# CRITICAL FIELDS OF TYPE II SUPERCONDUCTORS

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## INTRODUCTION

The purpose of this paper is to discuss the critical fields of type II superconductors. In order to develop a physical basis for the concept of the critical field, we start with a discussion of the magnetic behavior of type I superconductors, and particularly the intermediate state. The approach to type II behavior will be through the vortex model of deGennes which follows naturally from a consideration of surface energies in a type I superconductor. Finally, we will cover recent results from the Gor'kov microscopic Ginsburg-Landau equation which accurately predicts the effects of temperature, purity, normal electron spin paramagnetisms and variable coupling on the critical field behavior of a large class of type II superconductors. The exceptions to this theory and possible sources of their unique behavior will be discussed. Finally, we will consider recent experimental observations of critical field behavior in materials of practical interest.

## MAGNETOSTATICS AND THERMODYNAMICS OF TYPE I SUPERCONDUCTORS

Superconductors exhibit zero resistance below the transition temperature, $T_c$, but when relatively defect free, exhibit a diamagnetism that is field dependent and reversible.[1] This last fact, although of little practical utility, is the basis for the theoretical treatment of the superconducting state. For a uniformly magnetized ellipsoid three fields are introduced in addition to the microscopic local field h(r) and the applied field $H_o$. These three fields are B, the flux density or average local field $\overline{h(r)}$, M, the dipole moment per unit volume or magnetization, and H, the internal field. From magnetic theory:

$$B = H + 4\pi M = H_o + 4\pi (1 - D) M \quad . \tag{1}$$

In Eq. (1), D is the demagnetization coefficient of the ellipsoid. For a long cylinder, a sphere and a disk, D = 0, 1/3 and 1, respectively, where the applied field, $H_o$, is along the symmetry axis of the ellipsoid.

From considerations of the magnetic work, we are led to consider the specific Gibbs free energy g, which is a function of $H_o$ and T, and is a minimum under equilibrium at constant field and temperature. From the thermodynamic treatment,

$$dg = - sdT - Md\, H_o \quad . \tag{2}$$

In Eq. (2), s is the specific entropy. The Gibbs free energies of two phases in equilibrium can be shown to be equal, and this criterion for phase equilibrium is critical for understanding the gross features of field effects in superconductors.

For type I superconductors, when D = 0, it is observed experimentally that $M_s = - H_o/4\pi$ up to a critical field $H_c(T)$.[2] Thus B = 0 in the superconducting state. Above this field the magnetization of the superconductor, $M_s(T)$, is the same as that of the normal state, $M_n(T) = \chi_n H$ (the paramagnetic susceptibility, $\chi_n$, is of the order of $20 \times 10^{-6}$ for transition metals, but is considerably less for nontransition metals).

The discontinuous change of magnetization at $H_c(T)$ defines a type I superconductor, as well as the thermodynamic critical field $H_c(T)$.

If we consider Eq. (2) we can arrive at another view of $H_c(T)$ which explains its nomenclature. From simple integration and use of the equilibrium criteria we see that

$$g_n(H_c,T) \approx g_n(0,T) = g_s(0,T) + \frac{H_c^2}{8\pi} = g_s(H_c,T) \tag{3}$$

and thus $H_c^2/8\pi$ represents the free energy difference between the normal and superconducting state. Figure 1 shows the free energy and the magnetization $[M = -(\partial g/\partial H_o)_T]$ of a type I superconductor and illustrates the content of Eq. (3). The effect of the field on the free energy of the superconductor is to destroy the energy gained by the initial condensation to the ordered superconducting state ($H_c^2/8\pi$). From Eqs. (3) and (2) one can obtain the entropy s $[s = -(\partial g/\partial T)_{H_o}]$ and it can easily be seen that the superconducting state is the more ordered state ($s_s < s_n$ for $T < T_c$). Furthermore, in zero field $s_s(T_c) = s_n(T_c)$, which implies a second order transition. In a finite field the entropy remains at its zero field value, up to $H_c(T)$, but jumps discontinuously at $T[H_o = H_c(T)]$ to the normal entropy (a first order transition).

The absence of a field dependence to the entropy is accounted for by the observation that since $B = 0$ up to $H_o = H_c(T)$, the field plays no role in changing the order of the superconductor. Of course, this ignores the fact that there cannot be a discontinuity in the field at the surface of the superconductor. The field extends a distance into the superconductor, given by the penetration depth $\lambda(T)$. A penetration depth, $\lambda_L$, was first introduced by London, who derived on the basis of a dissipationless fluid the following equation for the field penetration, which when combined with Maxwell's equations are in semiquantitative agreement with experiment:

$$\lambda_L^2 \, \nabla x(\nabla x H) = - H \quad , \tag{4}$$

where

$$\lambda_L^2 = \left( \frac{mc^2}{4\pi \; ne^2} \right) = \left( \frac{3c^2}{4\pi \; N \; v_F^2 \; e^2} \right) \quad . \tag{5}$$

In Eq. (5) m and n are the mass per particle and the density of the fluid, respectively; in the second form of $\lambda_L$, N and $v_F$ are the total density of states and Fermi velocity, respectively. This second form is of greater generality than the fluid model. It is interesting to note that Eq. (5) is invariant under the transformation to pairs appropriate to the BCS theory of superconductivity ($m \to 2m$, $e \to 2e$, $n \to n/2$).

From Eqs. (4) and (5) we can associate $H_c(T)$ with the kinetic energy of the shielding currents that maintain the condition $B = 0$ in the bulk. It is simple to show that the kinetic energy density K is given by

$$K = \frac{1}{2} \, nmv_d^2 = \frac{1}{2} \, \frac{mJ^2}{ne^2} = \frac{4\pi}{2c^2} \, \lambda_L^2 \, J^2 = \frac{H^2}{8\pi} \quad , \tag{6}$$

where $v_d$ is the drift velocity and we have used the solution for Eq. (4) at a plane boundary: $J = cH/4\pi \, \lambda_L$. At $H = H_c(T)$, the kinetic energy density of the shielding electrons equals the quantity $g_n - g_s(0,T)$ and the material goes normal.

It clearly costs the superconductor to expel a magnetic field. Consider Fig. 2 where again we show the free energy of a type I superconductor. If there were a way to achieve a lower magnetization [$M = -(\partial g/\partial H_o)_T$] as shown by the dashed curve, the material could achieve a lower free energy and would presumably remain superconducting to considerably higher fields. Experimentally such a situation has been known since the thirties for systems where one dimension approached a size of the order of $\lambda$ ($\approx$ 300-600 Å). Under these conditions, field exclusion is not complete, $B = \overline{h} \neq 0$, and M is appreciably smaller than for bulk materials. Indeed, critical fields considerably higher than $H_c(T)$ were observed and were correlated with the London expressions with qualitative and semiquantitative agreement.[3] From these experiments, an important question emerges: namely, why a bulk specimen did not subdivide into domains of the order of $\lambda$, and hence remain superconducting to fields much higher than $H_c(T)$.

## INTERMEDIATE STATE OF TYPE I SUPERCONDUCTORS

A model for such a domained structure was developed in the thirties to explain magnetization data on ellipsoidal specimens where $D \neq 0$. While neither the experiments nor the model led to critical fields higher than $H_c(T)$, it led through the work of Pippard[4,5] to what might be described as the physical basis of type II superconductivity. Curve (1) in Fig. 3 shows the magnetization and free energy of a bulk specimen with $D \neq 0$. The magnetization in the state for which $B = 0$ (the Meissner state) is of the form $M = -H_o/4\pi(1-D)$, and hence the free energy rises considerably faster than the curve (2) for $D = 0$. If this high moment state persists, the specimen would enter the normal state at a field considerably less than $H_c(T)$. In fact the material follows the curve (3), branching off from (1) at $H_o = H_c(1-D)$ and finally enters the normal state close to $H_c(T)$. In this new state, the intermediate state, $M = (-1/4\pi D)(H_c - H_o)$ and

$$g(H,T) = g_s(0,T) + H_c^2/8\pi - (H_c - H)^2/8\pi D \quad . \tag{7}$$

In the new state Peierls[6] suggested that the system is subdivided into normal domains where $h = H_c$, and superconducting domains where $h = 0$. Thus if x is the concentration of normal domains

$$x = \frac{B}{H_c} = -\frac{1}{D}\left(1 - \frac{H_o}{H_c}\right) , \tag{8}$$

and x goes from 0 at $H_o = H_c(1-D)$ to 1 at $H_o = H_c$. It is easily shown that the entropy of the intermediate state is a continuous function of field and it, as well as M, goes continuously to normal state values at $H = H_c$. In view of the presence of normal domains this is not a surprising effect.

Given the possibility of domains, it is not apparent why they cannot reduce in size to such a degree that $M \to 0$, as for thin films which would permit the intermediate state to persist to fields above $H_c$. However, far from this being the case, a careful examination of the magnetic transition of the intermediate state shows that the critical field, $H_I$, is slightly less than $H_c(T)$.

In order to understand this phenomenon, an additional property has to be introduced, the surface energy. In the intermediate state with many normal-superconducting interfaces, it is clear that there may be surface tension or surface energy effects resisting the increase of the interface. If the surface energy is $\alpha$, an additional free energy $\alpha f(x)$ will be lost to the superconductor and the critical field will be less than $H_c(T)$, as shown in Fig. 4.

Pippard[4] gave a physical picture of the source of this surface energy. Consider the superconducting state to be associated with an order parameter, $n_s$. The order parameter may be identified with the density of superconducting electrons, or with the energy gap. In either case it is a quantity that varies from its full value at $T = 0^{o}K$, to zero at $T_c$. We consider a normal-superconducting boundary to be defined by $n_s = 0$, but we cannot permit $n_s$ to change discontinuously at the interface. As in the case of field penetration, we are led to consider a fundamental length $\xi^*$, over which the order parameter can vary.

In Fig. 5, we consider a normal-superconducting boundary where $H = H_c(T)$ in the bulk of the normal metal ($n_s = 0$) and $H = 0$ in the bulk of the superconductor [$n_s = n_s(T)$]. It is easy to see that there is a gain of energy of order $\lambda H_c^2/8\pi$ per unit area due to flux penetration. Conversely, there is a loss of condensation energy of the order $\xi^* H_c^2/8\pi$ per unit area, where $\xi^*$ is the distance over which the order parameter varies. Thus the surface energy is given by $\alpha = (\xi^* - \lambda)H_c^2/8\pi \equiv \Delta H_c^2/8\pi$. For a positive surface energy ($\xi^* > \lambda$) we cannot gain energy by infinite subdivision. The minimum size of a domain is of the order of $\xi^*$, and the limit of $x \to 1$ for the intermediate state corresponds to the vanishing of the last domain, not its shrinking in size. For thick disks ($D \approx 1$) in a perpendicular field, one can show that the critical field $H_\perp$,[7] is given by

$$H_\perp/H_c \approx [1 - (\Delta/d)^{\frac{1}{2}}] \tag{9}$$

and this relation, as well as the slope of $(\partial M/\partial H)_H = H_\perp$, can be used to determine $\Delta$.

Pippard[8] further suggested a relationship for pure metals between $\xi^*$ and the transition temperature and Fermi velocity. As later given by BCS[9] this is

$$\xi^* \approx \xi_o = \hbar v_F/\pi\Delta \quad , \tag{10}$$

where $2\Delta$ is the energy gap ($2\Delta = 3.56\ k\ T_c$). Calculations show that for most pure metals, $\xi_o \approx 2000 - 10\ 000$ Å, whereas $\lambda \approx 200 - 600$ Å. Hence $\Delta > 0$.

From these considerations we have been led to consider two fundamental lengths for a superconductor, $\xi^*$ and $\lambda$. If we define their ratio as $\sqrt{2}\kappa = \lambda/\xi^*$, we see that for $\sqrt{2}\kappa > 1$, $\Delta < 0$, and one might expect a general depression of the free energy below even the Meissner curve for $D = 0$. Furthermore, the experience with the intermediate state suggests that such a negative surface energy state might be a proper thermodynamic phase — homogeneous and reversible.

