A.

HISTORICAL OUTLINE:

H. Kamerlingh Onnes first successfully liquified helium by attaining 4.2°K in 1908. This great feat opened a new domain for scientific investigation: The unthinkably frigid zone just above the absolute zero of temperature. Onnes immediately recognized the vast potential his accomplishment created and decided to perform resistivity experiments at these heretofore unknown temperatures.

It was everyone's guess that electrical resistance would either cease, level off, or increase near absolute zero, either because of heat, impurity, or electronic condensation effects, respectively. See Figure A-1. Onnes decided to measure the resistive properties of mercury, to determine the nature of this electronic phenomenon, at liquid helium temperatures.[1]

Strangely, the resistance of mercury steadily declined with reduced temperature until suddenly at 4.152°K, which was remarkably close to the helium boiling point, the metal lost all resistance to electric currents, within the limits of his accuracy. See Figure A-2.

It was quickly speculated that this perfect or super-conduction of electric current was due to some new condition within the sample yielding a state of infinite conductivity.

Onnes and several other investigators performed tests with spheres of lead and other "superconductive" materials leading to the result that (A) conductivity was indeed perfect and (B) any incident magnetic field was excluded or not from the interior of such a lossless sample depending on its prehistory, that is, whether the field was applied before or after the material became superconducting. See Figure A-3.

It is not with little shock that the scientific community of 1933 was jolted by the news of an experiment by W. Meissner and R. Ochsenfeld which conclusively proved that the magnetic state of a superconductive sample is independent of its pre-history. Incredibly, the applied field which was present in their mono-crystal of tin above the transition temperature was summarily and completely expelled upon reducing the temperature below its critical value, Tc. Therefore, the internal field is *always* zero while the metal is in the superconductive state.[2] See Figure A-4.

How could such a wondrous mechanism, the so-called Meissner Effect, remain undetected for more than twenty years? (A) The previous experimenters had not been properly cautious and careful in taking readings on the fields outside their test samples.[3] (B) Often hollow lead, etc., spheres were used in order to reduce helium refrigerant requirements, resulting in honestly mistaken measurements.[4] (C) The theoreticians had created an entire body of experimentally and mathematically unquestionable phenomenological treatments based on the perfect conductor premise.[5] With the foregoing in mind it is with ease that we are able to understand how the entire scientific world was kept within the bounds of its own preconceived myth (save for a visionary few).[6]

In the intervening years between the discovery of the Meissner Effect and the introduction of the microscopic theory in 1957, investigators groped for two rather elusive points: (A) A theory which would explain the perfect electrical conduction and Meissner Effect coupled with the experimentally found limits underwhich superconductivity may occur: below a certain maximum applied magnetic field and under a particular highest ambient temperature, see Figure A-5, and (B) superconductive materials which would retain their unique properties in very high fields and temperatures.

During this period some confusion[7] resulted because of a lack of universal recongition for many years of two classes of superconductors and the distinction between various phases within each class. Eventually, experimentation proved that: (A) Class I superconductors of the soft metals had a low critical field and temperature and entered an intermediate state (see next section) of alternate domains of superconductive and normal material when the geometry of the sample was other than a thin cylinder in a longtitudinal magnetic field and the applied field reached a locally critical intensity, see Figure A-6, and (B) Class II superconductors of the hard metals and alloys had comparatively high critical fields and temperatures and entered a mixed state (see next section) above a certain less than critical magnetic field independent of sample geometry. The intermediate state and mixed state were often confused and generally research was somewhat minimal since practical use of this phenomenon looked very far away indeed due to temperature (max. around 8°K for N_b) and field (Max. around 1800g for N_b [Type II]) limitations.

The greater part of scientific research has actually been done since Yntema in 1955 created the first successful high field superconductive electromagnet by using unannealed niobium wire to attain 7.1 Kgauss. He was soon followed by other experimenters who made use of cold working technology to improve the performance of niobium windings. Finally, since 1961 Kunzler and others successfully developed alloying techniques which produced Type II superconductors capable of withstanding (N_bS_n: 200 Kgauss & 18°K) inordinately high fields and almost "warm" temperatures, before losing their superconductive properties. This ushered in a new era of applied research and development, including: computer switching elements, motors, generators, magnets, and lossless bearings, nearly lossless power transmission lines and transformers, etc.

The Bardeen Cooper Schrieffer Theory of 1957 explained the phenomenological theories of F. London on a microscopic basis.[8] Superconductivity was understood to be: (A) a condensation to lower energy by so-called super-electrons due to a quantum mechanical electron pairing process, (B) this pairing process was seen to occur only within a finite distance, the Coherence Length, which, if longer or shorter than the depth to which a field penetrates into the surface of a sample, meant it was either Type I or Type II, (C) the critical fields and temperatures were then just the necessary energy inputs to raise the super-electrons of zero resistance to normal electrons of finite resistance, that is, the electron "fluids" were separated by an energy-gap, and (D) the Meissner Effect was due to a sudden condensation energy outflux at the transition, an energy capable of doing magnetic work.

Today, research is pressing forward at an ever accelerating pace to achieve room temperature superconductors. Some feel that this may be possible by using the long and essentially one dimensional organic molecule, which possesses the necessary symmetry requirements. Some success has been reported, with the present high at 23.2°K.[9] Generators, motors, power lines, and rail transport levitation schemes, using superconductors, have been constructed and successfully tested.[10]

