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THE BEHAVIOR OF THE CRITICAL FIELD OF QUENCHED
THIN Pb, Sn, AND In FILMS:

MASTER

Its Angular Dependence and Its Relation
to Changes in Defect Concentration,
Crystallization, and Mean Free Path

by

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DISSERTATION ABSTRACT

THE BEHAVIOR OF THE CRITICAL FIELD OF QUENCHED
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Its Angular Dependence and Its Relation
to Changes in Defect Concentration,
Crystallization, and Mean Free Path

The critical field behavior of superconducting thin films of Pb, Sn, and In, quenched on substrates held at liquid He temperatures, was investigated. The experimentally determined angular dependence of the critical field, H_c , was compared with the prediction of the Tinkham (1) theory, which also provided a means for estimating the electronic mean free path, ℓ , from the measured critical field values. These ℓ values are compared with the nominal crystallite sizes for similarly formed films as determined by electron diffraction experiments performed by Bulow and Buckel (2,3).

Our films were formed by quenching the metal vapor on a perpendicular cut quartz single crystal substrate held at liquid He temperature. After the evaporation process measurements were begun of the dependence of H_c on θ , where θ is the angle between the field and the plane of the film. The transition was measured resistively, using currents of 0.80mA, orthogonal to the field and the normal to the film. The films were warmed up to successive

higher temperatures up to room temperature. After each annealing stage measurements would be made with the film recooled to liquid He temperature. The angular dependence measured was found to follow the theory for the Pb and Sn films for all annealing temperatures if H_c was defined as the field at which one-half of the normal residual resistivity was restored. For In the angular dependence follows the theory except for the 300°K anneal, for angles in the range from approximately 0° - 30°. This departure from the theory was suspected on the basis of the known preferred growth of In crystallites on annealing, determined from the electron diffraction experiments, and was a major consideration in our choice of this metal for the present work.

As mentioned above, the Tinkham theory also enables one to compute a value of the electronic mean free path, ℓ , from the measured $H_c(90^\circ)$ values, for all annealing temperatures. For the metals investigated it was found that there is a relation between the electron diffraction determined nominal crystallite size (a) and the calculated mean free path values (ℓ) where $a = c \times \ell$, for the temperature range of 6°K - 300°K. The value of c is dependent on the film under consideration.

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2. Hagen Bulow and Werner Buckel, Zeit. fur Physik 145, 141 (1956).
3. Werner Buckel, Zeit. fur Physik 138, 136 (1954).

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To Mimi

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I. Introduction

Kammerlingh Onnes first liquified helium in 1908, and shortly afterwards began an investigation of the electrical conductivity of metals at the "new" low temperatures below 4.2°K . To reduce the resistance caused by impurities, he studied mercury of high purity and was not surprised when he found no measurable resistance. However, when he found that the addition of impurities to the mercury did not increase its resistance, and furthermore, that the resistance did not decrease smoothly to zero but dropped almost discontinuously to zero within a temperature range of 0.01°K at about 4°K , he concluded that "mercury has passed into a new state which, on account of its remarkable electrical properties, may be called the superconductive state". (1)

The complexity of this phenomenon, at first thought to be characterized solely by infinite conductivity, proved to be so great that a generally acceptable theory on the microscopic level was not formulated until 1957 when Bardeen, Cooper, and Schrieffer (2) proposed a theory based on the quantum mechanics of

solids. That a theory might be based on the electron-phonon interaction was first suggested by Frohlich (3) in 1950, when he independently predicted the isotope effect at the same time it was being discovered experimentally. (4,5) Thus, even though the superconducting state has been investigated for over fifty years, only recently have acceptable theories been proposed, and there are many features of the phenomenon which are still not fully understood.

The object of the research to be described in this paper is to present some information on superconductivity as evidenced in thin metal films. We have investigated the critical field behavior of superconducting thin films of Pb, Sn, and In with the intention of gaining some knowledge of the parameters which are important in governing their properties, and to check the correctness of the theory proposed by M. Tinkham (6) in 1963. The films are evaporated on a substrate cooled to liquid helium temperature. The reasons for this "quenched film" method of formation are discussed in detail in Section III.

To form a background and justification for our research, it will be worthwhile to review some of

the devices that have been manufactured from bulk superconductors and follow with those fashioned from thin films, mentioning some of the advantages of the latter. In the past few years (1960 - present), especially in the areas of computer design and the generation of high strength magnetic fields, superconducting materials have become more important.

Much has been done in the area of devices manufactured from bulk material. In the past ten years technology has progressed to the point where the metallurgical fabrication problems have been solved, resulting in the commercial availability of both superconducting wire and ribbon. E. A. Lynton (7), in his book entitled Superconductivity, describes a number of research devices which have been developed to detect very small potential differences, with a typical instrument capable of detecting e.m.f.'s of 10^{-12} v. Templeton (8) and De Vroomen (9) designed chopper amplifiers in which a small d.c. signal is converted into an alternating one by passing through a superconducting wire which is modulated into and out of the normal state by being placed in an alternating magnetic field. These devices can operate stably with a noise level at about 10^{-11} v.