## THE MIXED STATE OF TYPE II SUPERCONDUCTORS

It is one of the triumphs of solid state physics that the negative surface energy state was predicted mathematically before there was any recognition of experimental justification. However, it remains a paradox, that the experimental evidence for such a state was largely ignored both prior to the theory and to its eventual experimental "verification." The theory, of course, is the Ginzburg-Landau theory[10] published in 1950, "discovered" in 1961,[11] and which has received numerous verifications since that time, but some of whose predictions were observable in the experiments of Shubnikov et al.[12] in 1937. The G-L theory, the theory of the microstructure of the negative surface energy state due to Abrikosov,[13] and the microscopic theory of Gor'kov[14] (the GLAG theory) have all been the subject of numerous reviews, and only the results will be considered in detail in the present paper.

In its original form the theory was based on an expansion of the free energy close to $T_c$ in terms of an order parameter, and was explicitly designed to take into account spatial variations of the order parameter as occur in the intermediate state and in thin films. It was shown by Gor'kov to be a natural consequence of the BCS microscopic theory when the energy gap was permitted spatial variations. As developed by Abrikosov,[13] Gor'kov,[14] deGennes,[15] Maki,[16,17] Helfand and Werthamer,[18-21] Eilenberger[22] and others, it is a sophisticated nonlinear highly mathematical theory which is in very good agreement with experiment.

Despite the mathematical complexity of the theory, there is a physical approach to the magnetic behavior of type II superconductors that follows naturally from our previout discussions of surface energy. As developed by deGennes,[23] this approach considers a specific domained structure — a vortex of circulating superconducting electrons around a normal state core. In the following sections we will follow this approach, and will later make contact with the exact mathematical results of Maki,[17] Helfand and Werthamer[18-19] and Eilenberger.[22]

The laminellar domains[24] of the intermediate state are clearly not the only configuration appropriate to a domained structure. Again the task is to lower the magnetic energy while doing minimum damage to the condensation energy. Let us consider a normal core of radius $\xi^*$, with a field dropping off from its maximum value at the center as in Fig. 6. To proceed further we require a generalization of the London equations to take into account the normal core, and the circulation electrons about that core.

The usual form of London's equation [Eq. (4)], when combined with the Maxwell Equation $\nabla \times H = 4\pi J/c$, can be written as

$$\nabla \times v = - \frac{q}{mc} H \quad , \tag{11}$$

where v, q, and m are the velocity, charge and mass of the superconducting fluid ($J = nqv$). If we write $P = mv + (q/c)A$, where P is the quantum mechanical momentum, we can write Eq. (11) as

$$\nabla \times P = 0 \quad . \tag{12}$$

However, from the presence of the normal core and the electron circulation, we know that Eq. (12) cannot hold everywhere. A suitable generalization of Eq. (12) is

$$\nabla \times P = \frac{q}{c} \Phi \, \delta(r) \quad , \tag{13}$$

where $\delta(r)$ is a two-dimensional $\delta$ function and $\Phi$ is the flux in the core. Consideration of the circulation $\oint P \cdot dS$ about the core suggests $\Phi$ to be quantized in units of $hc/2e$ ($q = 2e$), where $\varphi_o = (hc/2e)$ ($= 2 \times 10^{-7}$ G$\cdot$cm$^2$) is the unit of flux quantization. From Maxwell's Equations and Eq. (2) we obtain as a generalization[25] of Eq. (4)

$$\lambda_L^2 \nabla \times (\nabla \times H) + H = \varphi_o \, \delta(r) \quad . \tag{14}$$

Using cylindrical symmetry, a solution of Eq. (14) for $\xi^* < r < \lambda_L$ is

$$H = \frac{\varphi_o}{2\pi\lambda^2} \log \frac{\lambda_L}{r} \quad . \tag{15}$$

We next calculate the magnetic and kinetic energy, F, of the vortex, per unit length of vortex [the core energy $(H_c^2/8\pi)\, \pi\xi^{*2}$ can be shown to be less than 12% of the magnetic and kinetic energy]

$$F = \int da \left( \frac{H^2}{8\pi} + \frac{1}{2} nmv^2 \right) = \int da \left( \frac{H^2 + \lambda^2 (\nabla \times H)^2}{8\pi} \right) \quad . \tag{16}$$

Using the vector identity,

$$\nabla \cdot [H \times (\nabla \times H)] = (\nabla \times H)^2 - H \cdot [\nabla \times (\nabla \times H)]$$

and Eq. (14) we obtain

$$F = \frac{\lambda_L^2}{8\pi} \int_{r=\xi^*} ds\ H \times (\nabla \times H) = \left( \frac{\varphi_o}{4\pi \lambda_L} \right)^2 \log \frac{\lambda_L}{\xi^*} \quad . \tag{17}$$

Noting that the flux density B is given by $n\varphi_o$, and neglecting the interaction between vortices, we have for the total free energy

$$nF = B \frac{\varphi_o}{(4\pi \lambda_L)^2} \log \frac{\lambda_L}{\xi^*} \tag{18}$$

at equilibrium

$$H_o = 4\pi n \frac{\partial F}{\partial B} = \frac{\varphi_o}{4\pi \lambda_L^2} \log \frac{\lambda_L}{\xi^*} \quad .$$

Thus vortices will penetrate at $H_o = H_{c1}$ where

$$H_{c1} = \frac{\varphi_o}{4\pi \lambda_L^2} \log \frac{\lambda_L}{\xi^*} \quad . \tag{19}$$

We will find that the condition for $H_{c1} < H_c$ will be related to the previous negative surface energy requirement $\xi^* < \lambda_L$. We can further estimate the transition field where M = 0, ($H_{c2}$) as that field ($B \approx H$) where the vortices overlap. Thus

$$H_{c2} \approx B \approx \frac{\varphi_o}{4\pi \xi^{*2}} \quad . \tag{20}$$

The next step is to relate the fields $H_{c1}$ and $H_{c2}$ to $H_c$. In the G-L equations a parameter $\varkappa$ is introduced such that, as suggested previously, $\xi^* = \lambda/\sqrt{2}\varkappa$. Furthermore

$$\varkappa = \lim_{T \to T_c} \frac{2\sqrt{2\pi}\,\lambda^2 H_c}{\varphi_o} \quad . \tag{21}$$

If we ignore the restriction to temperatures close to $T_c$ (and consider local superconductors where $\lambda \approx \lambda_L$) we can rewrite Eqs. (19) and (20) as

$$H_{c1} = \frac{H_c}{\sqrt{2}\varkappa} (\ln \varkappa + 0.3) \tag{22}$$

and

$$H_{c2} = \sqrt{2}\varkappa\, H_c \quad . \tag{23}$$

Thus if $\varkappa > 1/\sqrt{2}$, $H_{c1} < H_c$ and $H_{c2} > H_c$, and we expect the superconductor to make a gradual magnetic transition from the state where B = 0 (Meissner state) at $H_{c1}$ to the normal state at $H_{c2}$ where a second order transition occurs. Materials for which $\varkappa > 1/\sqrt{2}$ are called type II superconductors and the region between $H_{c1}$ and $H_{c2}$ where vortices penetrate is called the mixed state. Figures 7 and 8 show the magnetization, free energy and phase diagram of this state.

The resemblances to the gross features of the intermediate state are obvious, however it must be emphasized that there are fundamental differences. The intermediate state is only macroscopically second order; the last superconducting domain vanishes discontinuously at $H_I$. However, the mixed state is microscopically second order at $H_{c2}$. In the intermediate state one expects supercooling, i.e., a lowering of the field until the volume free energy can overcome the positive surface energy. In the mixed state there can be no supercooling due to the negative surface energy. Indeed, in the original work of Ginsburg-Landau, $H_{c2}$ ($\sqrt{2}\kappa < 1$) is defined as the minimum field to which one can supercool a type I superconductor. As we shall see, this is only true for certain field orientations.

It is interesting to note that the vortex approach described here led Tinkham to consider the question of what happens to thin disks of type I superconductors in a perpendicular field. For example, for low $\kappa$, $\Delta \approx \xi^*$ and, given Eq. (9), one expects $H_\perp$ to approach zero as $d \approx \xi^*$. Tinkham,[26] from energy consideration, suggested that a vortex state at $H_\perp = \sqrt{2}\kappa\, H_c$ might be energetically favorable and replace the intermediate state. The transition field $H_\perp$ has been observed for lead,[27] tin,[28] and indium.[28] Figure 9 shows experimental data for lead films. In this figure the rise in $H_\perp$ for low thicknesses is related to a thickness dependence of $\kappa$. However, the bulk value of $\kappa$ ($< 1/\sqrt{2}$) can be obtained by extrapolation. This technique can be used instead of supercooling for the determination of $\kappa$ in type I material.

## EXACT THEORIES OF THE MIXED STATE

The picture of the type II superconductor is physically that of the reduction of magnetization due to the penetration of vortices with normal cores. The exact calculations of the Gor'kov equation leads to the following expressions for $H_{c1}(T)$, $H_{c2}(T)$ and the slope of the magnetization curve close to $H_{c2}$:[17]

$$H_{c1}(T) = \frac{H_c(T)}{\sqrt{2}\kappa_3(T)} \ln \kappa_3(T) \quad , \tag{24}$$

$$H_{c2}(T) = \sqrt{2}\kappa_1(T)\; H_c(T) \quad , \tag{25}$$

$$\left(\frac{\partial M}{\partial H}\right)_{H_{c2}} = -\frac{1}{(1.16)}\left(\frac{1}{4\pi}\right)\frac{1}{(2\kappa_2^2 - 1)} \quad , \tag{26}$$

where $\kappa_1(T)$, $\kappa_2(T)$, and $\kappa_3(T)$ approach $\kappa$ as $T \rightarrow T_c$ and[29,30]

$$\kappa \approx 0.96\,\frac{\lambda_L}{\xi_o} + 0.7\,\frac{\lambda_L}{\ell} \tag{27}$$

$$= 0.96\,\frac{\lambda_L}{\xi_o} + 7.53 \times 10^3\, \rho_o\, \gamma^{\frac{1}{2}} \quad . \tag{28}$$

In Eq. (27) $\ell$ is the mean free path, and in Eq. (28) $\rho_o$ is the residual resistivity ($\Omega$·cm) and $\gamma$ (erg/cm$^3$ $^o$K$^2$) is the coefficient of the linear term in the electronic specific heat. It should be emphasized that Eqs. (24)-(28) take band structure effects into account only in terms of a one-band effective mass model. In this sense they are restricted in the same sense as BCS. However, the two terms for $\kappa$ permit one to define an intrinsic type II superconductor ($\ell \gg \xi_o$) and an extrinsic type II superconductor ($\ell \ll \xi_o$). This classification coincides with the distinction between "clean" and "dirty" superconductors, and hence one expects poorer agreement with theory for clean materials where anisotropy and multiple band effects have not been washed out by scattering.

Equations (27) and (28) permit one to give a more precise definition of $\xi^*$. Using the BCS results that, for $T \to T_c$

$$\lambda \to \frac{\lambda_L}{\sqrt{2}} (1 - t)^{-\frac{1}{2}} \left( \frac{\xi_o}{\xi} \right)^{\frac{1}{2}} , \tag{29}$$

where

$$\frac{1}{\xi} = \frac{1}{\xi_o} + \frac{0.7}{\ell} , \tag{30}$$

we obtain

$$\xi^* \approx \frac{\xi_o}{\sqrt{2}} (1 - t)^{-\frac{1}{2}} , \tag{31a}$$

$$\xi^* \approx \frac{(\xi_o \ell)^{\frac{1}{2}}}{\sqrt{2}} (1 - t)^{-\frac{1}{2}} , \tag{31b}$$

in the clean and dirty limit, respectively. From Eq. (31b) one notes that for impure metals $\xi^* \approx (\xi_o \ell)^{\frac{1}{2}} \approx (v_F \ell)^{\frac{1}{2}}$ and is related to a diffusion length.[15]

The original theory of G-L and Abrikosov was confined to temperatures close to $T_c$, where the order parameter was small and the free energy expansion might be expected to be valid. However, the order parameter is also small close to $H_{c2}$, and one might expect the theory to have a wider range of validity. Calculations of Gor'kov,[14] Maki,[16,17] Helfand and Werthamer,[18-21] and Eilenberger,[22] have shown that the temperature dependence of either $\kappa_1(T)$, $\kappa_2(T)$ or $\kappa_3(T)$ is quite weak, and is of the order of 20% from 0 to $T_c$ for extrinsic type II superconductors. However, this result is correct only for low $\kappa$ material. The general temperature and impurity dependence of $\kappa_1(T)$ and $\kappa_2(T)$ is quite complicated, and an additional physical mechanism, the magnetic nature of the normal state has to be included before it can be discussed.