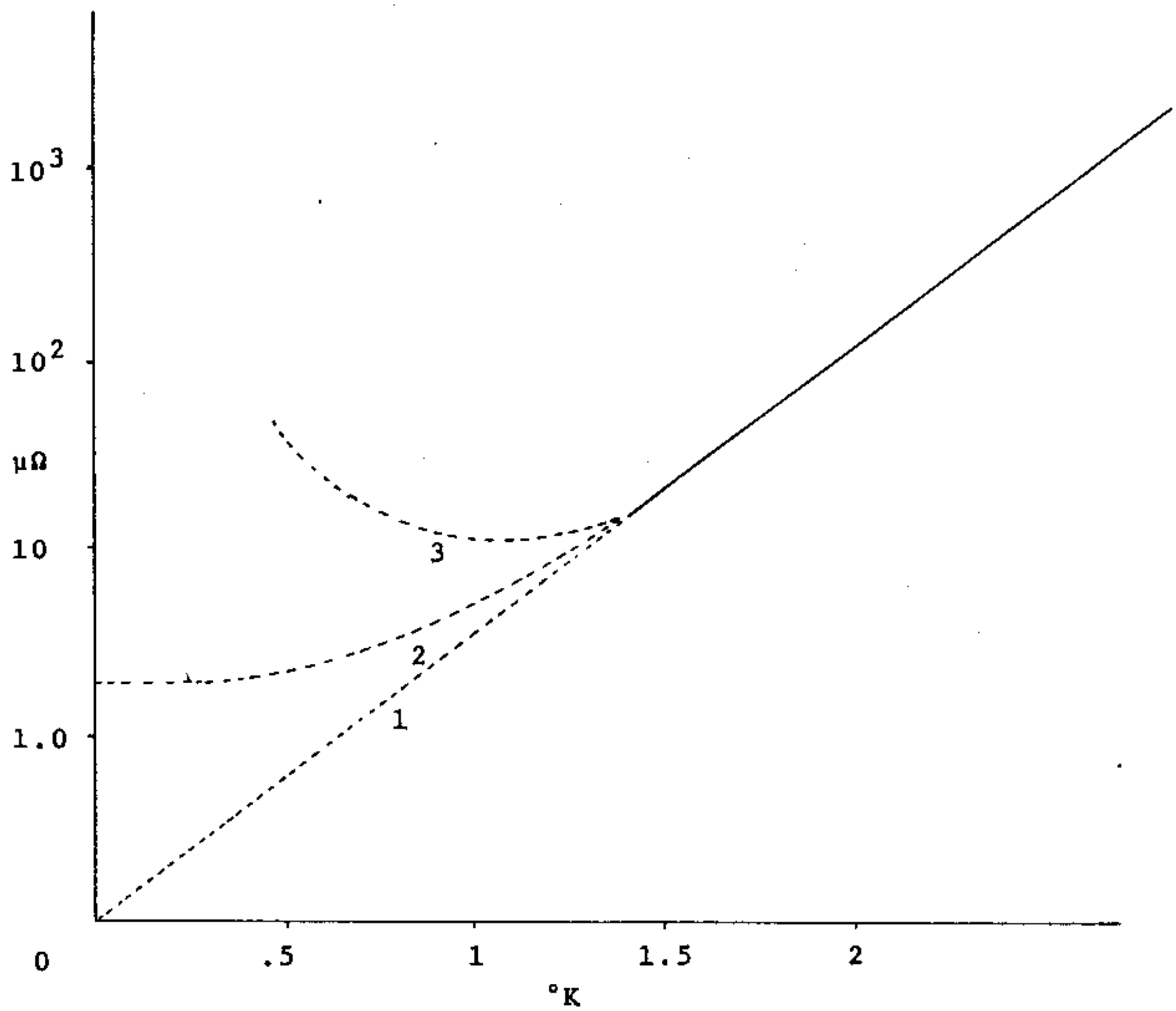


Fig. A-1. As temperature is lowered, the resistance of a metal might: 1. go to zero, 2. level off at a finite value, or, 3. increase, in the neighborhood of absolute zero.

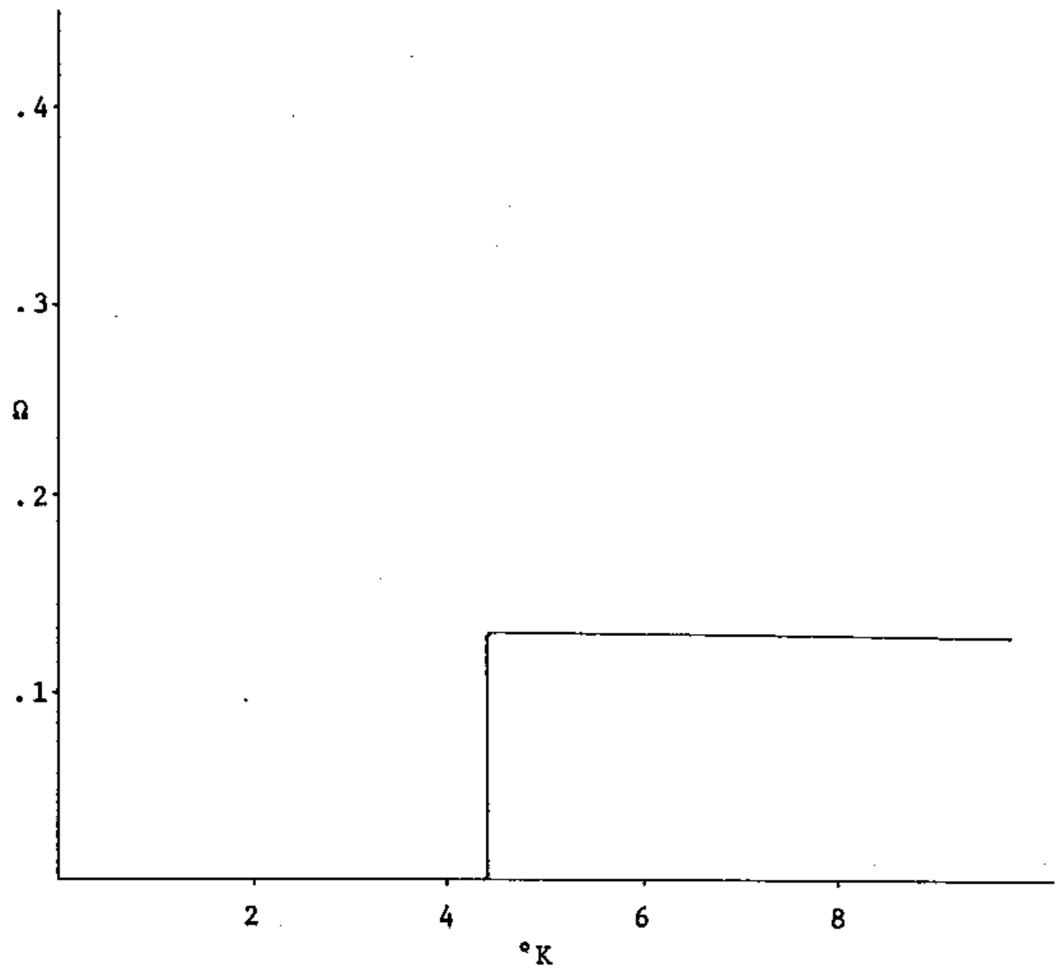


Fig. A-2. At the superconductive transition temperature, Onnes' sample of mercury suddenly lost all measurable resistance to electric current.