Olsen (10) has designed a superconducting rectifier and amplifier which, together with a low temperature transformer, allow one to feed a low alternating current through thin leads into a cryostat with resultant low thermal input. The rectification occurs as the current flows through a superconducting wire placed in an external, nearly critical field, such that the field due to the current in one direction is sufficient to make the wire normal during about one-half of each cycle.

The greatest commercial application to date has been in the construction of solenoids. Superconducting magnets with field strengths to 140 kilogauss and working volumes to 3" diameter x 8" length are currently in use. A superconducting magnet six feet in diameter has been constructed for the Air Force as a part of a feasibility study to establish whether or not large superconducting coils could be used as a means of shielding space vehicles against high energy radiation.

(11)

Qualitatively, thin films exhibit the same properties as the bulk materials, e.g., T_c , H_c , Meissner-Oschenfeld effect. The size of some of the effects, and the manner of their occurrence, is much different

for films however. These points will be amplified in Sections II and III.

As a result of our lack of understanding of how to control the parameters which will allow us to use thin superconducting films to perform useful functions, and of the difficulty of fabricating the films, they are at present only in limited use. But since there are many potential applications and advantages, there is considerable interest in the study of such films.

It is thought that magnets made from thin films rather than bulk materials will have several benefits. Most notable would be higher maximum field strengths, steeper field gradients, lower total weight per unit of field, increased homogeneity, and lower power input. There is also the likelihood that they will be easier to manufacture once fully developed, and thus be less expensive.

The basic idea for a superconducting switching element originated with Buck (12) who invented the "cryotron". Such a device could also be used to form computer memory elements. His design was for a wire-wound device, which was subsequently found to be severely limited by the fact that the switching time

could be no less than 10^{-5} sec. Thus all current research effort is directed toward making thin film cryotrons, which can have time constants of 10^{-8} - 10^{-9} sec. due to their lower self-inductance. A model with a switching time of 2×10^{-9} sec. has been successfully operated. (13)

Broad potential applications also exist in the area of large transformers, transmission lines, and associated equipment. The practicality of these devices depends on the feasibility of producing superconductors that can carry high a-c currents with little or no resistance. Presently a-c losses are substantial, but some recent work on superconducting delay lines using ultra high frequency pulses indicates that these losses can be substantially reduced. (11)

The future for bulk and thin film devices looks bright. With our rapidly increasing technological knowledge of the materials and better theoretical understanding of their behavior more and better applications are being discovered. Their great interest to both scientists and manufacturers is evident.

Before beginning a detailed description and analysis of our experiments, to be presented in Section III,

it is necessary to review some of the work of previous investigators to introduce and define new terms and to form a basis for interpreting our thin film results. This will be done in parts A and B of the following section, and in Section II C the theory of M. Tinkham will be presented.

II A

Properties and Basic Concepts of the Superconducting State

For a material to become a superconductor its temperature must be lowered below a critical value, T_c , which for most materials is $< 10^\circ\text{K}$, but which can be as high as 18°K for special alloys, e.g., Nb_3Sn , Nb-Zr . This means that all research on superconductors must be done at cryogenic temperatures (with the use of liquid helium, N.B.P. = 4.2°K) and the relative scarcity of this refrigerant was one reason for the delay until after World War II of a full scale attack on the problem. Fortunately, since the development of the Collins liquifier in 1947, now a familiar feature of low temperature laboratories throughout the world, the scarcity of refrigerant has been eliminated.

Kammerlingh Onnes also observed, in addition to the loss of resistance, that when a superconductor is placed in a sufficiently strong magnetic field (critical field H_c) it becomes normal. The magnitude of this field empirically depends on temperature according to:

$$H_c = H_0 \left[1 - \frac{T}{T_c} \right]^2 \quad (\text{IIA-1})$$

where H_0 is the critical field for $T = 0^\circ\text{K}$. We notice that the critical field decreases with rising temperature and becomes zero at T_c . If the transition takes place in the presence of a magnetic field it is a normal phase transition of first order, accompanied by the release or absorption of a latent heat. If the transition takes place in the absence of a magnetic field, i.e., at T_c , it is a transition of second order, in which there is no latent heat, and one observes only a discontinuity in the specific heat. (14)

Another important property of superconductors was discovered by Meissner and Oschenfeld in 1933. They observed that an external magnetic field does not penetrate into the body of a thick superconductor, and that on the transition into the superconducting state the field is expelled. This anomalous behavior occurs, naturally, only for applied fields smaller than H_c . It is observed that magnetic flux does penetrate to a depth of about 10^{-5}cm. , called the penetration depth, λ . However, since inside the bulk of the superconductor the magnetic induction B is zero, we consider the superconductor to behave as a perfectly

diamagnetic material. Moreover, magnetic flux is excluded whether or not the material is cooled down below the critical temperature before or after the application of the magnetic field. This is evidence for the fact that the superconducting and normal are true thermodynamical states, the transition between which is reversible.