## PARAMAGNETIC AND IMPURITY EFFECTS ON $H_{c2}$

Up to the present we have neglected the magnetic properties of the normal state. For transition metals such as Nb, or intermetallic compounds such as $Nb_3Sn$, $V_3Si$ or $V_3Ga$ the paramagnetic susceptibility, $\chi$, is of the order of $20 \times 10^{-6}$, with about equal orbital and spin contributions.[31] For a BCS superconductor the ground state consists of pairs of electrons with opposite spins, and hence the spin susceptibility is zero in the superconducting state. The unequal assignment of spin magnetic energy between the normal and superconducting states is the additional factor that has to be included to account in detail for the high field behavior of type II superconductors.

In the original suggestion of Clogston[32] and Chandrasekhar[33] the paramagnetic limiting field $H_P$ was obtained by equating the magnetic energy of the normal state to the condensation energy, i.e.,

$$\frac{1}{2} \chi_N H_P^2 = \frac{H_c^2}{8\pi} . \tag{32}$$

Using $\chi_N = N\mu^2$, and the BCS relations $H_c^2/8\pi = N\Delta^2/4$, $2\Delta = 3.5\ kT_c$, we obtain

$$H_p = 18.4 \times 10^3\ T_c \quad . \tag{33}$$

In these papers the prediction was made that $H_{c2}$ could not exceed $H_p$. A slightly more realistic calculation (although still incorrect) utilizes Fig. 10 to calculate the effect of normal state spin paramagnetism.

If we ignore spin contributions in the superconducting state we have for the magnetization $M = \chi_s(H - H_{c2}^*)$, where $\chi_s \approx 1/8\pi\kappa^2$ and therefore:

$$g_s(H) = g_n^o(H_{c2}^*) - \chi_s \frac{(H - H_{c2}^*)^2}{2} \quad . \tag{34}$$

In Eq. (34) $g_n^o(H_{c2}^*)$ is the normal state free energy without the spin paramagnetism, $\chi_N H$. The quantity $H_{c2}^*$ is the upper critical field in the absence of the paramagnetic limitation. If we include the spin paramagnetism in the normal state we have

$$g_n(H) = g_n^o(H_{c2}^*) - \frac{\chi_N H^2}{2} \quad . \tag{35}$$

Equating Eqs. (35 and (34) at the transition field $H_{c2}$, we obtain

$$\frac{H_{c2}^* - H_{c2}}{H_{c2}} = \left(\frac{\chi_N}{\chi_S}\right)^{\frac{1}{2}} = \frac{\sqrt{2}\kappa}{H_P} H_c = \frac{H_{c2}^*}{H_P} \quad , \tag{36}$$

where we have utilized Eq. (32). For a superconductor where $H_{c2}^* > 100$ kG, $T_c \approx 10^oK$, we estimate $(H_{c2}/H_{c2}^*) \approx 0.6$. Figure 11 shows the magnetization curve resulting from the above treatment and one notes the first order transition to the paramagnetic normal state at $H_{c2}$.

There are two objections to the above treatment. First, it is not clear how the normal cores will modify the free energy of the superconducting state. In terms of the simple vortex model, the essentially normal material of the core will have a tendency to lower the superconducting free energy, and lead to a magnetization that approaches that of the normal state at $H_{c2}$. Figure 12 shows the expected free energy curve and magnetization. One notes that the transition is second order, and that M crosses the H axis at a field where $g_s(H,T)$ has a maximum. Despite the change in the order of the transition, the magnitude of $H_{c2}$ is not very different from the simple relation Eq. (36). A second more significant effect arises from the fact that in highly disordered alloys there may be appreciable spin scattering in the superconducting state leading to a depairing of the spins in the superconducting state. This last effect, which is the dominant one, leads to a reduction of the paramagnetic effect on $H_{c2}^*$ due to an equalization of the spin paramagnetism in the normal and superconducting states.

The parameter to measure the effect of spin-orbit scattering can be estimated by comparing the energy uncertainty introduced by such scattering with the energy gap. If $\tau_{so}$ is the spin-orbit scattering time, from the uncertainty principle one expects depairing effects to be large when $[\hbar/\tau_{so}(3.5\ kT_c)] \geq 1$. The exact theories[17,19] to be discussed introduce two parameters to describe scattering effects:

$$\lambda_{so} \equiv (\hbar/3\pi\ kT_c\tau_{so}) \tag{37}$$

$$\lambda \equiv (\hbar/2\pi\ kT_c\tau) \quad , \tag{38}$$

where $\tau_{so}$ is the spin-orbit scattering time, and $\tau$ is the spin independent scattering time. In the work of Maki[17] and of Helfand, Werthamer, and Hohenberg,[18,19] $\tau$ is identified with the transport scattering time. As suggested by Eq. (36), the basic parameter of the paramagnetic effect is

$$\alpha \equiv [\sqrt{2}\, H^{*}_{c2}(0)/H_P] \tag{39}$$

and Maki[17] introduces a mixed parameter $\beta_o$ to characterize the paramagnetic effect, and its reduction by spin orbit scattering,

$$\beta_o^2 \equiv \frac{\alpha^2}{1.78\,\lambda_{so}} \quad . \tag{40}$$

To summarize the discussion to the present, we note that the results of the GLAG theory, Eqs. (24)-(28), are only exactly valid near $T_c$. Close to $H_{c2}$, at lower temperatures and when spin paramagnetism can be neglected, Eqs. (24)-(28) retain approximate validity, and departures from the exact theory will be measured by the parameter $\lambda$ [Eq. (38)]. For high $\kappa$ dirty materials the parameters $\alpha$ [Eq. (39)], $\lambda_{so}$ [Eq. (37)], and $\beta_o$ [Eq. (40)], determine the upper critical field and its temperature dependence.

Before we discuss the formal theories and their comparison with experiment it will be helpful to make three general observations about experimental results. First, it is important to note that in all of the theories, paramagnetic effects vanish at $T_c$. Physically, this arises because close to $T_c$ quasi-particle excitations dominate the superconductor, and hence the mixed state is depaired. Thus if we use the notation:

$$H_{c2}(\alpha,\lambda,\lambda_{so},T) \equiv H_{c2}(T)$$

$$H_{c2}(0,\lambda,\lambda_{so},T) \equiv H^{*}_{c2}(T)$$

we obtain

$$\left(\frac{dH_{c2}}{dT}\right)_{T_c} = \left(\frac{dH^{*}_{c2}}{dT}\right)_{T_c} = \sqrt{2}\kappa\left(\frac{dH_c}{dT}\right)_{T_c} \quad , \tag{41}$$

where $\kappa$ is given by Eqs. (27) and (28). Second, in the dirty limit, the parameter $\alpha$ does not have to be fit to the data, but can be obtained independently. This observation follows from the theoretical temperature dependence of $H^{*}_{c2}$, which will be discussed presently, and Eqs. (41) and (28) plus some results from BCS. In the dirty limit one obtains

$$\alpha = 2.35\,\rho\gamma \quad , \tag{42a}$$

where $\rho$ is in $\Omega\cdot$cm and $\gamma$ has been defined below Eq. (28). Further algebra shows that

$$\alpha = 5.33 \times 10^{-5}\left(-\frac{dH_{c2}}{dT}\right)_{T_c} \quad . \tag{42b}$$

Hake[34] has presented an admirable review of the effect of spin paramagnetism on the mixed state, and this review has an appendix which lists a variety of formulae showing relationships between experimental and theoretical quantities.

The third observation is the most important and must be taken into account before any discussion of experiment. In general there are two ways of presenting experimental data. One can use the usual relation $H_{c2} = \sqrt{2}\kappa_1 H_c$ and show $\kappa_1$ as a function of temperature. For greater generality it is convenient to introduce a normalized quantity

$$\kappa^*(t) \equiv \kappa^*(t,\alpha,\lambda,\lambda_{so}) \equiv \frac{\kappa_1(T,T_c,\alpha,\lambda,\lambda_{so})}{\kappa} . \tag{43}$$

This mode of presentation presents two difficulties: first, it combines two quantities $H_{c2}$ and $H_c$, and hence couples the mixed state with the zero field state; second, it requires the experimentalist to have data on $H_c(T)$ for the specimen under consideration, and these data often are not available. Werthamer, Helfand and Hohenberg[19] suggest the use of the normalized field

$$h^* = \frac{H_{c2}(T)}{-T_c\left(\frac{dH_{c2}}{dT}\right)_{T_c}} \tag{44}$$

for comparisons between theory and experiment, and they present data on impurity effects as well as spin paramagnetic effects in terms of $h^*$ (to be distinguished from $H^*_{c2}$).

Figure 13 shows the results of the calculation of Helfand and Werthamer[18] for $h^*$ as a function of $T/T_c$ for $\alpha = 0$, and for two values of $\lambda$. Figure 14 shows the same results expressed in terms of $\kappa^*(t)$. One notes the weak impurity dependence of $h^*$ and $\kappa^*$. However, it must be emphasized that the calculations shown in Fig. 14 are based on BCS values for $H_c(T)$, and the small variation in $\kappa^*(t)$ with temperature holds only for BCS-like superconductors.

This observation can be seen more clearly if we note that

$$\begin{aligned} \kappa^*(t) &= -\,h^*\,[T_c(dH_c/dT)_{T_c}/H_c(T)] \\ \kappa^*(t) &= -\,h^*\,\varphi(T) \quad . \end{aligned} \tag{45}$$

For all superconductors, from the normalization of $h^*$, $\kappa^* \to 1.0$ as $T \to T_c$. However, $\kappa^*(0)$ will depend strongly on the value of $\varphi(0)$. Table I shows values of $\varphi(0)$ for Sn, Pb, V, $Nb_3Sn$ and Nb. It also shows the value of $\varphi(0)$ predicted by BCS, and $\kappa^*(0)$ for pure ($\lambda = 0$) and dirty ($\lambda = \infty$) materials.

TABLE I

$\kappa^*(0)$ for BCS and Non-BCS Superconductors

| | $\varphi(0)$ | $[\kappa^*(0)]$ pure | $[\kappa^*(0)]$ dirty |
|---|---|---|---|
| Sn | 1.855 | 1.35 | 1.28 |
| Pb | 2.132 | 1.56 | 1.47 |
| V | 1.773 | 1.29 | 1.22 |
| $Nb_3Sn$ | 2.000 | 1.46 | 1.38 |
| Nb | 2.000 | 1.46 | 1.38 |
| BCS | 1.737 | 1.27 | 1.20 |

From Table I we see that the variation in $\kappa^*(0)$ between different materials is much larger than the variation induced by changing from completely pure to impure materials. Clearly the simple statement that $\kappa^*(0) > 1.27$ does not in itself constitute a departure from theory. For completeness we note that

$$H_{c2}(T) = h^* (\sqrt{2}\kappa)\ [-\ T_c(dH_c/dt)_{T_c}] \tag{45a}$$

and again any comparison between theory and experiment has to include a knowledge of $(dH_c/dT)_{T_c}$.

The results shown in Figs. 13 and 14 are in excellent agreement with low $\kappa$ materials where paramagnetic limitations are inoperative, and where impurity effects dominate. There is not good agreement for clean type II superconductors such as V and Nb.[35,36] Figure 15 shows the departures from theory for Nb, and similar departures are seen for V. For type I material such as Sn and In,[27,28] where measurements have been made of the transition fields of thin films in a perpendicular field, similar departures are noted. It is interesting to note that in all cases the departure from theory is expressed by the experimentalist as a preference for the two-fluid temperature dependence of $\kappa$ (Eq. 21), i.e., $\kappa = \kappa_0[1 + (T/T_c)^2]^{-1}$. For V, Nb and Sn use of the theory leads to $h^*(0) = 0.85$, 0.83 and 0.85, respectively, whereas the maximum value of Fig. 13 is about 0.72. The discrepancy ($\approx$ 20%), although small, is well outside experimental and theoretical uncertainty. It cannot be accounted for on the basis of strong coupling effects, and according to Hohenberg and Werthamer[21] may arise from Fermi surface anisotropy effects. Before we leave the area of nonparamagnetically limited type II superconductors, it is of interest to point out the extensive numerical calculations of Eilenberger[22] for $\kappa_1$ and $\kappa_2$ as a function of purity including both S-S and S-P scattering.

