

CHAPTER II

SUPERCONDUCTIVITY

II.1 Infinite Conductivity

Superconductivity was first discovered and so named by Kamerlingh Onnes¹ in 1911. He observed that a sample of mercury cooled to liquid helium temperature exhibits no measurable resistivity. Since that time many metals and alloys have been discovered which exhibited this property. We call the temperature at which the specimen changes from a state of normal electrical resistivity to a superconducting state "critical or transition temperature, T_c ". The transition width is very narrow. In good samples, it is sharp to 10^{-3} degrees, but in strained or inhomogeneous alloys, the transition may be a degree wide². The upper limit of T_c is about 21°K, for the alloy $Nb_3(Al_{0.8}Ge_{0.2})$.³

¹Onnes, H.K., Leiden Comm. 1206, 1226 (1911) ; quoted in D. Shoenberg, Superconductivity, Cambridge, New York, 1952, p.1

²De Haas, W.J. and J. Voogd, Leiden Comm. 214c (1931)
quoted in D. Shoenberg, Superconductivity, Cambridge; New York
1952 p.2

³Matthias, B.T., T.H. Geballe and V.B. Compton
" Superconductivity " Rev. Mod. Phys., 35, 1 (1963)

In the superconducting state the dc electrical resistivity is zero, or at least so close to zero that persistent currents have been observed to flow without attenuation in superconducting rings for more than a year. By such means, one can show that the resistance has dropped by a factor of more than 10^{15} below the normal residual resistance. Thus, for direct current we conclude that the resistance truly vanishes. Although the resistance is essentially zero up to megacycle frequencies, some resistive effects reappear in the microwave region, and there is no observable difference between normal and superconducting metals for optical frequencies⁴.

As we shall see in more detail later, there is a characteristic frequency for each superconductor associated with energy gap in its excitation spectrum. At $T = 0^\circ\text{K}$, this is given by

$$h\nu_g = E_g = 3.5 kT_c \quad (2.1)$$

as predicted by the BCS theory⁵. For typical superconductors, this gap frequency corresponds to roughly 1 mm wavelength radiation. At $T = 0^\circ\text{K}$, there is a sudden onset of absorption when this

⁴Pippard, A.B., " Impedance at 9400 Mc/sec of single crystals of normal and superconducting tin " Proc. Roy. Soc. Lond., A 203 98 (1950)

⁵Bardeen, J., L.N. Cooper and J.R. Schrieffer, " Theory of Superconductivity " Phys. Rev., 108, 1175 (1957).

frequency is reached. As T increases the equation (2.1) must be modified in the sense that the energy gap decreases and is equal to zero when the temperature reaches T_c .

For a number of years it was thought that a superconductor was simply a " perfect conductor," but the discovery by Meissner and Ochsenfeld⁶ led to the realization that the effect was of much wider significance than originally supposed.

II.2 Meissner's Effect.

In 1933 Meissner and Ochsenfeld found that a magnetic field is excluded from a superconductor, regardless of the past history of the specimen. (This is not valid if the magnetic field is greater than H_c , the critical field) This phenomena is called the " Meissner's effect " (Fig. 1). In fact, the field can penetrate into the superconductor but only to a depth λ (penetration depth) $\approx 10^{-6}$ cm. (see Sec. II.4).

This shows that a bulk superconductor behaves in an applied external field H_a as if inside the specimen $H = 0$. This important result cannot be derived merely from the characterization of a superconductor as a medium of zero resistivity or perfect conductor. This can be seen from the following.

From the Maxwell's equation

$$c \vec{\nabla} \times \vec{E} = - \frac{\partial H}{\partial t} \quad (2.2)$$

⁶Meissner, W. and R. Ochsenfeld, Naturwiss., 21, 787 (1933)
quoted in Boorse, H.A., AJP, 27, 47 (1959).