Application of thermodynamics shows that the superconducting state is lower in energy than the normal state, and also that the entropy difference between the normal and the superconducting state is:

$$S_n - S_s = \frac{-H_c}{4\pi} \frac{dH_c}{dT} . \quad (\text{IIA-2})$$

From Equation (1) we see that $\frac{dH_c}{dT}$ is always negative, and thus $S_s < S_n$ for any given temperature. This provides valuable insight into the nature of the superconducting state: the superconductor must be more ordered than the normal metal. In an analogous way, the entropy of a liquid is lower than that of a gas at the same temperature; the implication is that in the superconducting state a condensation takes place. (15)

As a metal becomes superconducting, experiments show that only the electronic properties are altered

appreciably; this implies major changes occur only in the electron system. Although the electrons make up a Fermi gas, they must undergo a condensation. One important characteristic of a condensed state, which will be amplified later, is that the component particles interact over macroscopic distances.

Cooper (16) established that in the presence of an attractive interaction the electrons in the neighborhood of the Fermi surface condense into a state of lower energy in which each electron is paired with one of opposite momentum and spin. This led to the Bardeen-Cooper-Schrieffer (BCS) theory, mentioned in Section I, which showed that a finite energy gap separates the state with the largest possible number of Cooper pairs from the state with one less pair. This gap at the Fermi surface has been experimentally verified. (17,18)

The attraction between electrons necessary to form Cooper pairs can in principle be due to any suitable kind of attractive interaction. The discovery that for many superconducting elements the critical temperature depends on isotopic mass (4,5) showed that for these substances the attractive interaction is one between the electrons and the lattice. There

is also a hypothesis that in transition metals the attractive interaction responsible for pairing may be a magnetic one. (19)

If a current is flowing in a superconductor, the electrons making up a Cooper pair will have momenta which can be expressed as: $m\mathbf{v} + \hbar\mathbf{k}$; $m\mathbf{v} - \hbar\mathbf{k}$, where the velocity $\mathbf{v}$ is the drift velocity of the pair, and $\hbar\mathbf{k}$ is the usual electron momentum. As a result the two electrons will have different energies. If the paired electron in the higher energy state mentioned above could be scattered into a lower energy state, leading to a decrease in momentum along the direction of electron current flow, there would be electrical resistance. Such scattering processes would necessitate the splitting up of electron pairs and their removal from the condensed state. It is just this that the correlated electron system resists most strongly: for a pair to be broken, the electrons must obtain sufficient energy to be excited across the energy gap. At low temperatures the energy available from single scattering processes is not enough to disrupt pairs. Scattering is thus suppressed, and current flow persists.

The wave function of a Cooper pair extends over a distance of about 10^{-4} cm., a comparatively long range in the lattice. This distance has been termed the "correlation length", ξ , and will be important in Section II B when we consider how its variation will affect the critical field.

F. London proposed (20), on the basis of a phenomenological theory of superconductivity, that the magnetic flux passing through the axial hole in a hollow, current-carrying, superconducting cylinder, should be quantized in multiples of $\frac{hc}{e}$. Careful experiments (21,22) verify that the magnetic flux is quantized, but that the magnitude of the flux quantum is $\frac{hc}{2e}$ ($\approx 2 \times 10^{-7}$ Gauss-cm²). This also indicates that the electrons are bound together in pairs.

Flux quantization gives a further insight into the stability of persistent currents in superconducting rings. If a supercurrent is to decay, the flux must jump to another state with an integral quantum number: the system as a whole must be altered; many particles must change states simultaneously. The probability of this happening is vanishingly small because typical scattering processes in the solid affect only a few

particles at a time. Hence supercurrents can persist.

(15)

Within the limits imposed by the relative simplicity of their model, the BCS theory provides an acceptable explanation of the phenomenon of superconductivity. At temperatures below T_c there are both normal and superconducting electrons. Intrinsic to the superconductor is an energy gap between the two types of particle states. In the lower energy state pairs of electrons are coupled by "virtual phonons". Overlap between pair wave functions gives rise to this condensed state, which is capable of sustaining persistent currents. Thus in a superconductor quantum effects are acting on a macroscopic scale.

Theoretical Developments Concerning the
Magnetic Transition of Superconductors,
with Emphasis on Thin Films

Superconducting materials have been divided into two types. Historically, there were hard and soft superconductors, referring to their physical form. More recently, a theoretical division with more meaning has been used, where materials are classed as Type I or II depending on the value of the dimensionless parameter κ being $\leq \frac{1}{\sqrt{2}}$. The two types behave differently in a magnetic field. For Type I superconductors the superconducting-normal critical field transition takes place in a very narrow range of field, and thus results in a single unambiguous critical value H_c . In Type II materials, a much different behavior is observed. As the field is increased, until a field H_{c1} is reached, all magnetic flux is excluded. Between H_{c1} and H_{c2} flux enters the sample, completely filling the sample only at H_{c2} . Measured resistively the transition will appear as in Figure 1. κ , first introduced in the Ginsburg-Landau theory, is fittingly termed the Ginsburg-Landau parameter, defined by $H_{c2} = \kappa\sqrt{2} H_c$.