Although the small departures from theory for clean type II superconductors are sufficiently large to bother theoreticians and experimentalists, the paramagnetically limited alloys (i.e. the dirty limit) appear to be well understood. Figure 16 shows the comparison between $h^*$ for Ti(0.56)Nb(0.44) and the predictions of the theory of Werthamer, Helfand, and Hohenbert.[19] In fitting the data, $\alpha$ is fixed by Eqs. (42) and $\lambda_{so}$ is chosen as a free parameter. The fit is excellent.

Maki[17] has expressed his results in terms of $\kappa_1/\kappa$ and $\kappa_2/\kappa$ as a function of t and $\beta_o$ as shown in Figs. 17 and 18, and one notes the depression of $\kappa_2(T)$ as well as $\kappa_1(T)$ below $\kappa$ where the paramagnetic effect is operative. In this connection it is important to note that $\kappa_2(T)$ is defined by $-\ 4\pi(M_s - M_n) = (H_{c2} - H)/[2\kappa_2^2(T) - 1)(1.16)]$. Figure 19 shows a comparison between the Maki theory for $\kappa_2(T)$ and the experimental results of Hake.[34] The agreement appears satisfactory. Figure 20 is an impressive example of the effect of spin paramagnetism from the work of Hake,[34] where the free energy as well as the magnetization is plotted as a function of field for a Ti16%Mo alloy with an $H_{c2}^*$ of about 100 kG, paramagnetically reduced to about 40 kG.

Figure 21 from the paper of Hake shows a comparison of the Werthamer, Helfand, and Hohenberg[19] (WHH) computer solutions for $h^*$ (t = 0) as a function of $\alpha$ and $\lambda_{so}$, compared to the analytic approximate form derived by Maki. The Maki[17] expression, corrected from the original paper, as quoted by Hake, is

$$h^*(t) = 1.39\ h_{c2}\ [1 + (1 + \beta_o^2\ h_{c2})^{\frac{1}{2}}]^{-1} \quad , \tag{46}$$

where $\beta_o$ is given by Eq. (4) and $h_{c2} = H_{c2}^*(t)/H_{c2}^*(0)$. A condition to be met for both theories is that the spin flip scattering time $\tau_{so}$ be large compared to the transport scattering time $\tau$; a condition which is physically realizable in high $\kappa$ transition metal alloys. As shown in the paper of Hake, one can get about equally good fits to either the Maki or WHH theory within the experimental uncertainties.

Finally, it is important to note that for $\lambda_{so} \to \infty$, there is no paramagnetic limitation of $H_{c2}$, and $H_{c2} \to H^*_{c2}$. Since $\lambda_{so} \propto (Z^4)$, where Z is the average atomic number, one might expect high Z alloys to have less paramagnetic limitations and hence achieve the upper critical field predicted from Eq. (28).

## CRITICAL FIELDS OF INTERMETALLIC COMPOUNDS

From the previous discussion it is apparent that dirty type II superconductors (extrinsic) are in excellent agreement with theory for both the paramagnetically limited and nonparamagnetically limited regime. Clean (intrinsic) type II superconductors exhibit characteristic departures from theory at low temperatures. Intrinsic high $\kappa$ materials (if they exist) have yet to be critically examined in the paramagnetic regime, although the theory exists. The departure from theory for low $\kappa$ materials has been ascribed to band structure and anisotropy effects, but no quantitative calculations have been made.

It is an interesting question whether similar departures from theory might be expected for the intermetallic compounds $Nb_3Sn$, $V_3Si$ and $V_3Ga$. These materials show significant departures from "normal-metal" behavior[31] above $T_c$, and there has been little success in correlating their superconducting behavior with existing free electron theories. One is inclined to believe that these materials exhibit band anisotropy and strong coupling, but they present experimental difficulties for both sample characterization and experiment. They are difficult to prepare in single crystal form, and the high critical fields and transition temperatures make it difficult to extract such parameters as the residual resistivity and electronic specific heat.

Table II gives data for $(dH_{c2}/dT)_{T_c}$, $(dH_c/dT)_{T_c}$, $\gamma$, $\rho$ and $\kappa$ for $Nb_3Sn$, $V_3Si$ and $V_3Ga$, as well as a calculation of $\kappa_\ell$ ($\kappa_\ell = 0.7\ \lambda_L/\ell$). Unfortunately, except in the case of $Nb_3Sn$, the $H_{c2}$ data do not necessarily refer to the same specimen for which the $\rho$ is given. Moreover, resistivity data on sintered specimens are often overestimated due to the problems of porosity. From the Table one notes that $Nb_3Sn$ and $V_3Si$ are intrinsic ($\kappa > 2\kappa_\ell$). However, the apparent insensitivity of $(dH_{c2}/dT)_{T_c}$ to sample preparation for $Nb_3Sn$, $V_3Si$ and $V_3Ga$ suggests that all are intrinsic and more so than

TABLE II

Parameters of Type II Intermetallic Compounds

| | $T_c$ ($^o$K) | $\rho$ ($10^{-5}$ $\Omega\cdot$cm) | $\gamma$ ($10^4$ erg/cm$^3$ $^o$K) | $(dH_{c2}/dT)_{T_c}$ (kG/$^o$K) | $(dH_c/dT)_{T_c}$ (G/$^o$K) | $\kappa$ b) | $\kappa_\ell$ a) |
|---|---|---|---|---|---|---|---|
| $Nb_3Sn$ | 18 | 1.0[31] | 1.18[37] | -18.0[37] | -590[37] | 22[37] | 8.2 |
| $V_3Si$ | 17 | 0.4[39] | 2.4 c) | -19.0[41] | -720[40] | 19 | 5.0 |
| $V_3Ga$ | 16 | 4.0[38] | 2.7 c) | -45.0[41] | -870[42] | 37 | <49.0 |

a) Eq. (28).

b) Eq. (25) at $T_c$.

c) Best values derived by L. Vieland from Ref. 40 and Ref. 42.

is suggested by the calculation of $\kappa_L$ from Eq. (28). For example, doubling the resistivity of $Nb_3Sn$ has no measurable effect on the slope $(dH_{c2}/dT)_{T_c}$.[43] Another example is the invariance of $dH_{c2}/dT$ under large changes in stoichiometry for $V_3Ga$.[41] Furthermore, both $V_3Si$ and $Nb_3Sn$ (and perhaps $V_3Ga$) exhibit specific heat anomalies at low temperatures that cast some doubt on the quoted $\gamma$'s. Since this Table includes two materials of practical interest, and three of great theoretical interest, it is of some importance to obtain critical field data on well characterized specimens.

Before leaving the intermetallic compounds, it may be of value to consider two-band effects. Roger Cohen of our laboratory has made some preliminary calculations of the dependence of $\kappa$ on the material properties of a two-band system with two energy gaps (e.g., an s gap and a d gap). Similar calculations have been made by Tilley[44] and Moskalenkov.[45] Cohen expresses his results as a function of $N_i$, the density of states in the $i^{th}$ band ($i = 1,2$); $v_{Fi}$, the Fermi velocity; $T_c$; and the energy gap, $\Delta$. A basic parameter is the quantity r, where near $T_c$

$$\Delta_1^2/\Delta_{BCS}^2 = [1 + (N_2/N_1)r^2]/[1 + (N_2/N_1)r^4] \tag{47}$$

$$\Delta_2^2 = r^2\ \Delta_1^2 \tag{48}$$

and $\Delta_{BCS} = \Delta_{BCS}(T)$, and $\Delta_{BCS}(0) = 3.5\ kT_c$. The result for $\kappa$ in the clean limit is

$$\kappa = \kappa_{01}^2\ \frac{[1 + (v_{F1}^2/v_{F2}^2)r^2]}{[1 + (N_2v_{F2}^2/N_1v_{F1}^2)r^2]}\ , \tag{49}$$

where

$$\kappa_{01}^2 = \left(\frac{9\pi}{7\zeta(3)}\right)\left(\frac{ckT_c}{\hbar e}\right)\left(\frac{1}{N_1v_{F1}^4}\right) = \left(\frac{0.96\ \lambda_{L1}}{\xi_{01}}\right)\ . \tag{50}$$

Figure 22 shows an approximately self-consistent variation of $\kappa$ with r for $Nb_3Sn$ as a function of various d-band Fermi velocities. The curves are based upon paramagnetic susceptibility, Hall data, specific heat data for $Nb_3Sn$. Unfortunately, it is not possible to fit all the existing data, in particular $\lambda$ and $\kappa$, with this model. It is clear that more data are required to satisfactorily understand $\beta$-W intermetallic compounds.

## SURFACE SUPERCONDUCTIVITY

Up to now, we have not touched upon the third critical field, $H_{c3}$. This field arises from a peculiar boundary condition of the G-L equations for a field parallel to the surface. Under these conditions a superconducting sheath of thickness $\approx \xi^*$ can exist up to a field $H_{c3} = 1.695\ H_{c2}$ (Fig. 23). Furthermore, for type I superconductors $H_{c3}$ is the supercooling field. There is good experimental agreement with the ratio $H_{c3}/H_{c2}$ when there is proper control of the surface. Calculations by Eilenberger and Ambegaokar[46] in the strong-coupling limit for pure superconductors close to $T_c$ show that the ratio is maintained. Recent calculations of Lüders[47] for clean superconductors suggest that $H_{c3}/H_{c2}$ at low temperatures can be as large as 2.2 due to the effect of electron reflection. Fischer[48] has interpreted microwave data for lead along these lines, and derived an $H_{c2}(T)$ for Pb which is in good agreement with the calculations of Werthamer and Helfand. However, in these measurements ($\kappa < 1/\sqrt{2}$, $1.695\ \sqrt{2}\kappa > 1$) $H_{c2}$ is not directly measurable and there is some question of interpretation. Moreover, given the disagreement of Nb and V with the calculations of Helfand and Werthamer,[18] there is a question as to whether one should expect good agreement for Pb. Finnemore et al.[36] measured $H_{c3}/H_{c2}$ for Nb, for samples with a residual ratio of 280 and 2000, and found $H_{c3}/H_{c2}$ of 1.69 and 1.50 respectively. However, the transitions were broad and extended to $H_{c3}/H_{c2}$ of 1.8 and 2.0 respectively.[49]

Saint-James[50] has derived the modification of $H_{c3}$ when there are paramagnetic effects with the following expression at T = 0°K:

$$\frac{H_{c3}(0,\alpha)}{H_{c2}(0,\alpha)} = \frac{1.695\ (1+\alpha^2)^{\frac{1}{2}}}{[1+(1.695\ \alpha)^2]^{\frac{1}{2}}} \quad . \tag{51}$$

As before, paramagnetic effects vanish close to $T_c$. When one includes spin orbit scattering one obtains

$$H_{c3}(T,\alpha,\lambda_{so}) = 1.69\ H_{c2}(T,1.69\alpha,\lambda_{so}) \tag{52}$$

and, as Saint-James points out, simultaneous measurement of $H_{c2}$ and $H_{c3}$ should permit direct determination of $\alpha$ and $\lambda_{so}$. Equation (52) does not appear to have received any experimental verification. Equation (51) for $\alpha \approx 1$ suggests $H_{c3}(0,\alpha) \approx 1.2\ H_{c2}(0,\alpha)$, which is in fair agreement with measurements of Kim et al.[51]

Finally, I present some recently measured data on practical materials made by Saur and Wizgall[52] (Fig. 24). Table III summarizes the results as well as giving some predictions of Hake[53] on possible values for $H_{c2}$ if their properties could be maintained under massive alloying to raise $\rho$. As noted, since I believe the intermetallic compounds are inherently intrinsic, this part of the Table should be considered with some discretion. In my own opinion the critical field of these materials is intimately related to their $T_c$, and poorly understood band structure and electronic interactions. It is quite possible that large enhancements in $H_{c2}$ beyond that realized today will only follow the understanding that leads to increases in $T_c$ above 20°K.

TABLE III

Upper Critical Fields of Intermetallic Compounds

| Material | $H_{c2}(0)$ (kG) | $H_{c2\ max}$ (kG) (after Hake[53]) |
|---|---|---|
| $Nb_3Sn$ | 245 | 880 |
| $V_3Si$ | 235 | 850 |
| $V_3Ga$ | 210 | 810 |
| NbN | 153 | 250 |

REFERENCES


1. An excellent review of superconductivity is E.A. Lynton, Superconductivity (Methuen, London, 1964), 2nd ed.
2. Ibid., p. 27.
3. Ibid., p. 76.
4. A.B. Pippard, Proc. Camb. Phil. Soc. 47, 617 (1951); Phil. Mag. 43, 273 (1952); Phil. Trans. Roy. Soc. A248, 97 (1955).