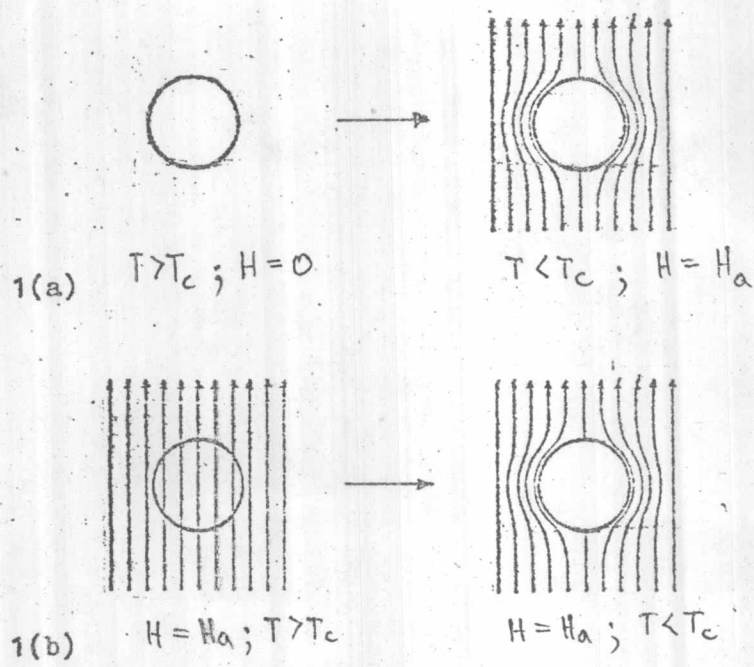


Fig. 1 The Meissner's Effect.

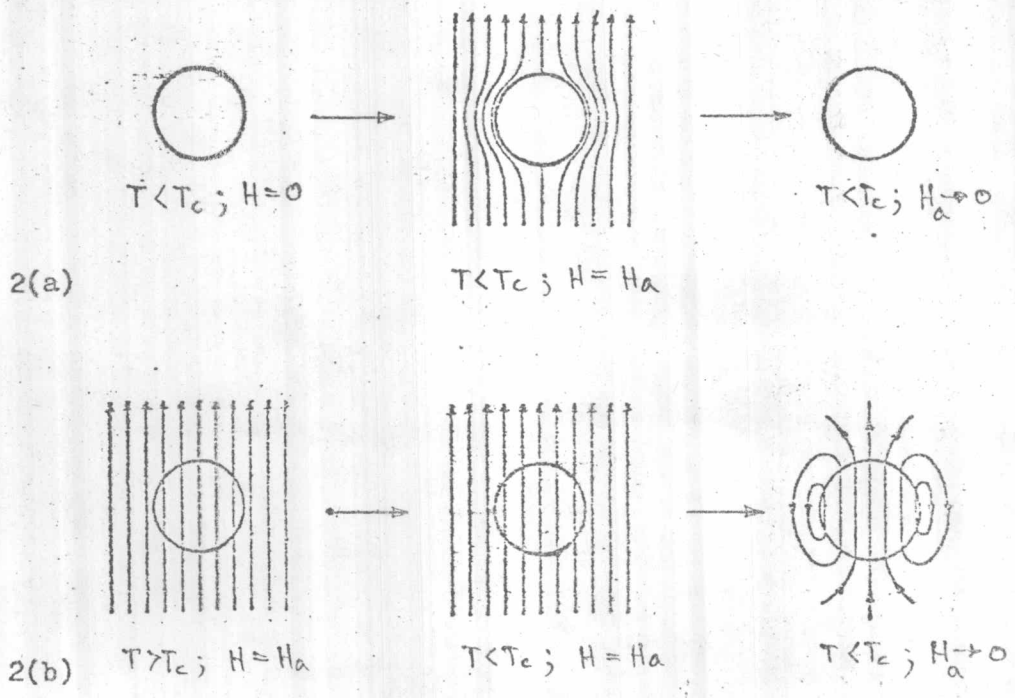


Fig. 2 The Behavior of a Perfect Conductor in an Applied Magnetic Field

Making use of Ohm's law, $\vec{E} = \rho \vec{J}$ where \vec{J} is the current density and ρ the electrical resistivity. We see that if the resistivity ρ goes to zero while \vec{J} is held finite, then \vec{E} must be zero. In the limit of zero resistance, therefore, $\partial \vec{H} / \partial t = 0$ or $\vec{H} = \text{constant}$ at all time after the attainment of this state (perfect conducting state). Some consequences of this result may be visualized with help of Fig. 2 .

This leads to the formulation of the Meissner's effect that a superconductor shows " perfect diamagnetism ". The perfect conductivity is a necessary but not sufficient condition for the perfect diamagnetism, and so these two properties are to be regarded as distinct fundamental characteristics of a superconductor.