It is known from flux penetration measurements

Figure 1. Resistively Measured Superconducting - Normal Transition for a Type II Material.

H_{c1} is the lower critical field; H_{c2} is termed the upper critical field, and may be several times greater than H_{c1} in very broad transitions. H_c is the choice we make for the critical field when applying Tinkham's theory to our results, and is discussed in Section III B.

that at H_{c1} nearly full flux penetration occurs, and it is thought that the establishment of filaments of current prevents the resistance from increasing as abruptly. (23)

What is the reason for the difference in behavior of the two types? If we consider the motion of a pair of electrons, it follows that the electric current at a given point in the metal will depend on the electromagnetic field (E-M) not only at that point, but in a region with dimensions of the size of the pair. This leads to an integral or "non-local" relation between current and field. There are two limiting cases. When the E-M field varies only slightly over distances of the order of the correlation length, ξ , the correlation effects are unimportant, and the current depends, practically speaking, only on the field at the same point. In that case one finds the London equations hold (proposed by F. and H. London (24,25) in 1935 on the basis of phenomenological arguments). In the opposite limit, one obtains an integral relation between current and field which was proposed by A. B. Pippard (26) in 1953, before the appearance of the microscopic theory. The parameter which characterizes the distance over which the field changes appreciably

is taken to be the penetration depth, λ . Thus we are concerned with the ratio of ξ and λ . For Type I materials (Pippard limit) $\xi \gg \lambda$, whereas for Type II $\xi \ll \lambda$. Most metals belong to the Pippard case, with the exception of a few "high field" superconducting metals and alloys, so named because for them H_{c2} can be very large. In Table 1 the bulk values of these parameters are listed for the metals used in this investigation.

It should be stated that when one is dealing with films, if the thickness of the film is less than the correlation length of the material of which it is made, then the thickness will play the part of the correlation length. If the film is also thinner than the penetration depth, then the film necessarily becomes a superconductor of Type II. The critical field of the film will therefore increase as the thickness is decreased. (14)

It is also found that any pure superconductor can be converted to Type II if ξ and/or λ are altered by adding impurities or creating defects in the lattice. This point is basic to our experiments, where films are produced on a cold substrate by means of evaporation. (See Section III A) A film formed in this manner

TABLE 1
SELECTED PROPERTIES OF BULK MATERIALS

Metal	$H_{cb}(0)$ [Gauss]	T_c [°K]	ξ_0 [Å]	λ_L [Å]
Pb	803 ^{a, b} 805 ^e	7.18 ^b	830 ^c	370 ^c 390 ^d
Sn	305 ^e 306 ^b	3.72 ^b	2100 ^f 2300 ^c	500 ^d 510 ^f
In	269 ^e 283 ^b 275-293 ^h	3.41 ^b	4400 ^g	640 ^d

^aAIP Handbook, edited by D. E. Gray (McGraw Hill Book Company, New York, 1963), p. 110.

^bP. G. De Gennes, Superconductivity of Metals and Alloys (W. A. Benjamin, Inc., New York, 1966), p. 17, after J. Bardeen and J. R. Schrieffer, Low Temperature Physics, edited by C. J. Gorter (North Holland Publishing Company, Amsterdam, 1961), Vol. III, p. 170.

^cibid., p. 24.

^dC. Kittel, Introduction to Solid State Physics (John Wiley & Sons, Inc., New York, 1956), p. 470, after J. M. Lock, Proc. Roy. Soc. (London) A208, 391 (1951).

^eM. Tinkham, Phys. Rev. 129, 2413 (1963).

^fD. H. Douglass, Jr., and R. H. Blumburg, Phys. Rev. 127, 2308 (1962); T. E. Faber and A. B. Pippard, Proc. Roy. Soc. (London) A231, 336 (1950).

^gE. A. Lynton, Superconductivity (John Wiley & Sons, Inc., New York, 1964), p. 65.

^hM. D. Reeber, Phys. Rev. 117, 1476 (1960).

will have a high defect concentration and thus the characteristics of a Type II material. The electronic correlations will be disrupted, with a shortened correlation length ξ as a consequence. ξ is easily reduced to $< 10^{-5}$ cm. and its ratio with λ is reversed.

