on T and thickness d for films of type II superconductors.

dependent quantity in Eq. (12) (a departure from earlier convention in this paper) which yields the same temperature dependence for H_{c2} as Eq. (11). As the film thickness is decreased the increase of H_{c2} above the bulk value becomes significant in the vicinity of a critical thickness[53]

$$d_c = 2(\sqrt{5})\lambda/\kappa(T) = (10/\pi)^{\frac{1}{2}}d_v\,, \qquad (13)$$

where d_v is the vortex lattice spacing characteristic of a bulk sample at the bulk upper critical field. For very thin films, H_{c2} asymptotically approaches the form

$$H_{c2}(d \ll \lambda/\kappa)/H_c = 2(\sqrt{6})\lambda/d\,, \qquad (14)$$

which also applies to type I superconductors. Recent longitudinal-field measurements by Khukhareva[54] on disordered elemental films ($\kappa \sim 2$ to 7) deposited at low temperatures appear to support this picture for $T \approx T_c$ and yield penetration depths of the order of several thousand Å. Also of interest are her graphs of $\ln H_{c2}$ vs $\ln \Delta T$ where $\Delta T = T_c - T$. For each film thickness two straight-line segments, of slope $\frac{1}{2}$ and 1, are obtained. In analyzing her data from a purely empirical viewpoint, we have found that these lines intersect at upper critical field values H_{c2} which accurately satisfy the relation

$$d = (\phi_0/H'_{c2})^{1/2}\,, \qquad (15)$$

where $\phi_0 = hc/2e$ is the flux quantum appropriate to superconductivity, i.e., as T is decreased, the change from $H_{c2} \propto (\Delta T)^{\frac{1}{2}}$ to $H_{c2} \propto \Delta T$ takes place abruptly when the vortex lattice spacing which corresponds to the transition field becomes small enough to fit within the film thickness. Equation (15) is compared with experiment in Fig. 5, where values of $(\phi_0/H'_{c2})^{\frac{1}{2}}$ deduced from Khukhareva's data are plotted against d.

The thickness dependence of H_{c1} has apparently not been treated theoretically. However, we may *speculate* that as d is decreased the large λ typical of type II superconductors might provide a magnetic stress relaxation mechanism capable of delaying

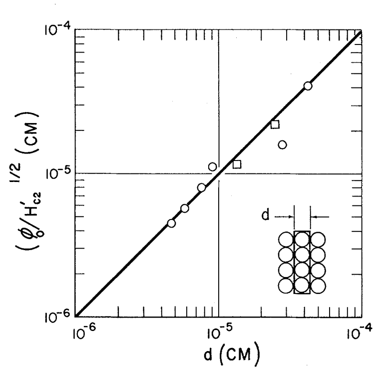

FIG. 5. Illustration of empirical correlation [solid line represents Eq. (15)] between film thickness d and field H_{c2} at which the temperature dependence of H_{c2} changes character in a type II superconductor. Circles and squares represent, respectively, values deduced by the author from the Hg and Al data of Khukhareva. As shown at the lower right this correlation corresponds to an exact match between vortex diameter and film thickness.

entry into the mixed state, and that the mixed state might be completely suppressed in films considerably thicker than d_c. Pertinent to this point are the recent longitudinal-field tunneling and magnetization studies of Tomasch and Joseph[55] on alloy films. Conventional

[53] J. J. Hauser and H. C. Theuerer (to be published).

[54] I. S. Khukhareva, Zh. Eksperim. i Teor. Fiz. **41**, 728 (1961); **43**, 1173 (1962) [English transl.: Soviet Phys.—JETP **14**, 526 (1962); **16**, 828 (1963)].

[55] W. J. Tomasch and A. S. Joseph (to be published).

interpretation of the tunneling characteristics of a 23 000-Å Pb–9.2 at.% Tl film with $\kappa \approx 2.3$ yielded an energy gap (~1% less than for pure Pb) which remained sharp and constant (to within 1%) at 1.1°K in fields nearly twice the bulk specimen lower critical field, i.e., this experimental quantity was not indicative of vortex smearing of the gap or vortex reduction of the effective gap in fields well in excess of those at which flux penetration commences in bulk specimens. On the other hand, the area between the normal and superconducting current–voltage characteristic curves decreased approximately linearly with field. Torque magnetometer studies (though not definitive on this point) suggested that a conventional penetration-depth shielding current (i.e., one diamagnetic multiquantum vortex), rather than a myriad of single-quantum vortices, was responsible for the magnetization in fields approaching the bulk sample upper critical field (even though at this field the sample thickness could have accommodated ~30 vortex–lattice layers).

Cody and Cohen[56] and Goldstein,[57] respectively, have carried out longitudinal-field thermal conductivity and tunneling studies on Nb_3Sn specimens of intermediate thickness ($\sim 6 \times 10^{-3}$ cm). Their results imply a field independence of the energy gap in fields ($\sim 0.05\ H_{c2} \gg H_{c1}$) where a change of at least a few percent might be expected for a bulk sample. Attempts to explain such behavior on the basis of an enhanced H_{c1} as discussed above would presumably require a much larger λ than reported for this material.[58]

56 G. D. Cody and R. Cohen, Rev. Mod. Phys. **36**, 121 (1964).

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58 G. D. Cody, J. J. Hanak, and M. Rayl, in *Proceedings of the Eighth International Conference on Low Temperature Physics* [Butterworths Scientific Publications, Ltd., London (to be published)].

The evidence presented in this section indicates that the theoretical and experimental characterization of samples in the intermediate thickness range ($\sim 10^{-4}$ to 10^{-2} cm) is less complete than for thicker and thinner samples. Clarification of this aspect could be of considerable practical significance because layers a few microns in thickness are often utilized in supermagnet applications.

IV. CONCLUSIONS

The past few years have marked the resolution of problems in high-field superconductivity which perplexed low-temperature physicists for 30 years. Nevertheless, it must be conceded that the picture remains incomplete. Direct observation of the vortex lattice (or alternate laminar structure[8,11,23,59]) would add confidence to our understanding. However, by analogy with recent developments in the physics of superfluid helium,[60] progress could be more reliant upon man's imagination than upon experimental knowledge of vortices.

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