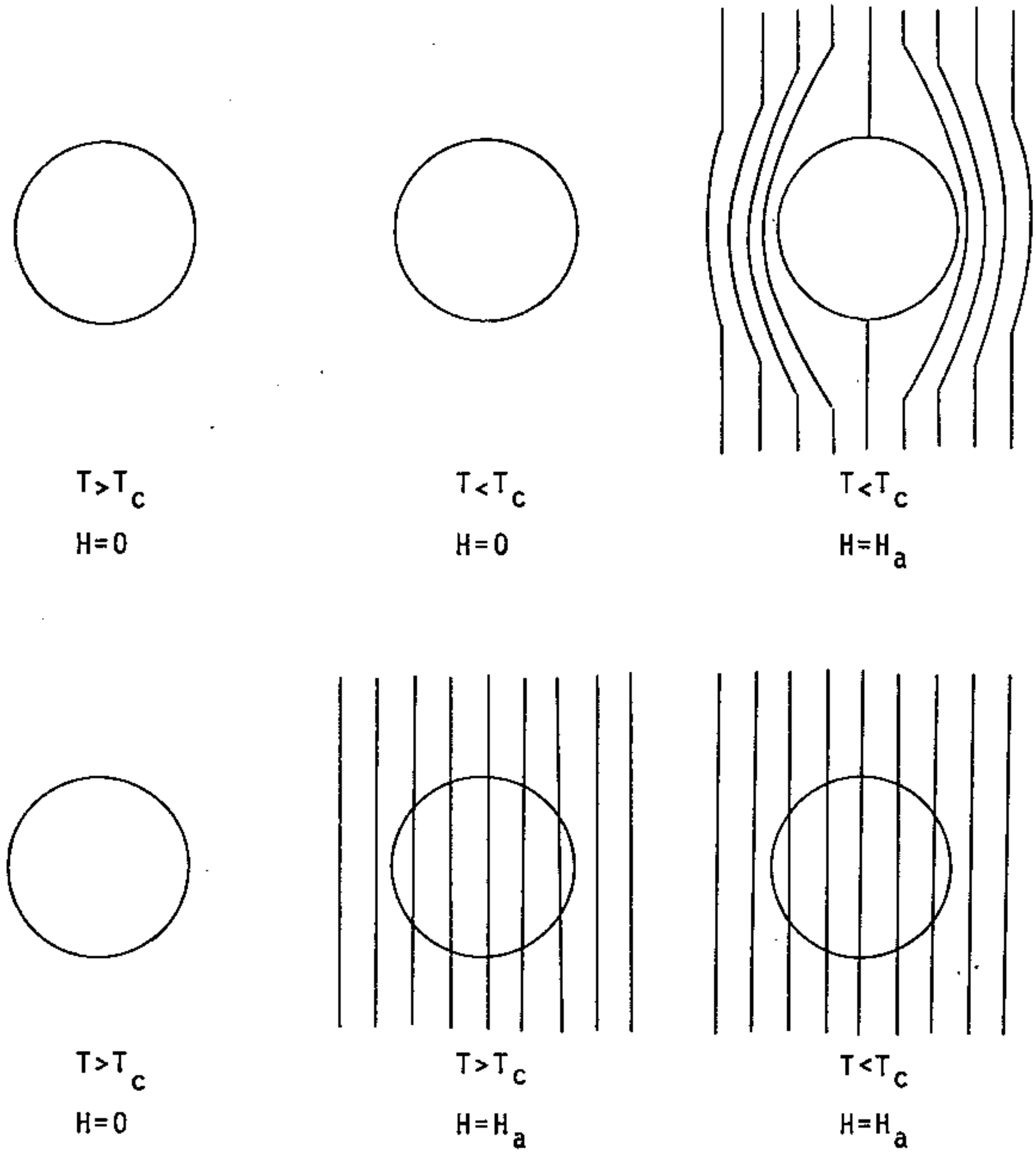


Fig. A-3. A perfect-conductor can exclude an applied field only depending in its pre-history. In order that surface currents be generated, the field must be applied after the material becomes perfect-conducting.