The work of Bardeen, Cooper, and Schrieffer was based on the concept of an "ideal" superconductor, and is not directly applicable to the analysis of experiments performed on Type II materials, especially thin films. Ginsburg and Landau (28) in their work considered in detail only the case $\kappa \ll 1/\sqrt{2}$, since is small for pure metals. Abrikosov (29) was the first to extensively investigate the case $\kappa > 1/\sqrt{2}$, where he noted that the upper critical field rises in proportion to the concentration of defects, i.e., with the decrease of the correlation length. Gorkov (30) and Shapoval (31,32) further developed his theory, but considered thin films only when parallel with the applied magnetic field. M. Tinkham (6) extended their work to result in a theory specifically for thin films in perpendicular fields. It is this theory whose validity we wish to check against the results of our experiments, and which will be presented in Section II C.

Having outlined the types of superconductors which are found, and the theories which have been proposed, it will now be worthwhile to review some of the observed properties of Type II materials.

Some of the characteristic properties which are found in varying degrees in Type II materials are:

- a) Large critical fields are found for the restoration of resistance.
- b) Critical currents are small.
- c) Resistive transitions are very broad.
- d) Flux trapping occurs.
- e) The Meissner Oschenfeld effect is incomplete.
- f) The resistive and magnetic transitions are separated.

It will be instructive to look at these properties individually.

The large values of critical field observed for Type II materials were discussed at the beginning of this section, with reference to Figure 1, and need not be expanded on here in reference to point (a).

In reference to (b), the absence of resistance for sufficiently weak currents has been found to persist right up to the upper critical field, which may be

very large. Experimentally Autler (33) found that his Nb wire samples could remain superconducting even above the accepted value of H_{c2} , in contrast to the theoretical predictions, if the measuring current was low enough. This may be due to the existence of a few defects, which would increase the value of H_{c2} .

That resistive transitions are very broad, listed as (c), was also discussed at the beginning of this section. We might add here that Seraphim (23) has found a broadening for tantalum wires in longitudinal fields similar to the broadening we observe for thin films. In his experiments he reported a nearly discontinuous rise in resistance at a certain value of the field, followed by a gradual increase until the full resistance was restored.

In amplifying (d) we note that hysteresis is found, in that on lowering the applied magnetic field below the upper critical field, the decrease in resistance does not appear as soon as one would expect. The behavior has been termed "supercooling" but the name is not accurate since the temperature is constant. In the model proposed by Faber (34) to explain the occurrence of supercooling, he assumes that there always

are flaws in the material which are superconducting, even at very high fields. From an energy argument he shows that superconducting nuclei cannot immediately grow when the magnetic field is reduced below H_c . It is not until the field has been lowered below H_c that growth becomes favorable, and then the specimen becomes superconducting.

His explanation is incompatible with the idea of a simple mean free path effect, and the question of the explanation of supercooling must be considered still open.

Finally considering (e) and (f), we note that along with the fact that the Meissner-Oschenfeld effect, expulsion of field upon normal - superconducting transition, is often incomplete, it does not always occur at the same field at which the loss of electrical resistance takes place. Currents flowing in the specimen often affect the transition, as measured by resistance techniques, in a manner which suggests that the supercurrent is localized in small regions of the specimen. (35)

In attempt to explain the appearance of this phenomena, the concept of the superconducting filament

was formulated (36). These filaments were believed to be associated with some sort of crystalline imperfections, usually referred to as "flaws" (34) or "strains and inhomogeneities" (37) and which could give rise to a negative interface surface energy in their vicinity (34,38,39). (Here, and subsequently, the term "interface" will refer to the boundary between normal and superconducting regions.) Such a negative surface energy could be used to explain the existence of threads or laminae in the presence of fields well above the "bulk" critical field of the material. This agrees with the known large effect of the measuring current on the resistive transition. With the localized filaments carrying the current the current density would be very high and thus able to produce a large effect.

If the idea of a negative interface surface energy is correct in this connection, one is led to the possibility that it can be negative everywhere, for sufficiently short mean free paths. Such a condition would favor the subdivision of the material into arbitrarily small normal and superconducting regions, with no exclusion of the magnetic field. (23) The idea of a negative interface surface energy is also

contained in the theory of Ginsburg and Landau (28) and its modifications, although its introduction is different.

In summary, present explanations of high field superconductivity invoke, directly or indirectly, the thermodynamic argument (40) that if a superconducting region is thin enough to permit substantial field penetration, it will remain superconducting for $H > H_{cb}$. These theories fall into two classes:

- i) Inhomogeneities such as filaments exist which have a higher H_{cb} than the surrounding material. In a strong field the current flows along these filaments, which may be dislocations (41). As the applied field is increased, these filaments shrink in size, raising their critical fields. A model of this type has been used (42) to explain the observed dependence of current carrying capacity on the direction of the applied field.
- ii) In the presence of a magnetic field the sample can lower its free energy by breaking up into normal and superconducting regions thin enough to allow field penetration into the superconducting regions. This flux penetration

is often described in terms of vortices, which will be discussed in connection with Tinkham's theory in the next section. The result is an increase in the normal-superconducting surface area, and may be thought of in terms of a negative surface energy. This is one of the bases of Abrikosov's theory (29), and more recently of the theories of Goodman (43,44) and of Yntema (45). Ginsburg and Landau (28) in their theory showed that the parameter κ determines to a great extent the surface energy at the normal-superconducting interface, and that for $\kappa > \frac{1}{\sqrt{2}}$ the surface energy is negative. Tinkham's theory is also based on a vortex picture, where the flux contained in a vortex is quantized.