5. P.R. Doidge, Phil. Trans. Roy. Soc. A248, 553 (1956).

6. R. Peierls, Proc. Roy. Soc. A155, 613 (1936).

7. E. Guyon, C. Caroli, and A. Martinet, J. Phys. Radium 25, 683 (1964).

8. A.B. Pippard, Proc. Roy. Soc. A216, 547 (1953); T.E. Faber and A.B. Pippard, Proc. Roy. Soc. A231, 336 (1955).

9. J. Bardeen, L.N. Cooper, and J.R. Schrieffer, Phys. Rev. 108, 1175 (1957); J. Bardeen and J.R. Schrieffer in Prog. in Low Temp. Phys., Vol. 3, C.J. Gorter, Ed. (North Holland, Amsterdam, 1961), p. 170.

10. V.L. Ginzburg and L.D. Landau, J. Expt. Theor. Phys. (U.S.S.R.) 20, 1064 (1950). An excellent review of the theory is B.B. Goodman, Reports on Progress in Physics 29, II, 445 (1966).

11. B.B. Goodman, IBM J. Research and Development 6, 631 (1962).

12. L.W. Shubnikov, W.I. Khotkevich, J.D. Shepdev, and J.N. Riabinin, J. Expt. Theor. Phys. (U.S.S.R.) 7, 221 (1937).

13. A.A. Abrikosov, J. Phys. Chem. Solids 2, 199 (1957).

14. L.P. Gor'kov, Sov. Phys. JETP 9, 1364 (1959); Sov. Phys. JETP 10, 593 (1960); Sov. Phys. JETP 10, 998 (1960).

15. P.G. deGennes, Rev. Mod. Phys. 36, 225 (1964); Phys. Kondens. Materie 3, 79 (1964).

16. K. Maki, Physics 1, 127 (1964); Physics 1, 21 (1964).

17. K. Maki, Phys. Rev. 148, 362 (1966).

18. E. Helfand and N.R. Werthamer, Phys. Rev. 147, 288 (1966).

19. N.R. Werthamer, E. Helfand, and P.C. Hohenberg, Phys. Rev. 147, 295 (1966).

20. N.R. Werthamer and W.L. McMillan, Phys. Rev. 158, 415 (1967).

21. P.C. Hohenberg and N.R. Werthamer, Phys. Rev. 153, 493 (1967).

22. G. Eilenberger, Phys. Rev. 153, 584 (1967).

23. P.G. deGennes, Unpublished Lecture Notes, Herzengnovi Summer School; P.G. deGennes and J. Matricon, Rev. Mod. Phys. 36, 45 (1964).

24. T.E. Faber, Proc. Roy. Soc. A248, 460 (1958).

25. B.B. Goodman, Reports on Progress in Physics 29, II, 445 (1966).

26. M. Tinkham, Phys. Rev. 129, 2413 (1963); Rev. Mod. Phys. 36, 268 (1964).

27. G.D. Cody and R.W. Miller, Phys. Rev. Letters 16, 697 (1966); Phys. Rev. Sept. 1968 (to be published).

28. G.K. Chang and B. Serin, Phys. Rev. 145, 274 (1966).

29. B.B. Goodman, Rev. Mod. Phys. 36, 12 (1964).

30. T.G. Berlincourt, Rev. Mod. Phys. 36, 19 (1964).

31. R.W. Cohen, G.D. Cody, and H. Halloran, Phys. Rev. Letters 19, 840 (1967).

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

33. B.S. Chandrasekhar, Appl. Phys. Letters 1, 7 (1962).

34. R.R. Hake, Phys. Rev. 158, 356 (1967).

35. R. Radebaugh and P.H. Keesom, Phys. Rev. 149, 209 (1966); Phys. Rev. 149, 217 (1966).

36. D.K. Finnemore, T.F. Stromberg, and C.A. Swenson, Phys. Rev. 149, 231 (1966).

37. L.J. Vieland and A.K. Wicklund, Phys. Rev. 166, 424 (1968).

38. L.J. Montgomery and H. Wizgall, Phys. Letters 22, 48 (1966).

39. J.J. Hauser, Phys. Rev. Letters 13, 470 (1964).

40. J.E. Kunzler, J.P. Maita, H.J. Levinstein, and E.J. Ryder, Phys. Rev. 143, 390 (1966).

41. J.H. Wernick, F.J. Morin, F.S.L. Hsu, D. Dorsi, J.P. Maita, and J.E. Kunzler, in High Magnetic Fields, ed. Kolm, Lax, Bitter, Mills (The M.I.T. Press, 1962), p. 609.

42. F.J. Morin, J.P. Maita, H.J. Williams, R.C. Sherwood, J.H. Wernick, and J.E. Kunzler, Phys. Rev. Letters 8, 275 (1964).

43. J.L. Cooper, RCA Review 25, 405 (1964).

44. D.R. Tilley, Proc. Phys. Soc. 84, 573 (1964).

45. V.A. Moskalenkov, Sov. Phys. JETP 24, 780 (1967).

46. G. Eilenberger and V. Ambegaokar, Phys. Rev. 158, 332 (1967).

47. G. Lüders, Z. Physik 202, 8 (1967).

48. G. Fischer, Phys. Rev. Letters 20, 268 (1968).

49. For recent work on niobium, see G. Webb, Sol. State Comm. 6, 33 (1968).

50. D. Saint-James, Phys. Letters 23, 177 (1966).

51. Y.B. Kim, C.F. Hempstead, and A.R. Strnad, Phys. Rev. 139A, 1163 (1965).

52. E. Saur and H. Wizgall, in Proc. Intern. Conf. High Magnetic Fields, Grenoble, 1966, p. 223.

53. R.R. Hake, Appl. Phys. Letters 10, 189 (1967).

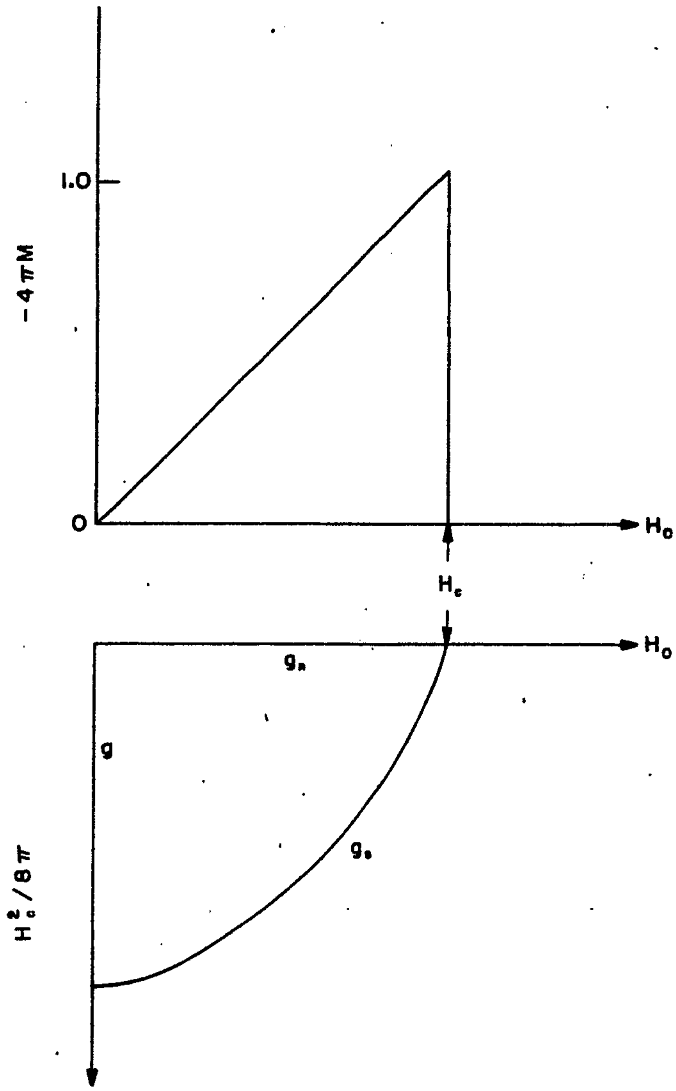


Fig. 1. Magnetization and free energy (type I).

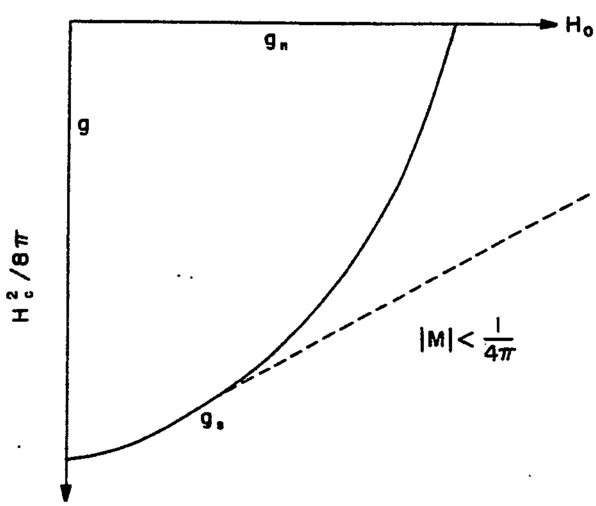


Fig. 2. Effect of reduction of magnetization on free energy.

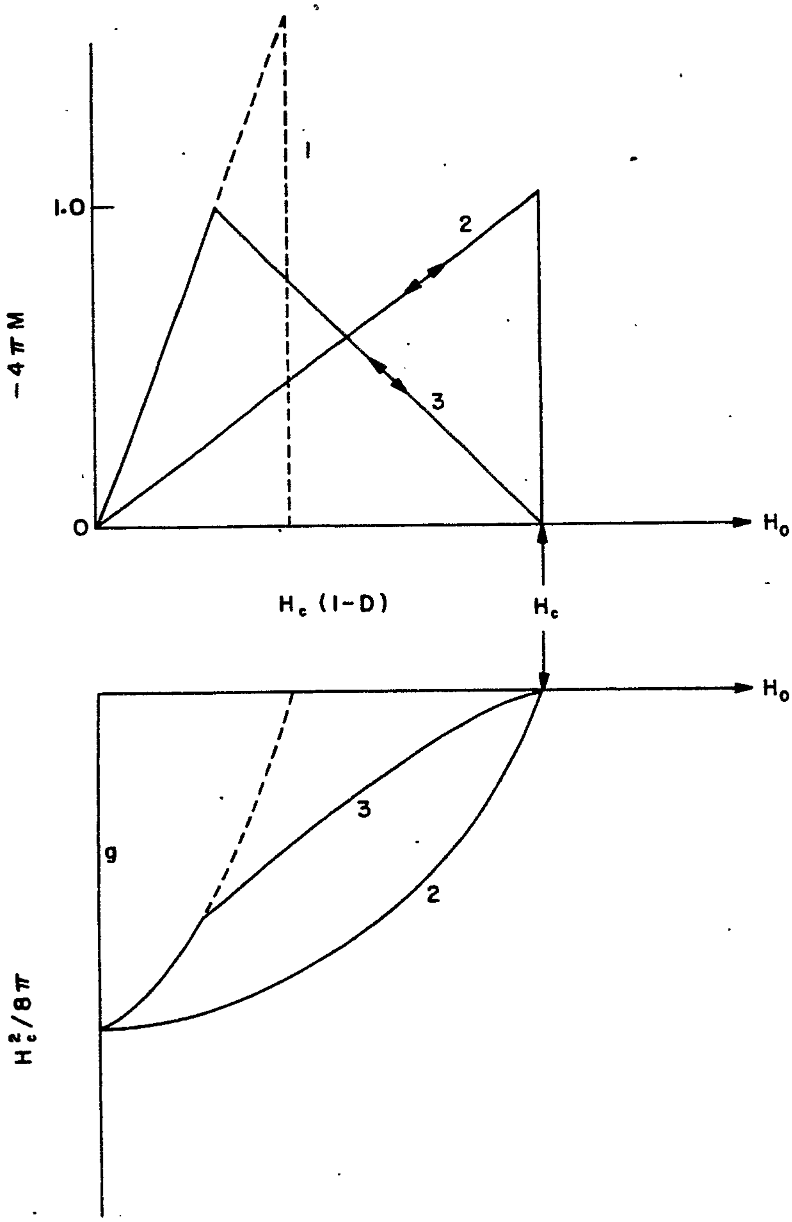


Fig. 3. Magnetization and free energy intermediate state.