II.3 Critical Field and Critical Current.

A sufficiently strong magnetic field will destroy superconductivity⁷. The critical value of the applied magnetic field for the destruction of superconductivity is denoted as $H_c(T)$, the critical field; it is a function of temperature. At the critical temperature the critical field is zero. The variation of the critical field with temperature for a superconductor is shown in Fig. 3 schematically. The curve separates the superconducting state in the lower left of the figure from the normal state in the upper right.

⁷Onnes, E.K., Leiden Comm., 139f (1913) ; quoted in Chandrasekhar, B.S., Superconductivity, Vol. I , Edited by R.D. Park, Marcel Dekker, Inc., New York 1969; p.2 .

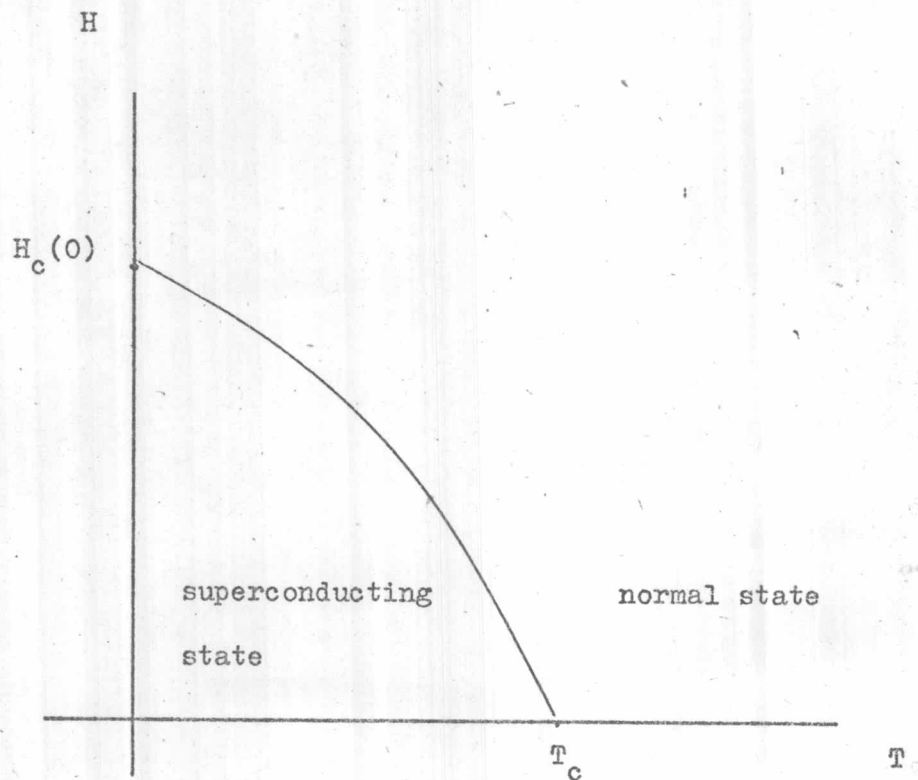


Fig. 3 The Variation of the Critical Field with Temperature
($H_c(T)$ curve) for a Superconductor.

The current can destroy superconductivity also, if the current increases to the value which produces a field H_c at the surface of the superconductor. This current is called the critical current. At the critical current the superconducting state changes to the normal state. This is Silsbee Effect⁸.

II.4 Penetration Depth.

The magnetic field can penetrate into a superconducting metal to the characteristic length λ (penetration depth). The value of λ is about 10^{-6} cm. Its dependence on various physical parameters can provide a sensitive test of the quantitative aspects of any theory of superconductivity⁹.

The penetration depth occurs only if the magnetic field is parallel to the surface of the superconductor. This can be seen from the London equations (London, 1935). These equations which apply to a superconductor in a static field are

$$\vec{E} = 0 \quad (2.3)$$

$$\vec{\nabla} \cdot \vec{H} = 0 \quad (2.4)$$

$$c \operatorname{curl} \Lambda \vec{j}_s = -\vec{H} \quad (2.5)$$

$$c \operatorname{curl} \vec{H} = 4\pi \vec{j}_s, \quad (2.6)$$

⁸Shoenberg, D., Superconductivity, Cambridge University Press, 1952; p. 10, 130

⁹See for instance, Pippard, A.B., " Field Variation of the Superconducting Penetration Depth ", Proc. Roy. Soc. Lond., A 203 210 (1950)

where $\lambda = \sqrt{\Lambda c^2 / 4\pi}$, is the penetration depth and $\Lambda = m/n_s e^2$ with m , n_s and e are mass, density and charge of superelectron.