With the exception of Tinkham's theory, all of the theories are concerned with the prediction of quantities which may be experimentally checked only with magnetization and specific heat data, and do not consider the behavior of the resistivity or the effect of transport currents. However, from Tinkham's theory we are able to extract an estimate of the electronic mean free path and relate it to the measured resistivity.

along with being able to check the predicted angular dependence of the critical field. We now present his theory.

II C

The Theory of M. Tinkham

Tinkham (6) proposed an elementary theory in 1963 describing the superconducting transition for thin films in perpendicular magnetic fields. His work was based on the theories of Ginsburg and Landau (28) and Abrikosov (29) mentioned previously. Using the concept of fluxoid quantization, he was able to derive an equation to predict the perpendicular transition field, and also to predict the variation in critical field with angle for intermediate positions of the film between parallel and perpendicular to the applied field. In this section we will review the fundamental argument of his theory and show how it can be applied to our results.

Most all treatises on superconductivity begin by defining a thermodynamic critical field, H_{cb} , as follows:

$$F_n(T) - F_s(T) = \frac{H_{cb}^2}{8\pi} \quad (IIC-1)$$

F_n and F_s are the free energies in the normal and superconducting states, respectively. This equation results

from the fact that the S-N transition occurs when the magnetic energy resulting from the diamagnetic flux exclusion overcomes the condensation energy of the superconducting state.

If one considers a thin film (thickness $\approx$ penetration depth) with a field applied parallel to the surface, the critical field H_c at which the transition to the normal state occurs is increased above H_{cb} . According to the G-L theory, the transition field for such a thin film is

$$\frac{H_{c||}(T)}{H_{cb}(T)} = \frac{2(\sqrt{6}) \lambda_e(T)}{d} \quad (\text{IIC-2})$$

where $\lambda_e(T)$ is the penetration depth in the equilibrium state, i.e., in weak fields. This result is valid for films of thickness d satisfying the inequality $d < \sqrt{3} \lambda_e(T)$, which is the condition for the transition to be of second order.

When the field is applied perpendicular to the film plane, or when it has a perpendicular component, the situation is very different. The transition to the normal state occurs at a lower value than $H_{c||}$, but it is still greater than H_{cb} . What are the causes of such a difference in behavior?

In our experiment we have purposely made a film with a high number of defects, so that we can expect ξ to be much less than λ , and that the behavior will be characteristic of a Type II superconductor, with a range of field where penetration is only partially complete. For all Type II superconductors, bulk and thin film, energy considerations show that in the intermediate state the most probable form of field penetration will be as vortices (filaments of magnetic flux). At fields close to the lower critical field H_{c1} penetration begins with the formation of separate filaments of magnetic flux. A pictorial representation of a vortex is given by De Gennes (46), and is reproduced in Figure 2. A vortex is physically a cylindrical core of normal metal with a very small radius through which magnetic flux can penetrate the superconductor. As described in Section II A the flux is quantized. When the applied field is increased, the number of vortices also increases, until finally the penetration is total and the superconductor becomes a normal conductor.

What makes this state preferable for the system? Earlier it was pointed out that the superconducting state is one of lower energy than the normal state.

Figure 2. Structure of One Vortex Line in a Type II Superconductor.

The magnetic field is maximum near the center of the line. In (a) the screening current required by the Meissner-Oschenfeld is sketched. In (b) H decreases because of the screening in an "electromagnetic" region of radius $= \lambda$. The number of superconducting electrons per cm^3 n_s is reduced only in a small "core region" of radius ξ , as shown in (c).

However, if we increase the magnetic field while maintaining the temperature below T_c , the superconductor expels the field, according to the Meissner-Oschenfeld (M-O) effect. This requires energy which must be supplied by the superconductor. The energy appears in the form of the kinetic energy of the moving electrons that make up the surface currents required by the M-O effect. Increasing the field means that more energy has to go into the electron system and, at the critical field, the energy of the superconducting state becomes greater than the energy of the normal state, in which case the material reverts to the normal state.

If there were some mechanism whereby the magnetic field could partially penetrate the superconductor, the energy required to expel the magnetic field could be reduced, and the superconducting state could persist in higher magnetic fields. This mechanism is provided by the formation of vortices, which reduce the magnitude of the required M-O effect energy.

If we now limit our considerations to thin films, since vortices are always along the field directions, we might expect a large change in behavior for parallel

and perpendicular geometries due to the change in area normal to the field. This is fundamental to the theory of Tinkham, and in Figure 3 his schematic diagram of the arrangement of vortices is shown.