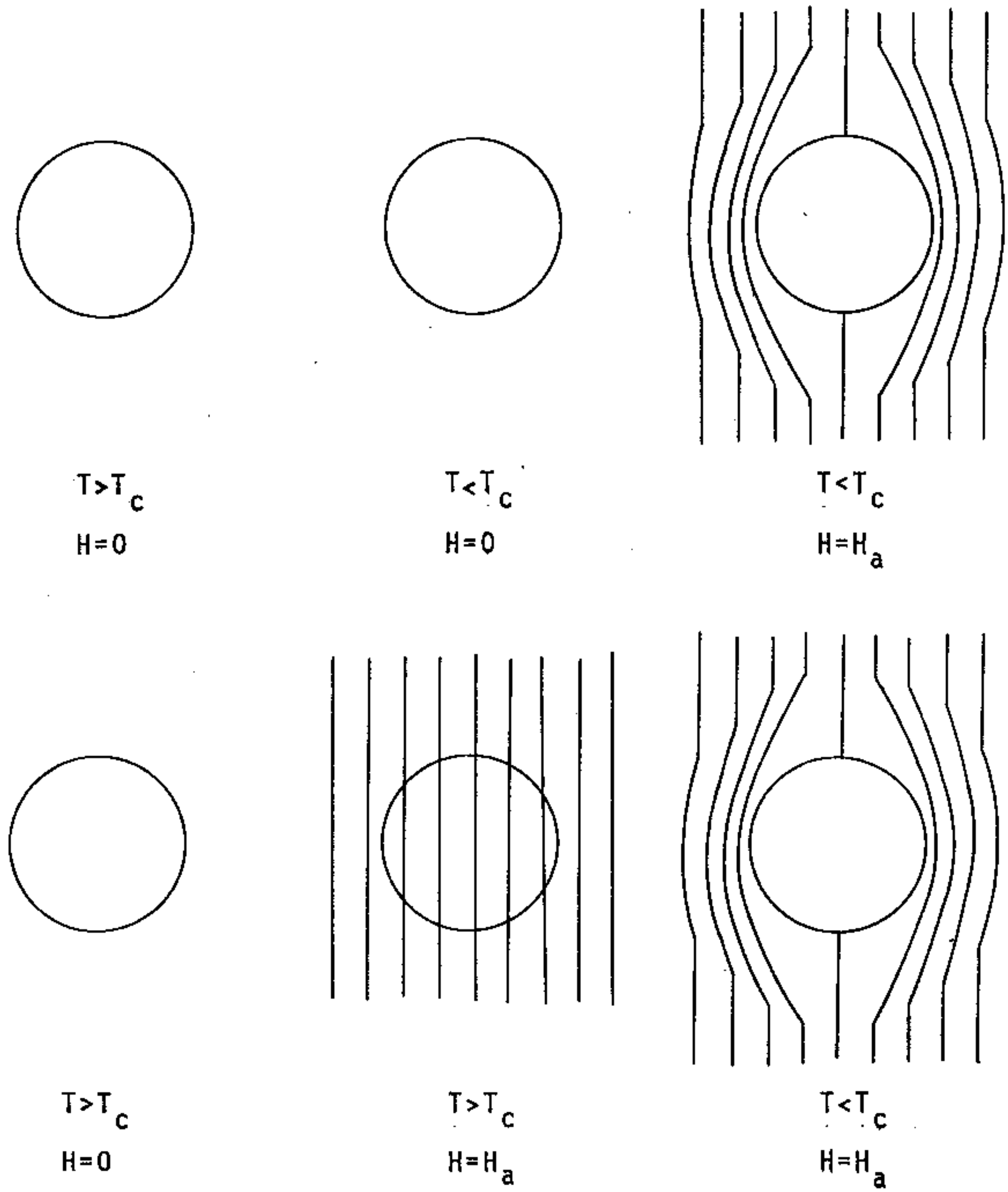


Fig. A-4. A superconductor can exclude an applied field independent of its pre-history. When the temperature is reduced below the critical value, some internal energy of the sample does work to expel the internal field.

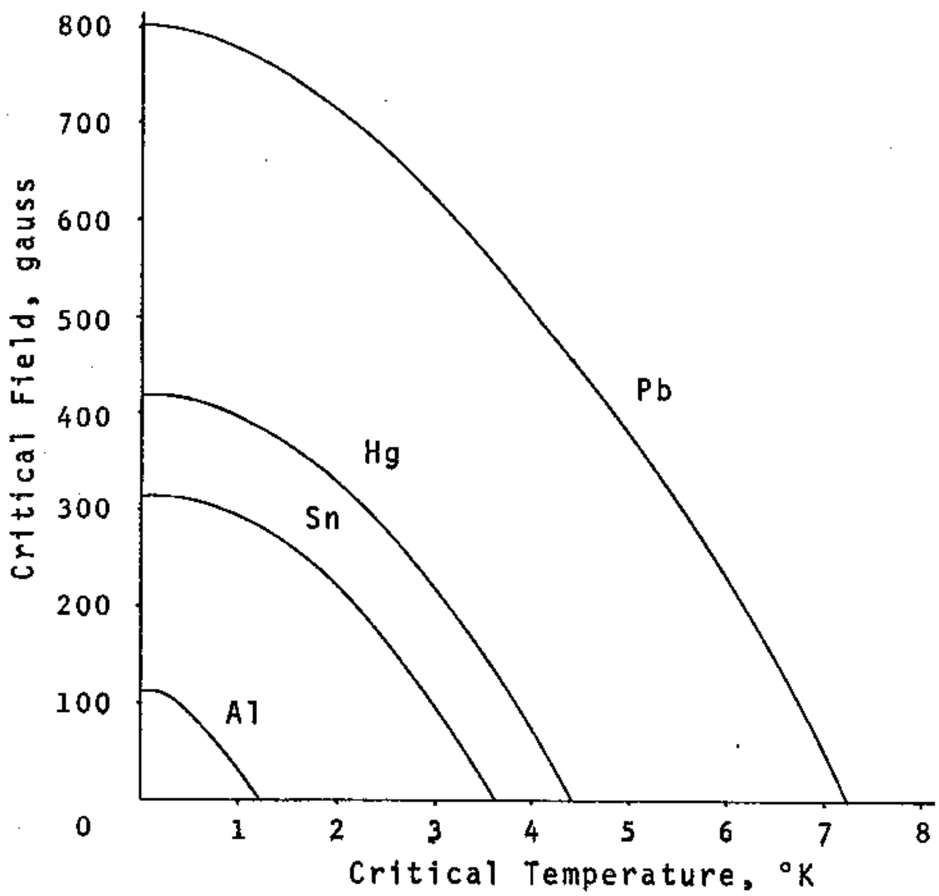
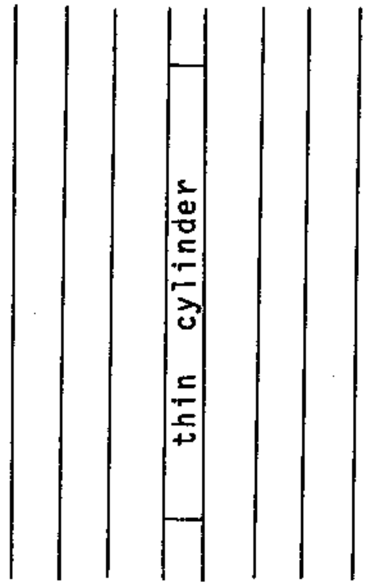


Fig. A-5. Critical field vs. temperature curve. Superconductivity can occur only below these limits; if one should exceed them the material becomes normal. Example: at 600 gauss and 6°K Pb is a normal conductor, at 600 gauss and 3°K Pb is superconductive.



Above: A thin cylinder parallel to the applied field does not distort the flux lines, therefore, H_c is reached at all points at the same time.

Below: A cylinder in a transverse field distorts the field. The intensity at the equator is $2 \cdot H_a$. Therefore, an applied field of $.5H_c$ will cause a critical field on the equator, thus necessitating the onset of the intermediate state.

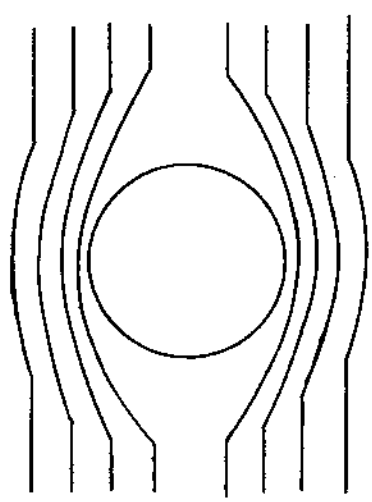


Fig. A-6. The intermediate state occurs when the sample geometry is such that somewhere on the surface H_c is reached before anywhere else.