The latter two may be combined to give,

$$\vec{H} + \lambda_L^2 \text{curl curl } \vec{H} = 0 \quad (2.7)$$

Let the surface of a specimen be on xy plane and the region $z < 0$ being empty.

We will consider two cases.

(i) An applied magnetic field is parallel to z , from (2.4) $\partial H / \partial z = 0$, or H is spatially constant. Thus $\vec{\nabla} \times \vec{H} = 0$ and $\vec{j}_s = 0$. Substituting these into (2.7) yields

$$\vec{H} = 0$$

Hence it is not possible to have a field normal to the surface of the specimen.

(ii) An applied magnetic field is along x direction, from (2.6) \vec{j}_s is along \hat{y} ,

$$\frac{dH}{dz} \hat{y} = \frac{4\pi}{c} j_s \hat{y} \quad (2.8)$$

Substituting this into the equation (2.5) yields

$$\frac{dj_s}{dz} = \frac{n_s e^2}{mc} \vec{H} \quad (2.9)$$

$$\frac{d^2 \vec{H}}{dz^2} = \frac{H}{\lambda_L^2} \quad (2.10)$$

where $\lambda_L^2 = mc^2 / 4\pi n_s e^2$. Hence the solution that remains finite in the superconductor is exponentially decreasing,

$$H(z) = H(0) \exp(-z/\lambda_L) \quad (2.11)$$

where λ_L is the penetration depth in the London theory.

II.5 The Specific Heat Capacity.

At low temperature the specific heat capacity (c_n) may be expressed as

$$c_n = \gamma T + \beta T^3 \quad (2.12)$$

The first term on the right is due to the electrons and the second is due to the lattice. The properties of the lattice are unchanged between the normal and superconducting states¹⁰. We shall consider only the electronic contribution to the specific heat capacity, and denote it by c_{es} and c_{en} , for the superconducting state and normal state.

When the transition occurs in zero magnetic field, the behavior of electronic specific heat is as the following,

(i) There is a discontinuous jump in the specific heat capacity at T_c with $c_{es}(T_c) \simeq 3 c_{en}(T_c)$.

(ii) c_{es} drops rapidly and nonlinearly for $T < T_c$; going to zero at $T = 0^\circ\text{K}$, (Fig. 4).

This behavior was first demonstrated by Keesom and Kok¹¹ in

¹⁰Wilkinson, M.K., et al, " Neutron Diffraction Observation on the Superconducting State " , Phys. Rev., 97 , 889 (1955)

¹¹Keesom, W.H. and J.A. Kok, Leiden Comm., 230c, (1934) quoted in Chandrasekhar, B.S., Superconductivity, Vol.I, Edited by R.D. Park, Marcel Dekker, Inc., New York 1969; p. 7

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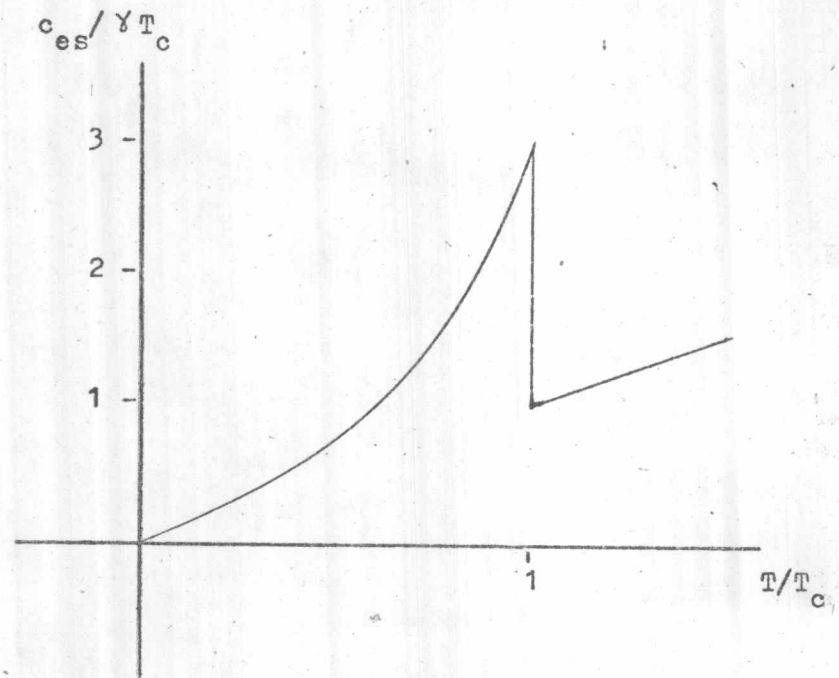