In his analysis, Tinkham begins with the London equation

$$-H = c \operatorname{curl}(\Lambda J_s), \quad (\text{IIC-3})$$

where J_s is the supercurrent density and

$$\Lambda = \frac{m}{n_s e^2} = \frac{4\pi\lambda^2}{c^2},$$

and uses this to obtain an expression for the current density $J_s(r)$ of a circular loop of radius r centered on a normal spot, i.e., containing one or more quanta of flux. Associated with this circulating current will be a kinetic energy density given by

$$T(w, r) = \frac{w}{2\Lambda_0} \left[\frac{n\phi_0 - \pi r^2 H}{2\pi r c} \right]^2 \quad (\text{IIC-4})$$

the physical basis of which was described more fully earlier. (See p. 32) In this expression the variable w is the order parameter:

$$w = \frac{n_s}{n_0} = \frac{\Lambda_0}{\Lambda}. \quad (\text{IIC-5})$$

Figure 3. Diagram of the Vortex Configuration (as Represented by the Circular Screening Currents) in Parallel and Perpendicular Field Cases.

In parallel field geometry (a), the width of the current loop is limited by film thickness. In the perpendicular field geometry, the size of the vortex can adjust depending on the field strength so as to minimize energy. Configuration (c) corresponds to a higher field strength than (b), so that smaller vortices contain one flux quantum.

The above kinetic energy term, along with a term proportional to $[\nabla w]^2$, which represents the energy increase associated with a spatial variation of the magnitude of the order parameter, is added to the G-L free energy difference expression (28,47):

$$f(w,T) = -a(T)w + \frac{1}{2}b(T)w^2, \quad (\text{IIC-6})$$

where

$$a(T) = \frac{H_{cb}^2}{4\pi} \left[\frac{\lambda_e(T)}{\lambda_e(0)} \right]^2 \quad (\text{IIC-7})$$

and

$$b(T) = a(T) \left[\frac{\lambda_e(T)}{\lambda_e(0)} \right]^2. \quad (\text{IIC-8})$$

From Equation 4 we see that if $n = 0$, i.e., field penetration without fluxoids, then $T(w,r) \rightarrow \infty$ as wH^2r^2 . This would soon lead to values in excess of the condensation energy, Equation 6, and the critical field would depend on specimen size and be very small for macroscopic specimens. It implies that to maintain a superconducting state in the presence of reasonably strong fields as found, we must have flux penetrating through in a uniform way, with a nearly uniform density of closely packed "vortices" of current everywhere. This argument is the justification for Figure 3.

If we consider one such vortex containing n flux quanta, since the field penetrates uniformly, the

overall radius R of the vortex will be such that

$$\pi R^2 H = n \varphi_0, \quad (\text{IIC-9})$$

if errors due to the fact that circular cells will not pack to cover a surface are ignored.

Application of the calculus of variations shows that to minimize the total free energy w should approach zero as r^{2n} , where n is the number of flux units in a vortex of radius r . This suggested to Tinkham a trial function $w(r) = w_0 \left(\frac{r}{R}\right)^\alpha$ be used to compute the free energy difference per unit volume with $H_{c\perp}$, n , and α as parameters. The resulting expression

$$\begin{aligned} \Delta G = \frac{H \varphi_0 w_0}{4\pi c^2 \Lambda_0} & \left[\frac{8n}{\alpha(\alpha+2)(\alpha+4)} + \frac{\alpha}{4n} \right] \\ & - a w_0 \left[\frac{2}{\alpha+2} \right] + \frac{b}{2} w_0^2 \left[\frac{1}{\alpha+1} \right] \quad (\text{IIC-10}) \end{aligned}$$

will yield the maximum field in which $w_0 > 0$ can be sustained if the term linear in w_0 is set equal to zero. In Equation 10 $\varphi_0 = \frac{hc}{2e} = 2.07 \times 10^{-7} \text{ G-cm.}^2$, is the flux quantum for pairs and $\Lambda_0 = \Lambda(T=0^\circ\text{K})$.

The expression obtained for $H_{c\perp}$ is:

$$H_{c\perp} = \frac{4\pi c^2 \Lambda_0 a}{\varphi_0} \frac{1}{[4n/\alpha(\alpha+4) + \alpha(\alpha+2)/8n]}. \quad (\text{IIC-11})$$

The variational problem is equivalent to finding n and

α so as to maximize $H_{c_{\perp}}$. Treating α and n as continuous variables, the optimum value occurs as α and n both approach zero, maintaining the relation $\alpha = 2n$, in which case the bracketed term goes to unity. However, to get the best physical solution, n must take its lowest non-zero integral value, namely, $n = 1$. In this case the minimum value of the bracketed quantity is approximately 1.1. If one goes to the opposite extreme, and lets $n \rightarrow \infty$, the minimum value increases only to $\sqrt{2}$. From these results Tinkham concluded that the optimum configuration is one in which the flux penetrates in fluxoids, each containing a single unit of flux. The variation with n is weak enough that physical inhomogenieties could shift this result to allow a coarser grained current pattern. Because of the limited class of variation functions used, and also because of the circular approximation to the vortex shape, this qualification is necessary.