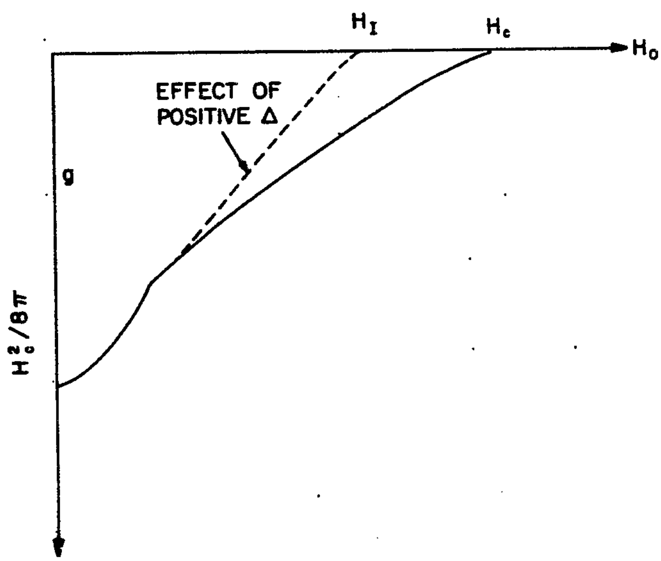


Fig. 4. Effect of positive surface energy on free energy of intermediate state.

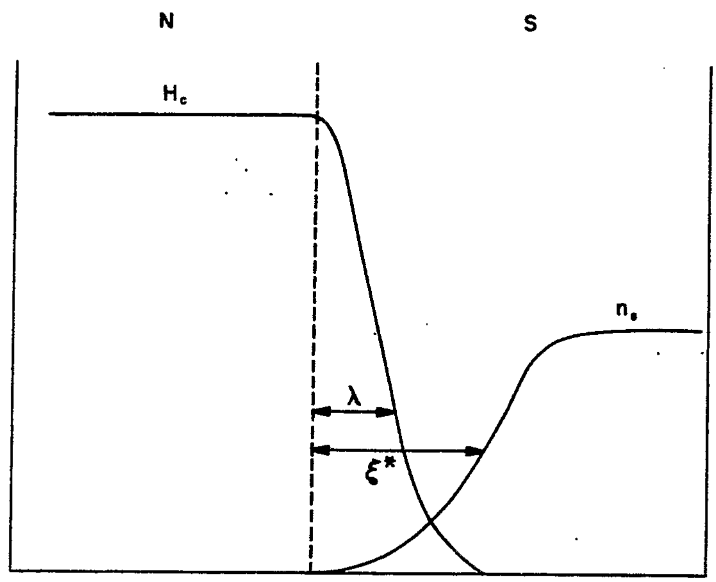


Fig. 5. Normal-superconducting boundary.

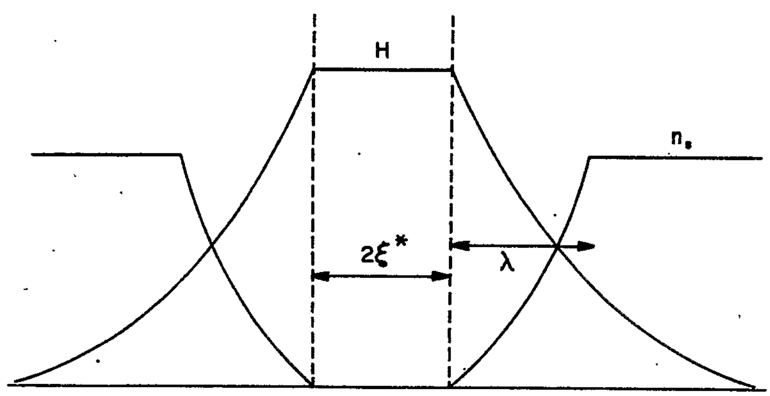


Fig. 6. Schematic of vortex structure.

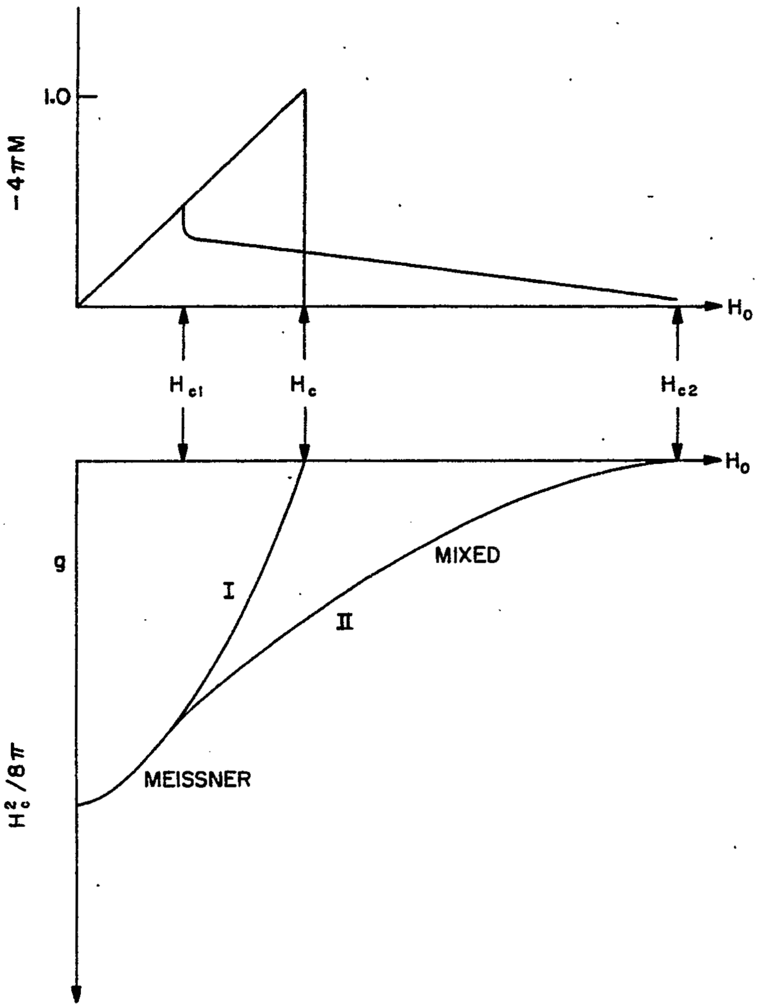


Fig. 7. Magnetization and free energy of type I and type II superconductors.

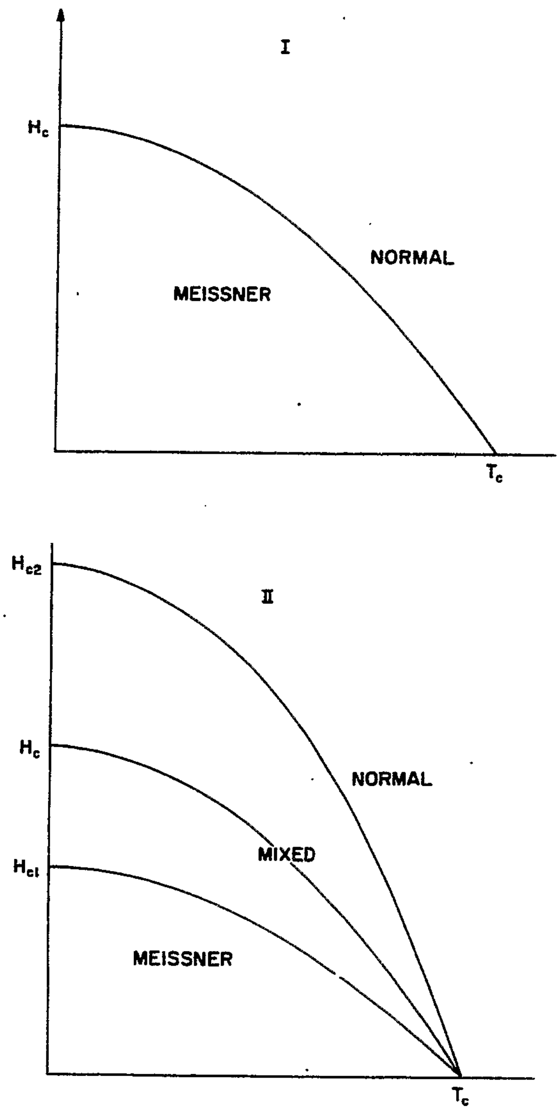


Fig. 8. Phase diagrams of type I and type II superconductors.

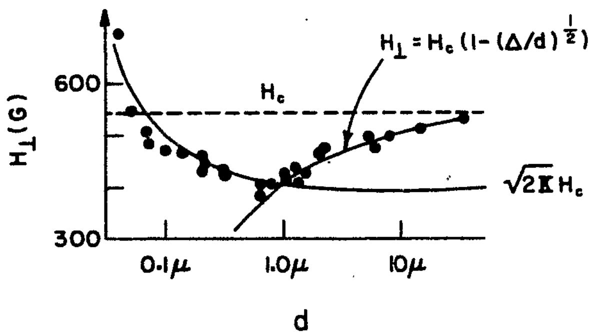


Fig. 9. Thickness dependence of perpendicular critical fields in thin Pb films and foils.

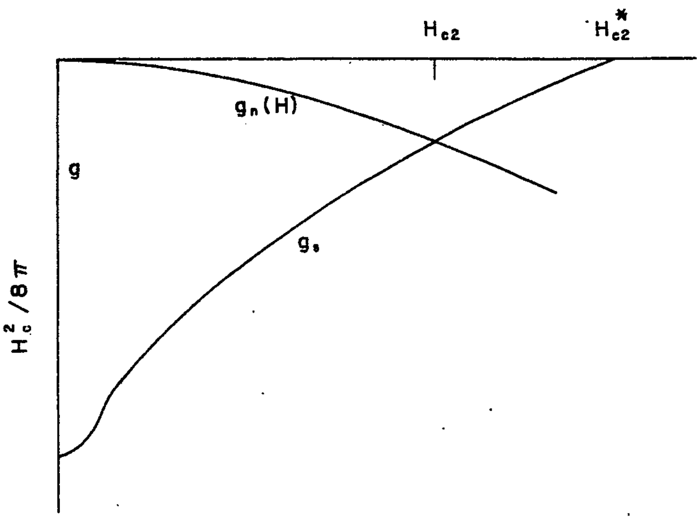


Fig. 10. Free energy, including spin energy, of normal state — first order transition.

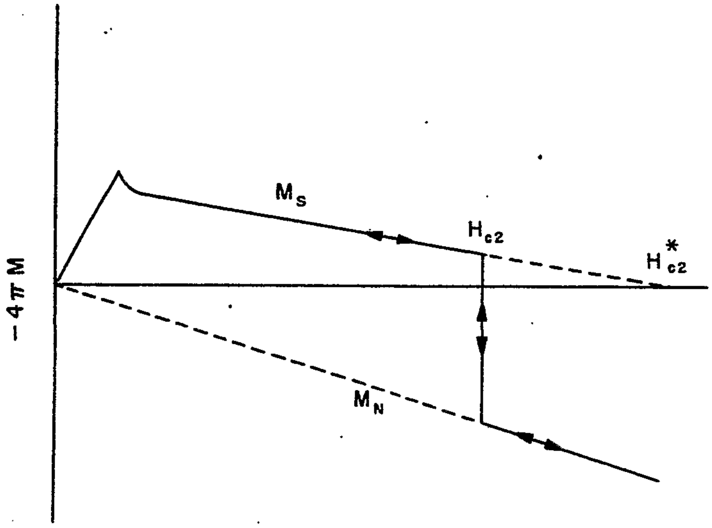


Fig. 11. Magnetization corresponding to free energy of Fig. 10 — first order transition.