REFERENCES:

1. Shoenberg, D. *Superconductivity.* Cambridge, 1962. Pgs. 1-5.

2. London, F. *Superfluids Vol. 1.* New York, 1950. Pg. 14.

3. Ibidem. Pg. 13.

4. Ibidem. Pg. 103.

5. Shoenberg. Pg. 16.

6. London. Pg. 27.
   Lynton, E.A. *Superconductivity.* London, 1962. Pg. 13.

7. Blatt, J. *Theory of Superconductivity.* New York, 1964. Pg. 13.
   Shoenberg. Pg. 111.

8. Lynton. Pg. 12.

9. *Science News*, September 22, 1973. Pg. 179
   March 31, 1973 Pg. 206.
   March 16, 1974. Pg. 176.

10. Newhouse, V. *Applied Superconductivity.* New York, 1964.

B.

PHYSICS OF SUPERCONDUCTORS:

Science has catalogued superconductors into two general types, I and II. I shall address myself to each respectively, and consecutively.

Type I superconductors are familiarly known as the elemental or soft kind. Basically, they show no resistance to electric currents and reject incident magnetic fields below a critical temperature, T_c and critical field, H_c. These critical conditions are parabolically given according to: (See Figure A-1)

$H_c = H_o(1-(T_a/T_c)^2)$. $H_o \equiv$ the critical field @0°K.

The exclusion properties are further fully reversible, in that irrespective of the mode of field application (above or below T_c) the material will exclude such applied field, within such critical conditions.

This latter effect, the Meissner-Ochsenfeld (Meissner) Effect, is in many ways the basic phenomenon of this activity of nature, and is specifically the basis of the herein described work. We may assume that the expulsion of magnetic field requires some internal energy utilization, as this produces a net external potential energy. This energy is given by the difference in the free energies of the normal and superconductive states as per some applied T_a. Since a field of application equivalent to H_c is required for normalization, the above difference must be of the order of:

$$G_n - G_s = H_c^2/8\pi \cdot V,$$

as

$$\int_0^{H_c} M(H)\,dH = -H_c^2/8\pi \cdot V.$$

This is available energy to do work.

It is the propensity of any system in nature to obtain a condition of lowest free energy. When a superconductor is immersed in an ambient magnetic field, a fine mixed state of flux penetration should ensue to lower attendant magnetostatic energy, while maintaining maximum superconductive volume. This does not occur when the conditions involve the existence of a surface energy, whereby the penetrating field will cause internal phase boundaries and an associated energy increment. This condition can be expected when the finite field penetration zone, λ, into the superconductor is less than the range of coherence of the superconductive mechanism, ξ. Type I superconductivity will occur when the ratio, $\kappa = \lambda/\xi < .71$. Thus, a condition of positive interphase boundary surface energy will yield a Meissner-Ochenfeld exclusion required for the expulsion of the flux within the sample.

Microscopically, the manifestations apparent are due to the pairing of electrons into a state of reduced free energy, through lattice intervention. An energy gap is established which must be overcome to raise the super-electrons to normalcy, on the order of $\varepsilon = 3.5kT_c$ @ 0°K/pair. This lowers the free energy, giving rise to macroscopic characteristics. The range of coherence then, (on the order of 10^{-4}cm) is the distance over which superelectrons interact. (See Appendix B-2)

As has been described, a field H_c is required to drive the material into a state of normalcy. This field is just sufficient to raise the superelectrons across the energy gap. Current-induced transitions are related to the attendant field production. If the applied field is not uniform over the superconductive sample, a condition will result where, at some point, H_c will be reached earlier than at some other juncture at a field of $H_a<H_c$. As H_c must exist in normal regions and $H_a<H_c$ in superconductive regions, a complex state of alternate domains of normal and superconductive substance within the material ensues, called the intermediate state, at field values above $H_a = H_c(1-N)$. (See Figure A-6)

The demagnetization Factor, N, is a geometrical condition which causes the applied, normally uniform field, to be locally displaced. This factor may be approximated for plates (transverse field) as: (See Figure B-3)

$N = 1-(t/2a)$ (where t = Thickness, a = Radius)

Magnetization curves depend directly upon the N factor resulting from the geometry of a sample: (See Figure B-1)

$M = -H_a/(4\pi(1-N))$.

Thus in considering energies of a superconductor in a magnetic field:

$\int_0^{H_c} M(H)dH = -H_c^2/8\pi$ = constant for any material N.

In the intermediate state, the surface energy acts to limit the minimum size of said domains. The magnetization changes linearly with increasing field, as per N factor conditions. The magnetic flux will penetrate a sample in such intermediate state as:

$B_i = H_c - (H_c-H_a)/N$.

With an N equal to 1, flux penetration immediately ensues as per application of H_a, thereby magnetization is a maximum at low field and decreases linearly with increasing H_a. An N equal to 0 will yield no flux penetration until H_a equals H_c, so that magnetization is zero at initial application of H_a, rising linearly to a maximum at H_c equal to H_a. Areas of resulting curves are always: (See Figure B-2)

$H_c^2/8\pi \cdot V$.

The thermodynamics of superconductivity are related to the condensation of the electrons, so that contributions to any unique heats are related to the electrons, not the lattice. A difference in entropy exists between the two phases: (See Appendix B-1)

$$S_n - S_s = -\mu H_c dH_c/dT \cdot V.$$

Thus we may examine the specific and latent heats:

$$C_s - C_n = (T\mu H_c d^2H_c/dT^2 + T\mu(dH_c/dT)^2) \cdot V.$$

and,

$$L = -T\mu H_c dH_c/dT \cdot V.$$

In the absence of an applied field the latent heat is zero, as it is at T_c and T = 0°K with an applied field. These thermodynamic properties will be treated in Appendix B-1.

All Type I materials discovered to present generally have rather low critical fields and temperatures. (Pb, for instance, normalizes at 803 gauss at 0°K and 7.2°K at 0 gauss). It is hoped future discovery will yield higher critical limit superconductors.

Class II superconductors are different from Type I in that this alloy or hard type has a negative interphase boundary surface energy. The range of coherence is shorter than the appreciable penetration depth of the applied field; in other words: $\kappa > .7071$.