Fig. 4 The electronic specific heat capacity

tin and has since been observed in other superconductors.

The qualitative features of this transition was predicted by thermodynamical arguments. Thermodynamical equations can be used since the transition is reversible according to the Meissner's effect. When a superconducting specimen is placed in a magnetic field, H_a , its total free energy (Gibb's free energy) is

$$G_s(T, p, H_a) = g_s(T, p) - \int_0^{H_a} \mu dH_a \quad (2.13)$$

where $g_s(T, p)$ is the free energy of the superconducting specimen in the absence of a magnetic field, μ is the total magnetic moment of the specimen, p is the pressure and T , the absolute temperature. In the normal metal if we neglect the small susceptibility, then $\mu = 0$ and the free energy of the normal metal is independent of field.

$$G_n(T, p, H_a) = g_n(T, p) \quad (2.14)$$

To avoid the extraneous effects due to geometry, it is simplest to consider initially the case of a long cylinder with its axis longitudinal to the field direction. We know that under these circumstances the specimen remains superconducting until the applied field attains the critical value, H_c , at which point it passes into the normal phase. Thus, $G_s(T, p, H_c) = G_n(T, p, H_c)$ and from the Eq. (2.13), Eq. (2.14) and the fact that the magnetization of long cylinder superconductor is equal to $-\frac{H_a}{4\pi}$ we get

$$g_n(T, p) - g_s(T, p) = \frac{VH_c^2(T, p)}{8\pi} \quad (2.15)$$

where V is the volume of the specimen.

Differentiation of (2.15) with respect to the temperature yields

$$S_n(T) - S_s(T) = (V H_c / 4\pi) \frac{dH_c}{dT} \quad (2.16)$$

where S is the entropy, and a second differentiation gives

$$c_n(T) - c_s(T) = -\frac{V T}{4\pi} \left[H_c \frac{d^2 H_c}{dT^2} + \left(\frac{dH_c}{dT} \right)^2 \right] \quad (2.17)$$

We must stress that these equations are valid along the curve

$H_c = H_c(T)$. Since $H_c(T_c) = 0$, it follows that at the critical temperature we have $S_n = S_s$. From the curve in Fig. 3 we see that dH_c/dT is always negative. From (2.16) it follows that $S_n > S_s$ and hence that the superconducting state is more ordered than the normal one. Moreover, for $T = T_c$ (i.e. $H_c = 0$) we obtain from (2.17)

$$c_s - c_n = (V T_c / 4\pi) (dH_c/dT)^2 > 0$$

Therefore the theory gives a jump in the specific heat, as has been observed experimentally.

The discovery¹², in 1954, that the electronic specific heat capacity of superconducting vanadium and tin could be fitted to an expression of the form

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¹²Corak, W.S., et al, " Exponential Temperature Dependence of the Electronic Specific Heat of Superconducting Vanadium " Phys. Rev., 96 , 1442 (1954)

$$a \exp(-b/t) ; t = T/T_c ; a, b = \text{constant}$$

was a significant contribution to the understanding of superconductivity. This suggested the existence of an energy gap in the excitation spectrum.

II.6 Type I and Type II Superconductors.

The magnetization curve expected for a superconductor under the condition of the Meissner's effect is sketched in the Fig. 5(A). Pure specimens of many materials exhibit this behavior, they are called type I superconductors or soft superconductors. The values of H_c are low for type I superconductors, in the order of 10^2 gauss.