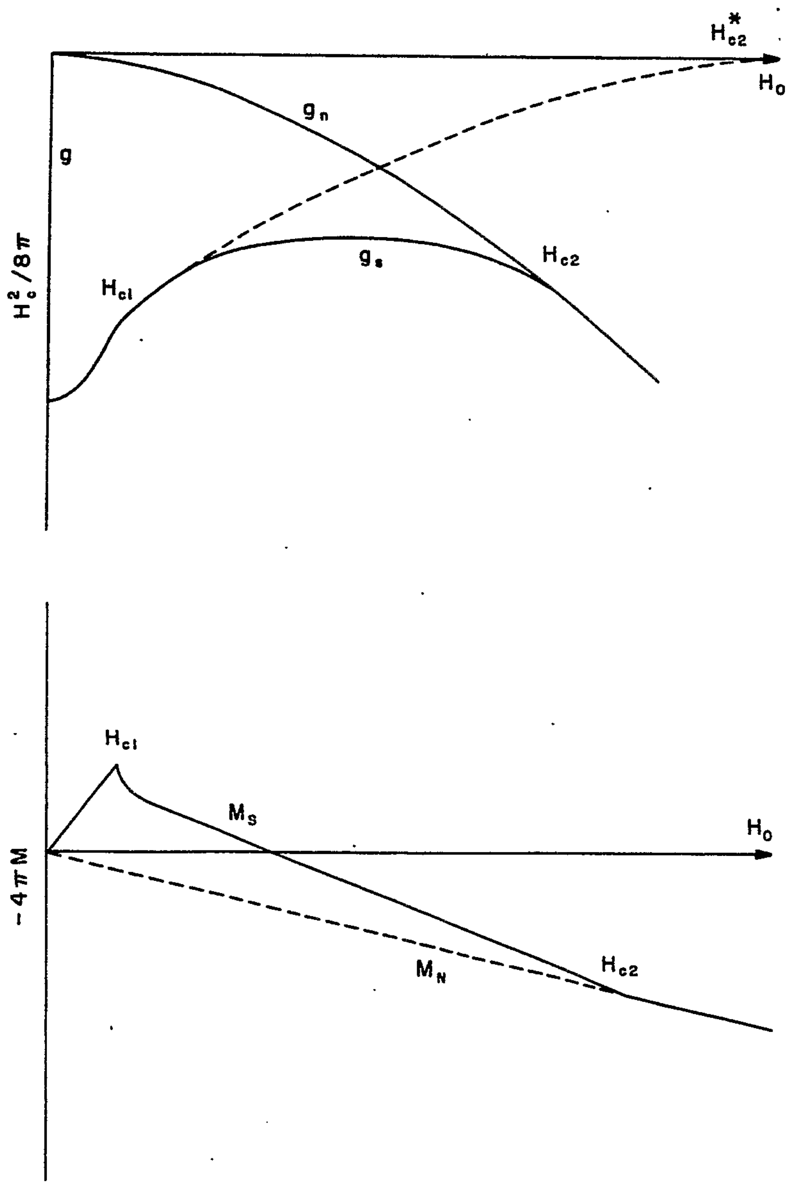


Fig. 12. Free energy and magnetization, including spin energy, of normal and superconducting states — second order transition.

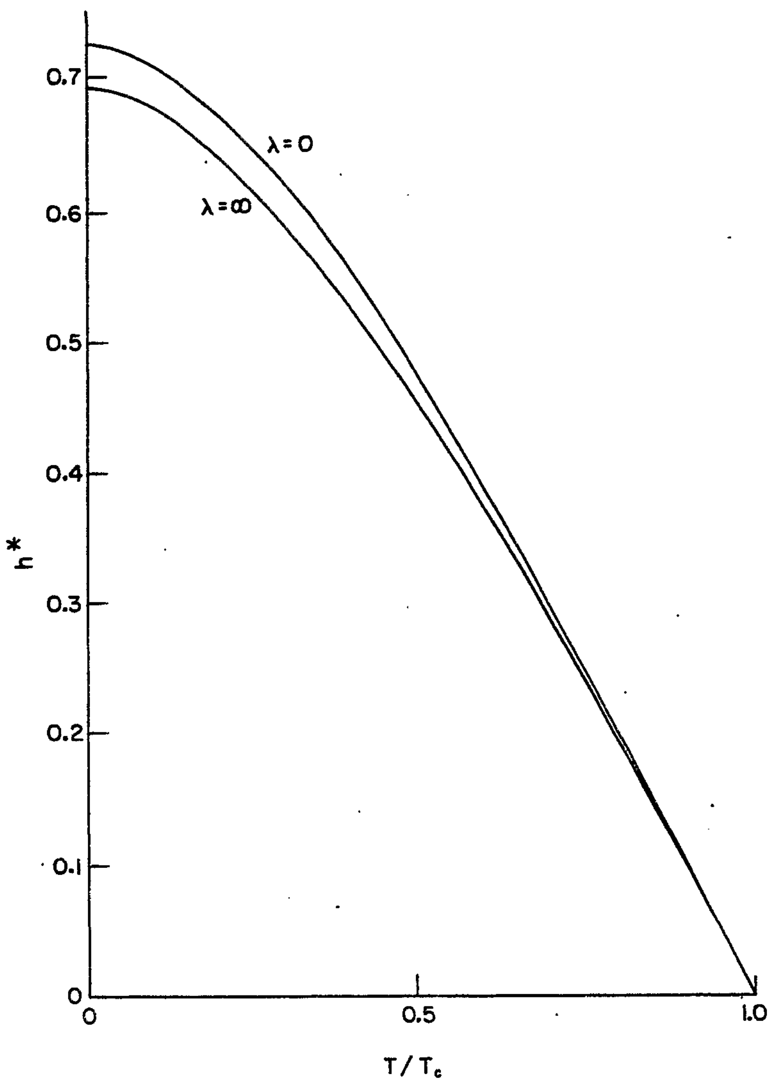


Fig. 13. Reduced field $h^*$ as a function of $T/T_c$, after Ref. 18.

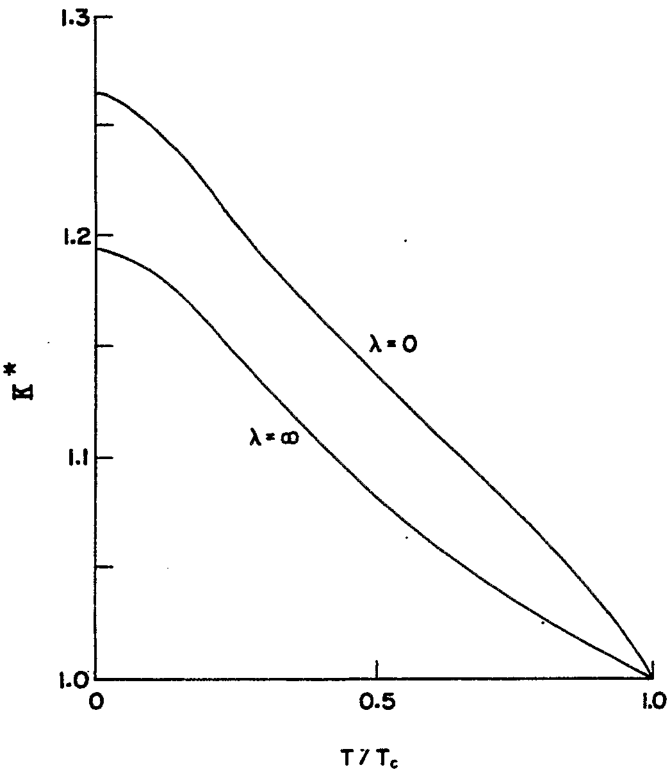


Fig. 14. Reduced parameter $\kappa^*$ as a function of $T/T_c$, after Ref. 18.

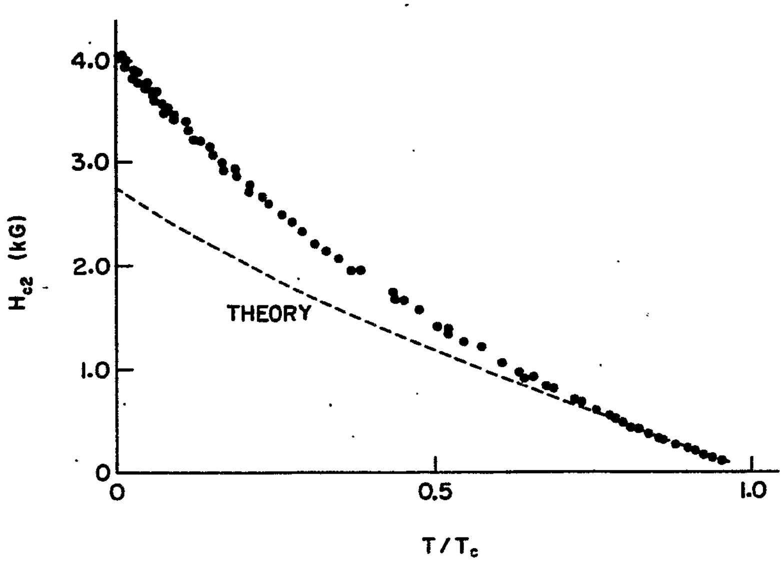


Fig. 15. Measured $H_{c2}$ for Nb compared with theory of Hohenberg and Werthamer, after Ref. 36.

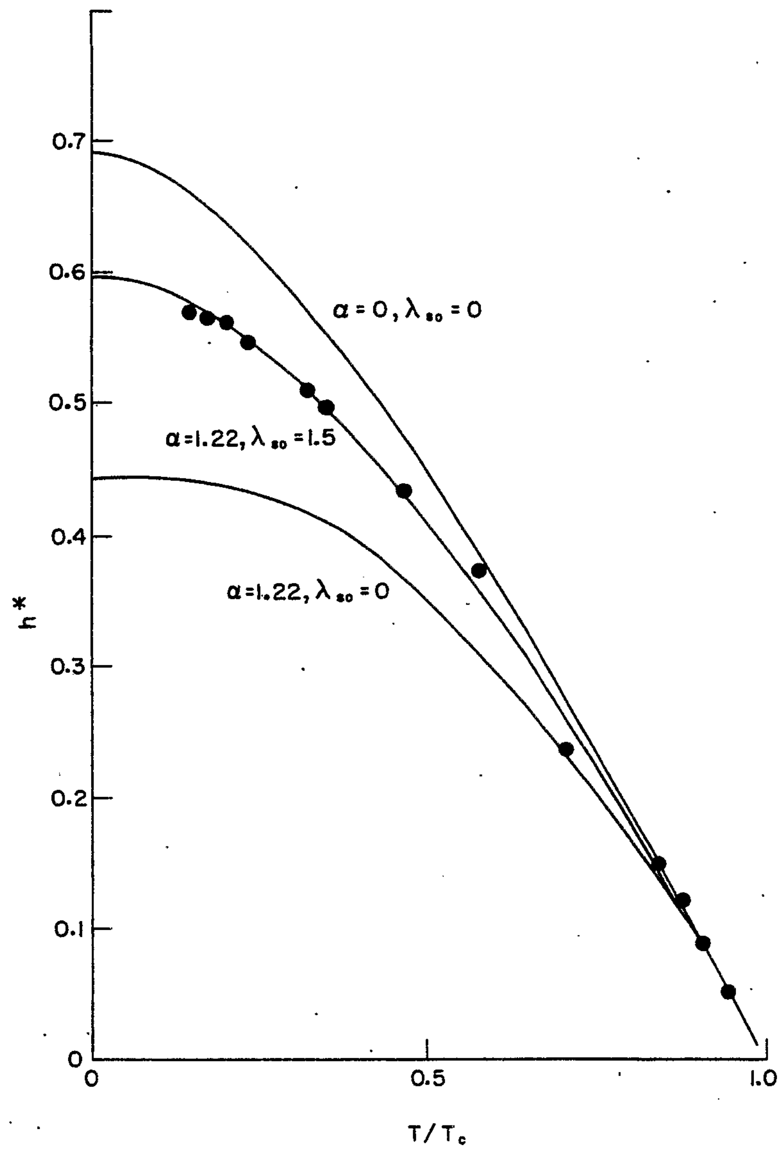


Fig. 16. Reduced field $h^*$ as a function of $T/T_c$ for Ti(0.56)Nb(0.44), after Ref. 17.

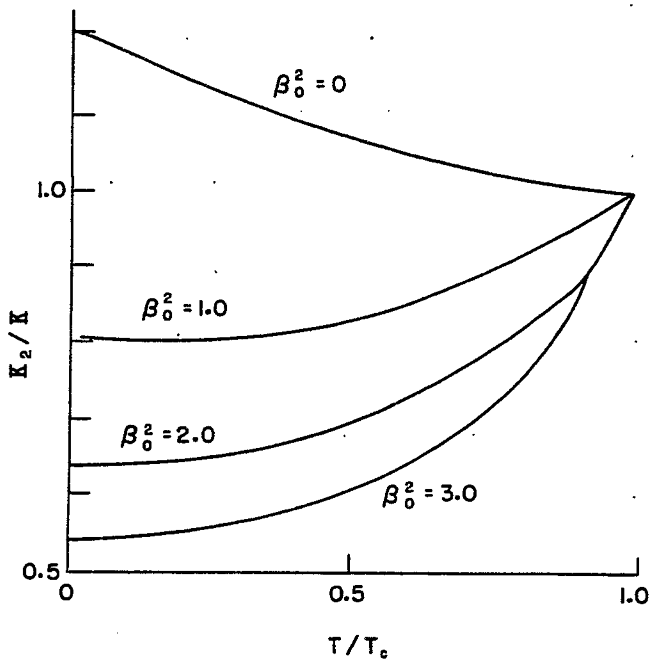


Fig. 17. Reduced parameter $\varkappa_2/\varkappa$ as a function of $T/T_c$, after Ref. 17.