Specifically, due to atomic structure arrangement, the electronic mean free path is low in these materials with an attendant reduction in the coherence length. (Impurities may cause the same condition in type I). The material will enter a mixed state of an extremely small and uniform arrangement of superconductive-normal regions, as was intimated previously concerning the surface energy. Said fine structure consists of fluxon penetrations on the order of 2×10^{-7} gauss, ie., a Cooper pair. Since the penetration depth is more dependent on the applied field than in type I, a certain field of application is required to cause said penetration to exceed the range of coherence, called H_{c1}. The mixed state will continue to some higher (N_b-S_n: 200,00 gauss) H_{c2}. The areas of magnetization curves are equivalent to the thermodynamic critical field, H_c: $H_c^2/8\pi \cdot V$. (See Figure B-1)

Superconductivity can exist in higher fields than that permitted by H_{c2}, ie., to some critical field H_{c3}, on the surface regions only, denoted as "surface superconductivity". Such may occur in type I or II materials where the coefficient $\kappa > .41$. Said H_{c3} is largely determined by angle of field incidence, with maximum parallel to the surface:

$$H_{c3} = 2.4\kappa H_c,$$

and minimum for perpendicularity of incidence:

$$H_{c3} = 1.414\kappa H_c.$$

This condition only transpires when the surface boundary involves an insulatory medium; therefore, the elimination of the above is effected via metallic contact thereat, ie., elimination of the insulator.

Thin films of superconductive material, in which the thickness 2a is less than the penetration depth, will necessitate flux penetration. This condition will yield a reduction in the magnetization. To obtain an area of $H_c^2/8\Pi \cdot V$ for the magnetization curve, a higher critical field is required:

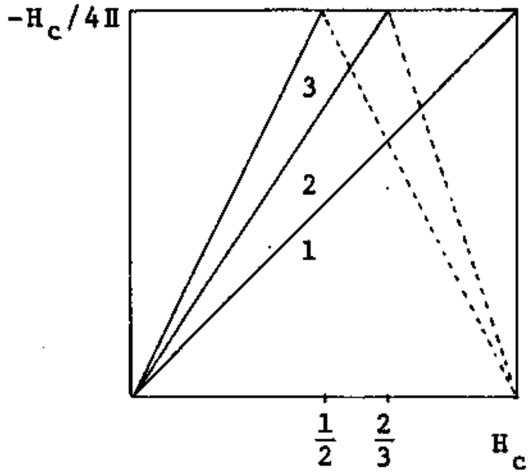
$H_s/H_c = \sqrt{3}(\lambda^2 \xi/a^3)^{1/2}$ λ and ξ are bulk values.

This state is analogous to the mixed state of type II materials.

Very highly annealed macroscopic specimens may experience a hysteresis effect, supercooling-superheating, in which the flux entrance or expulsion occurs above or below H_c, respectively. This activity is related to the surface energy and the requirement for the formation of nucleation sites, similar to super-cooling-heating vapor-liquid conditions at familiar temperatures. The indicated transition sites are always 10^{-3} to 10^{-4} cm below the surface, whereat the boundary propagates along the surface and then interior regions. The net effect is to alter the general shape of the magnetization curve, necessitating a larger <u>mechanical</u> magnetic work function in one direction, smaller in the other.

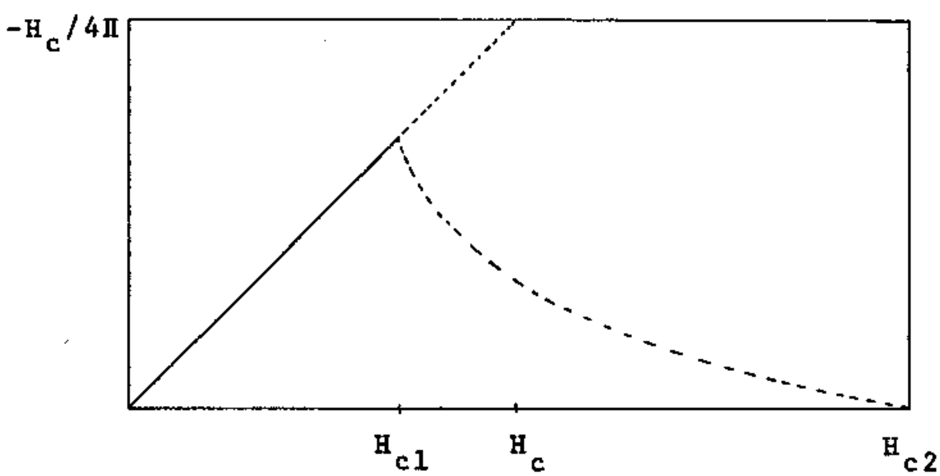
Hence, a heat influx is necessary to establish energetic equality.

Type I:



1. N=0 The material does not enter the intermediate state.
2. N=$\frac{1}{3}$ The material enters the intermediate state above $H_a=2/3H_c$.
3. N=$\frac{1}{2}$ The material enters the intermediate state above $H_a=1/2H_c$.

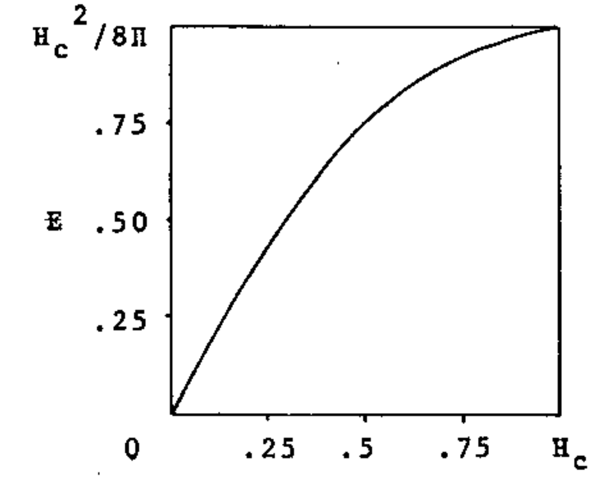
Type II:



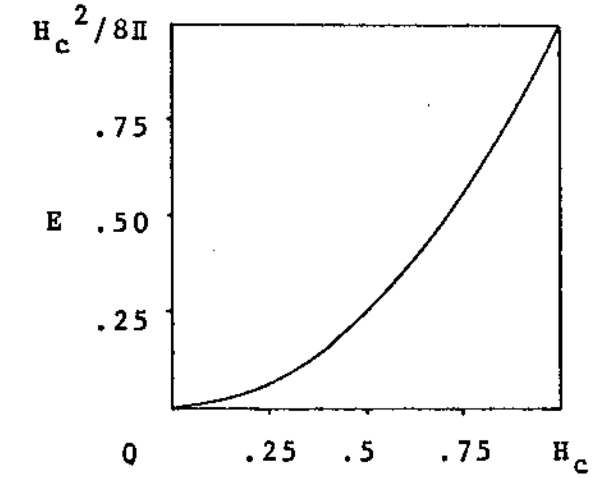
The material behaves as essentially Type I until H_{c1} is reached, whereupon the mixed state ensues, continuing through H_{c2}. Above H_{c2} normalcy is complete. The entire area is equivalent to that obtained with the extropolated curve to the thermodynamic critical field, H_c.