Other materials exhibit a magnetization curve of the form of Fig. 5 (B) and are known as type II superconductors or hard superconductors. They tend to be alloys and transition metals. Type II superconductors have superconducting electrical properties upto a field denoted by H_{c2} . Between the lower critical field H_{c1} and the upper critical field H_{c2} the flux density $B \neq 0$ and the Meissner's effect is said to be incomplete. The value of H_{c2} may be 100 times or more higher than the value of H_c calculated from the thermodynamics of the transition. In the region between H_{c1} and H_{c2} the superconductor is threaded by flux lines and is said to be in the vortex state. A field H_{c2} of 410 kG. has been attained in an alloy of $Nb_{79}(Al_{73}Ge_{27})_{21}$ at the boiling point of helium¹³.

¹³Foner, S., et al, Physics Letters, 31A, 349 (1970)
quoted in Kittel, C. Introduction to Solid State Physics, John Wiley & Sons, Inc., Fourth Edition, 1971, p. 408.

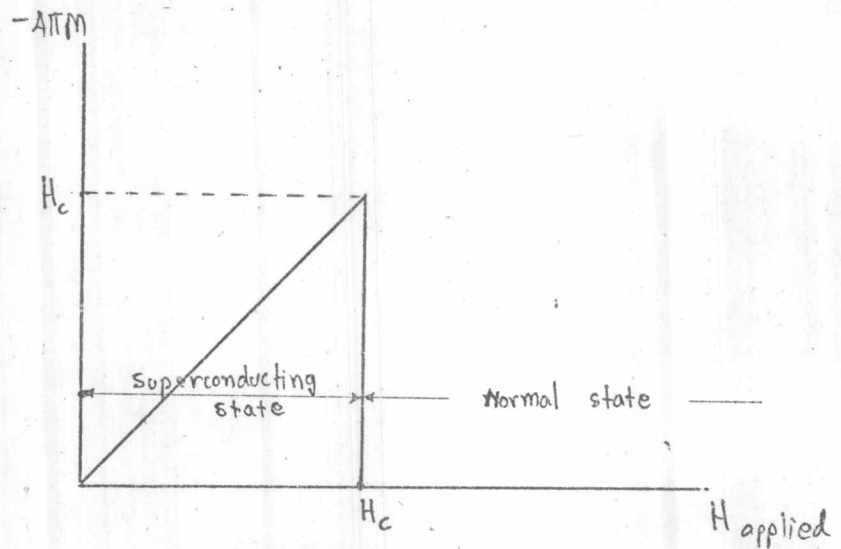


Fig. 5(A) The Magnetization Curve of Type I Superconductors

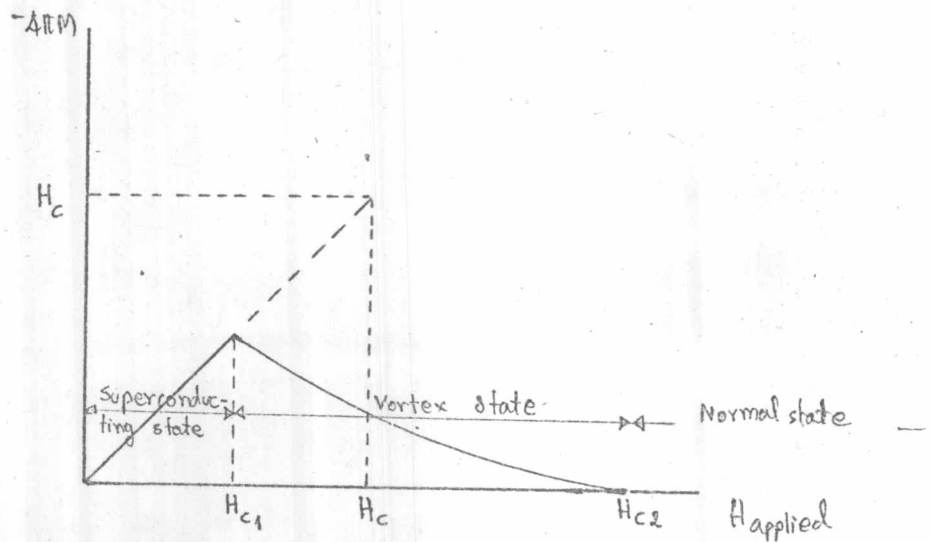


Fig. 5(B) The Magnetization Curve of Type II Superconductors

Fig. 5 The Magnetization Curve of Superconductors.