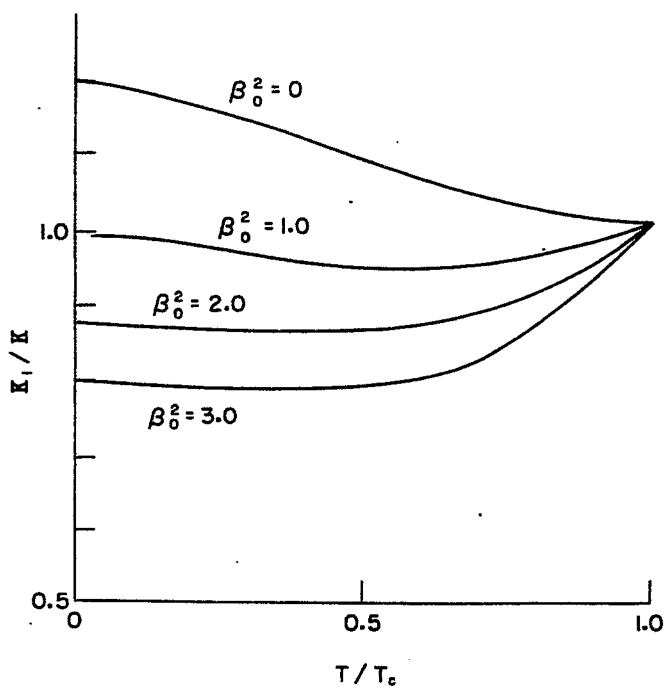


Fig. 18. Reduced parameter $\varkappa_1/\varkappa$ as a function of $T/T_c$, after Ref. 17.

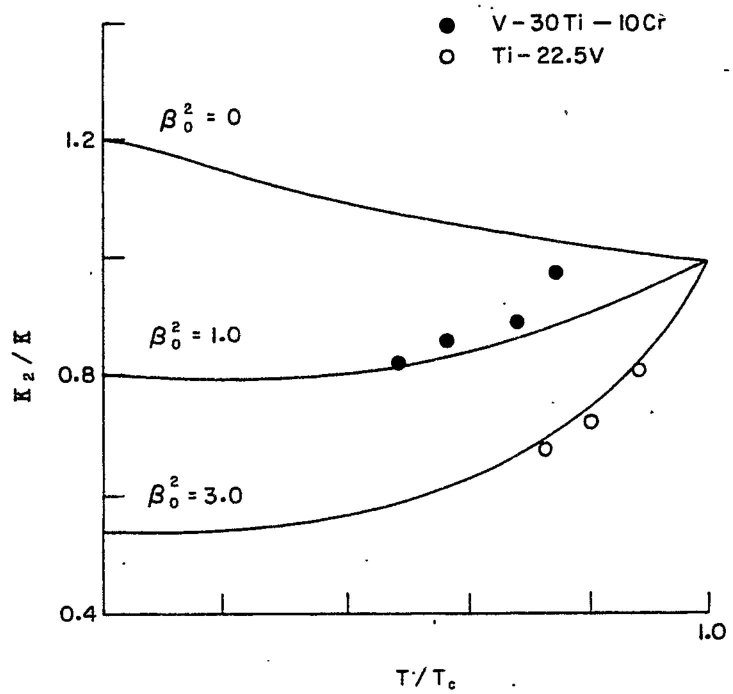


Fig. 19. Reduced parameter $\kappa_2/\kappa_1$ for two alloys as a function of $T/T_c$ compared to Maki theory after Ref. 34.

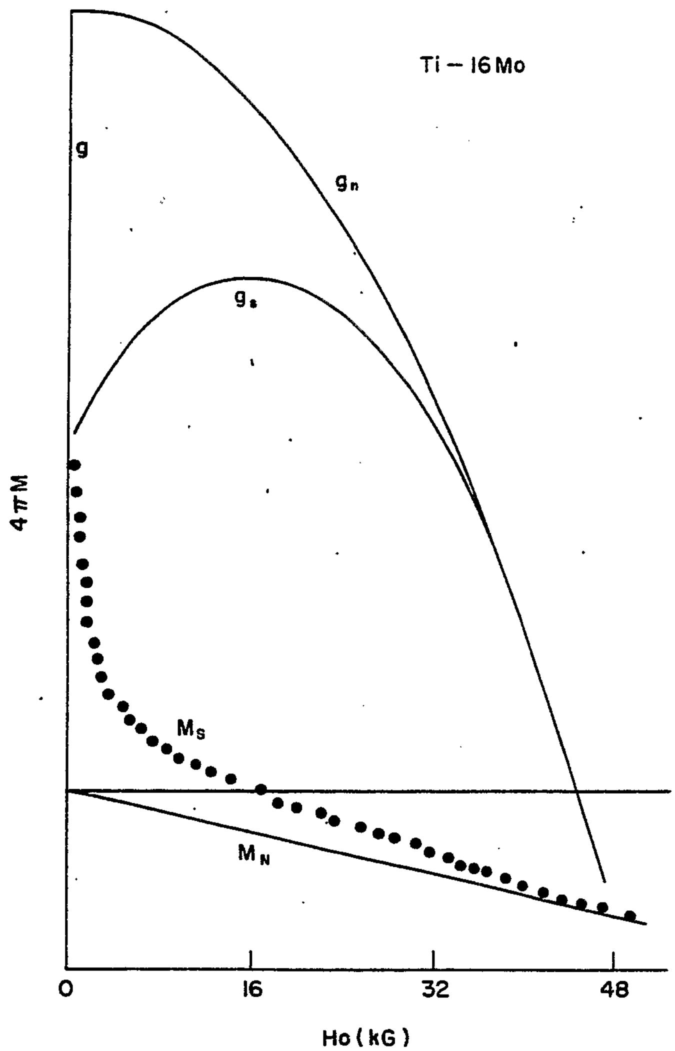


Fig. 20. Magnetization and derived free energy for Ti16%Mo alloy after Ref. 34.

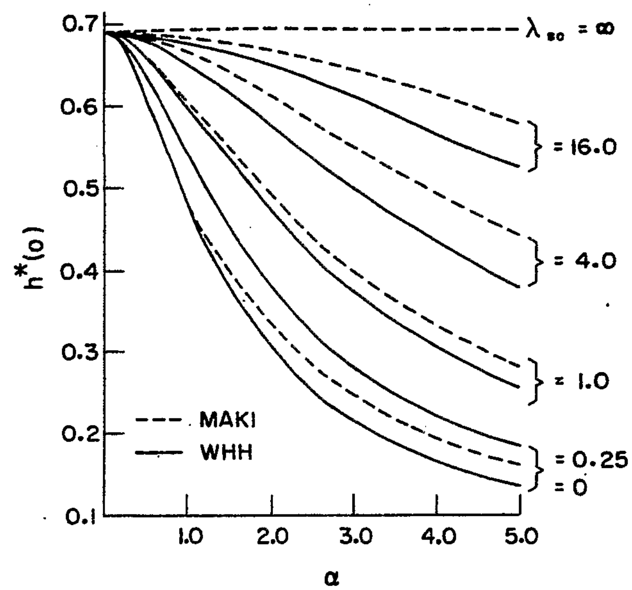


Fig. 21. The reduced field $h^*(0)$ as a function of $\alpha$ and $\lambda_{so}$ from theories of Maki and WHH after Ref. 34.

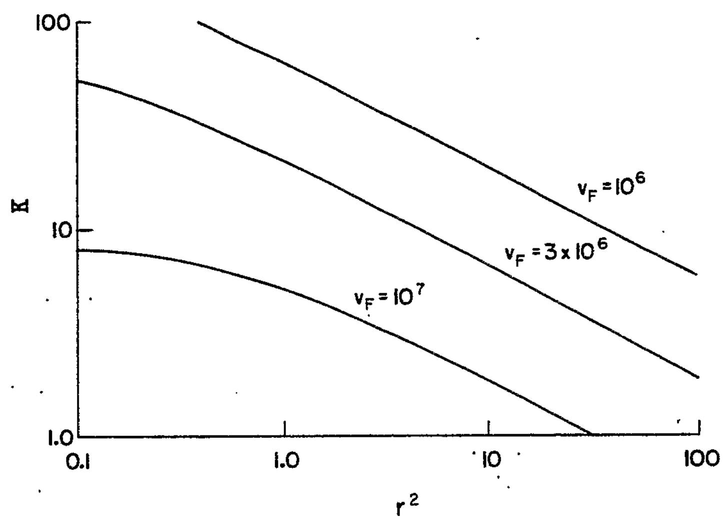


Fig. 22. Dependence of $\kappa$, in two-band model for $Nb_3Sn$, on Fermi velocity and parameter $r^2$.

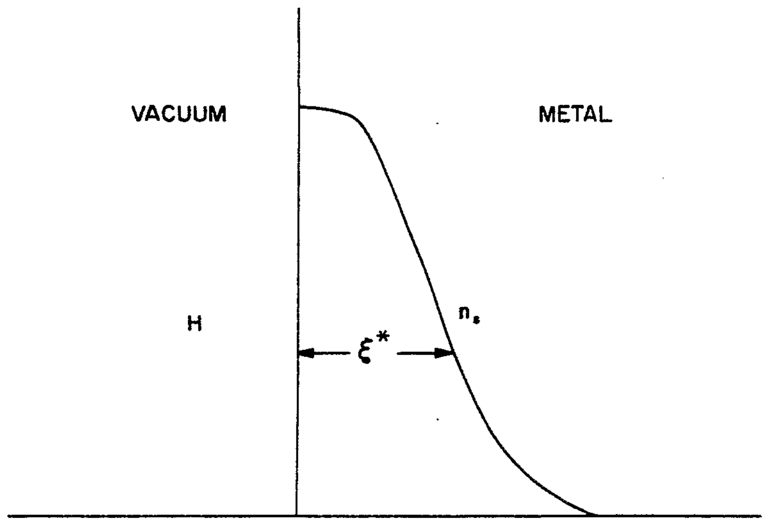


Fig. 23. Spatial variation of order parameter for surface superconductivity ($H_{c2} < H < H_{c3}$).

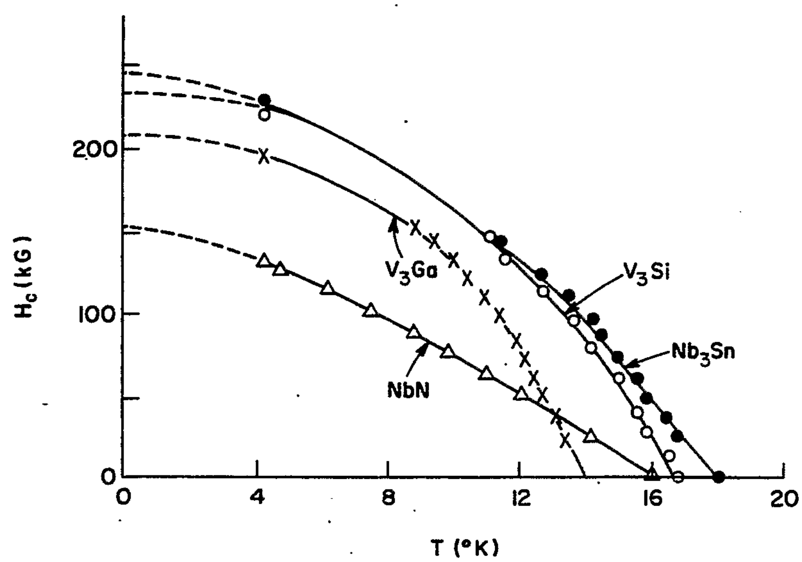


Fig. 24. Critical field curves of $Nb_3Sn$, $V_3Si$, $V_3Ga$ and NbN after Ref. 51.