Fig. B-1. Typical Magnetization Curves.

Magnetostatic energies of an N=1 superconductor in applied field H_a



Magnetostatic energies of an N=0 superconductor in applied field H_a



Amount material superconductive with N=1 in applied field H_a

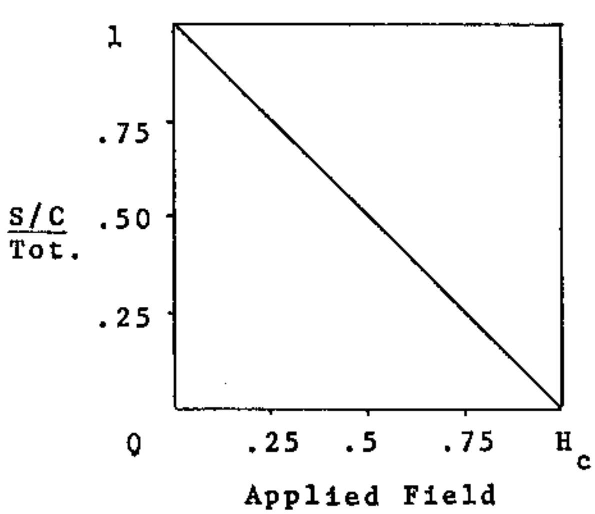
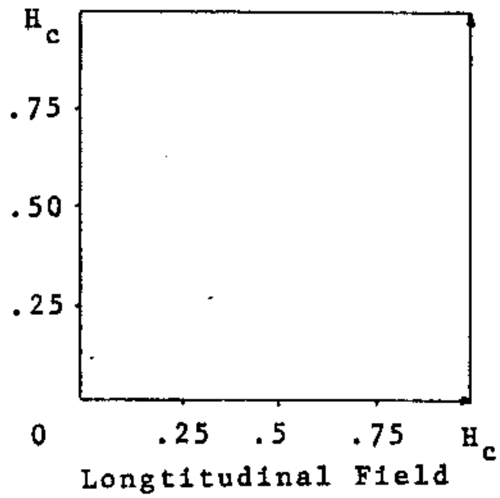


Fig. B-2. Some effects of demagnetization factor.

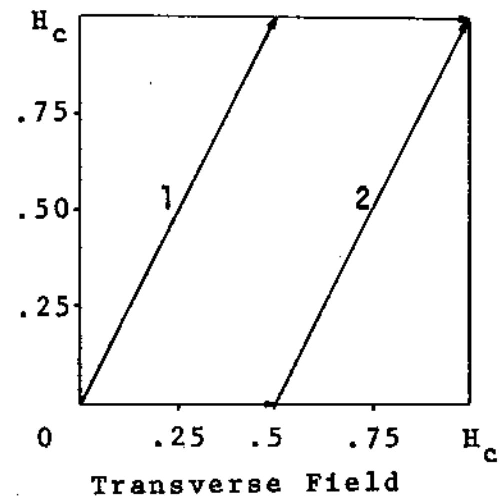
Fig. B-3. Effects of certain geometries in an applied field.

Cylinder:



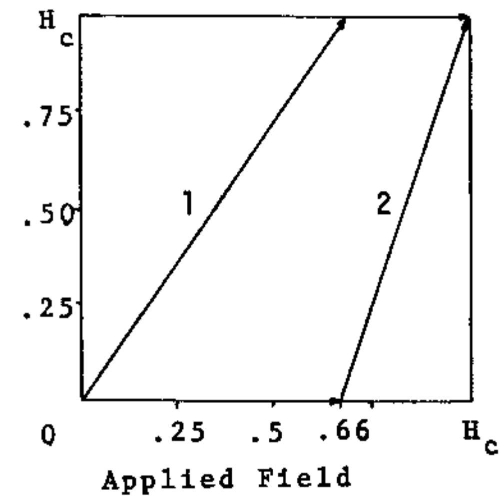
There is no intermediate state onset. The field is homogeneously distributed. Full normalcy transpires when H_a=H_c. The surface field is everywhere H_a.

Cylinder:



The intermediate state onsets at .5H_c. The equatorial field is given by 1. The polar field is given by 2. The equatorial field is a constant H_c in the intermediate state. The polar field remains zero until H_a=.5H_c. Field penetration is given by 2.

Sphere:



The intermediate state onsets at .66H_c. The equatorial field is given by 1. The polar field is given by 2. The equatorial field is a constant H_c in the intermediate state. The polar field remains zero until H_a=.66H_c. Field penetration is given by 2.

APPENDIX B-1:

THEORETICAL SURVEY:

A superconductor may be considered as a diamagnet whose internal peculiarities enable a certain magnetic work at 0°K. This implies an involvement of the internal energy, ie, magnetic work plus the superconductive state free energy at 0°K yield normalcy.

Specifically:

The magnetic Gibbs Potential may be written as:

$$G = U-TS+PV-\mu H_a M$$

We have then:

$$dG = dU-TdS-SdT+PdV+VdP-\mu H_a \cdot dM-\mu M \cdot dH_a$$

For a gas, dU = TdS - PdV. so, in our magnetic case:

$$TdS = dU-HdM+PdV$$

Substituting for TdS and cancelling terms in the equation for dG:

$$dG = -SdT-MdH-VdP$$

dP is negligible, Therefore:

$dG = -SdT - MdH$

At constant temperature: $dG = -MdH$

Now, using (O) and (Hc) to denote whether there is an applied field present and n and s to denote the phase:

We have: $Gn(0) = Gn(Hc) = Gs(Hc) = Gs(0) - MdH \cdot dV$

Therefore, $G_n(0)-G_s(0) = -\int_0^{H_c} M(H_c)\,dH \int_0^V dV.$

Integrating, we have finally:

$Gn(0) - Gs(0) = Hc^2/8\pi \cdot V$

This is the difference in free energies between the superconductive and normal states.

(After Lynton and Zemansky, Heat and Thermodynamics, 1968, 5th ed.)

SPECIFIC HEAT:

$C = VT \cdot dS/dT$

Taking the partial of S with respect to T:

$Cn - Cs = -VT \cdot d/dT \cdot (Hc \cdot dHc/dT)$, or

$Cn - Cs = -VTHc/4\pi \cdot d^2Hc/dT^2 - VT/4\pi \cdot (dHc/dT)^2.$

Integrating:

$$\int_0^{T_c} (C_n - C_s)dT = -\int_H^0 TV/4\pi \cdot (H_c \cdot dH_c/dT), \text{ generally, or,}$$

$$\int_0^{T_c} (C_n - C_s)dT = \int_{H_c}^0 VH_c/4\pi \cdot dH_c/dT \cdot dT - VTH_c/4\pi \cdot dH_c/dT \Big|_0^{T_c}.$$

The former term relates the magneto-mechanical heat energy and the latter concerns the latent heat contribution.

We have finally: $\int_0^{T_c} (C_n - C_s)dT = -H_c^2/8\pi \cdot V$,

the magentostatic available energies. (After Zemansky)

During some process, if the temperature varies, via design, leakage, joule heating, or latent evolutions, the above specific heat will exhibit itself.

In any transition 3 thermodynamic functions must be considered: the heat capacity of the normal regions and the superconductive regions plus the latent heat.

THE LATENT HEAT OF TRANSITION:

Recall: $dG = -SdT - MdH$

An incremental change in temperature, while H is constant gives:

$dG = -SdT$

ie, $S = -dG/dT$

Since $Gn(0) - Gs(0) = Hc^2/8\pi \cdot V$

Differentiation yields:

$Sn - Ss = -VHc/4\pi \cdot dHc/dT.$

This is just the entropy change between phases at temperature Ta. The heat absorbed or evolved at the transition is:

$dQ = VTdS.$

$Q = VT(Sn - Ss)$

$Q = -VTHc/4\pi \cdot dHc/dT.$

This is the latent heat of transition above 0°K and below Tc. It is evolved when phase change is present above absolute zero while in a magnetic field.

(After Lynton)

THE MAGNETODYNAMICS:

The minimum volume such that expulsion of flux transpires:

The energy density of a magnetic field of H gauss is:

$E = H^2/8\pi$.

It is well known that: $dW = Pdx$.

Consider the case of a superconductor in such field, an infinitesimal exterior contraction would yield a work of:

$dW = \mu H^2/8\pi \cdot dx$.

Therefore, $P = \mu H^2/8\pi$ dynes/cm^2. (After Newhouse)

It is necessary for a superconductor to expel a magnetic field below critical conditions (considering N=0 for simplicity). This can only transpire with sufficient free energy such that the Meissner-Ochsenfeld pressure can overcome the Maxwell stress. Since a condensation of electrons, resulting in free energy difference, occurs, per unit volume, to accomplish the above, we have:

$$dW = M(H)dH$$

$$W = 1/4\pi \cdot \int_0^{H_c} M(H)dH$$

$W = 1/8\pi \cdot H^2 = Gn(0) - Gs(0)$, the energy per cubic centimeter.

These results may immediately be applied to two interesting cases: (A) a superconductor completely surrounded by an applied magnetic field and (B) a superconductive plane upon one side of which a magnetic field is applied while on the other side there is no applied field, ie, this superconductor is acting as a magnetic field confinement shield.

(A) On the basis of the results, reversible exclusion of flux can only occur under conditions when the sample wholly occupies the volume of displacement. A hollow sample, for instance, could not possibly expel completely a magnetic field from its interior with a simple reduction of temperature below Tc. A Meissner Effect will only be noted in solid materials.

(B) Since we have found how surface pressure and free energies per unit volume are related, a shield wall, which might find practical application in magnetic circuit design, can only reversibly expel an interior field via the Meissner Effect if for every cm^2 of surface experiencing a pressure of $H_c2/8\pi$ there is a superconductive volume of 1 cm^3 present.

In either of the cases above the superconductor will exclude any incremented magnetic field until its intensity reaches Hc, independent of thicknesses, etc. Upon reduction of the field below Hc, however, frozen-in flux will surely nearly equal Hc (depending on the degree of variance from (A) & (B)).

APPENDIX B-2:

A FEW NOTES ON THE MICROSCOPIC THEORY:

This presentation is intended as a background for the phenomenological discussions that follow.

Frolich and Bardeen (1950) presented an hypothesis that the electrons moving in a crystal lattice set up a swarm of virtual phonons, due to lattice distortions as a result of the coulomb interactions.

Bardeen, Cooper and Schrieffer (1957) showed that this phonon cloud could be responsible for the superconductive state if it were able to mask the coulomb repulsion between electrons and in fact result in a net attraction.

The BCS Theory, as it has become known, succeeded in demonstrating that the basic interactions resulting in superconductivity were due to electron pairs.

If, for example, an electron interacted with the lattice, a phonon would be emitted that would eventually be absorbed by a neighboring electron. If the electronic energy change (which results from scattering) is less than the quantized phonon energy, $h/2\Pi \cdot \omega_q$, then the interaction between these two electrons is in fact attractive.

Cooper (1956) showed that if a net attraction between electrons just above the Fermi surface occurs, then a bound state can result. This, being a result of phonon interaction, can happen only to electrons lying within a shell of width $h/2\Pi \cdot \omega_q$.

This bound state is lower in energy than that for a normal metal of "non-condensed" electrons by an amount $Hc^2/8\Pi \cdot V$ at 0°K. An energy gap is therefore present separating super-electron pairs from the normal electron sea (3.52kTc per pair at 0°K).

The results of mixed state investigations in type II materials have revealed that flux penetrates in discrete quanta, called fluxons. A fluxon is that field which would be produced by an electron pair (2×10^{-7} gauss, ie, hc/2e).

The specific heat and the other macroscopic mainfestations may be derived directly from the theory.

See Lynton pp. 109-131.