Substitution in Equation 10 then yields the following equation for $H_{c_{\perp}}$:

$$H_{c_{\perp}}(T) = \frac{4\pi\lambda_e^2(T)H_{cb}^2(T)}{\varphi_0}$$

$$= 6.06 \times 10^7 \lambda_e^2(T)H_{cb}^2(T). \quad (\text{IIC-12})$$

This is Tinkham's prediction for the perpendicular critical field, which depends only on known quantities, $\lambda_e(T)$ and $H_{cb}(T)$, and thus leads to a parameter free determination of H_{c1} . This result is equivalent to that of Abrikosov (29) for the critical field H_{c2} of bulk Type II superconductors, in which the flux is shown to penetrate in a vortex structure similar to that described by Tinkham.

The angular dependence of the critical field was then considered. From the free energy expression, Equation 10, one can see that a perpendicular field component produces a term linear in the applied field to be balanced against the condensation energy. A field component in the plane of the film produces a quadratic effect. Figure 3 shows the basis for this difference. In the parallel orientation the important dimension of the current loops is fixed by the film thickness, and hence is constant, and the energy increases as H^2 ; on the other hand, in the perpendicular orientation, the size of the current loops scales down as H increases, leaving only a residual linear dependence. From this argument Tinkham predicts a critical field versus angle relation of the form:

$$\frac{H_c \sin \theta}{H_{c\perp}} + \left[\frac{H_c \cos \theta}{H_{c\parallel}} \right]^2 = 1 \quad (\text{IIC-13})$$

where $H_{c\perp}$ is given by Equation 12 and $H_{c\parallel}$ by Equation 2.

θ is the magnitude of the angle between the field and the plane of the film. For a thin film $H_{c\perp} \ll H_{c\parallel}$, and the first term will dominate over a considerable angular range. The fact that the variation is with $\cos \theta$ rather than $\cos^2 \theta$ is important for explaining the extreme sensitivity of critical field measurements to small perpendicular field components.

In the analysis of our experimental results we use Tinkham's theory in two ways. The angular dependence results are compared directly with Equation 13. Knowing the extreme values $H_{c\perp}$ and $H_{c\parallel}$, Equation 13 predicts a curve for intermediate values of θ which can be compared directly with our measured values.

We can also make use of Equation 12 in the following way: $H_{c\perp}(T)$ is measured, $H_{cb}(T)$ is known, and thus we can solve for $\lambda_e^2(T)$. We then make use of the relation, valid for $\ell \ll \xi_0$, $\lambda_e^2(0) = \lambda_L^2(\xi_0/\ell)$ which implies

$$\ell = \lambda_L^2 \xi_0 / \lambda_e^2(0). \quad (\text{IIC-14})$$

With ξ_0 and λ_L taken from the literature and $\lambda_e^2(0)$

determined from $H_{c_{\perp}}(T)$ we have an estimate of the electronic mean free path.

From earlier work performed by Bulow (46) in which electron diffraction patterns were taken of thin films formed in the same manner as ours, we can obtain an estimate of the nominal crystallite size. In our analysis in Section III B this work will be elaborated upon and compared with electronic mean free paths obtained from the Tinkham theory.

The temperature dependences for $\lambda_e(t)$ and $H_{ob}(t)$ are approximated by the usual Gorter-Casimir relations:

$$\lambda_e^2(t) = \lambda_e^2(0)(1 - t^4)^{-1} \quad (\text{IIC-15})$$

$$H_{cb}(t) = H_{cb}(0)(1 - t^2) \quad (\text{IIC-16})$$

where $t = T/T_c$. If these are used in connection with Equation 14 we obtain

$$\ell = \lambda_L^2 \xi_0 H_{cb}^2(0) (6.06 \times 10^{-9}) \frac{(1 - t^2)^2}{H_{c_{\perp}}(t)(1 - t^4)}, \quad (\text{IIC-17})$$

which depends only on known and measured quantities. All fields are expressed in gauss and lengths in angstroms.

It should be noted that the parameters entering into the theory are those of the bulk material, although the

predictions are for the behavior of the material in thin film form.

III A

The Experimental Equipment and Techniques

i. Experimental Concept

The purpose of our investigation was to examine the angular dependence of the critical field, and its relation to changes in defect concentration, crystallization, and mean free path. There are two commonly used approaches for studying the effects of defects in solids which can accomplish this.

It is possible to begin with a very pure material into which defects may be introduced by doping, alloying, radiation, plastic deformation, or other similar methods. A second procedure, the one which was employed in the experiments described herein, is to begin with as high a concentration of defects as possible, and subsequently anneal them. A similar approach is taken, for instance, in radiation damage experiments where depletion zones are produced and then annealed. (27)

In our case we form, by means of evaporation, a metal film on a quartz substrate held at liquid helium

temperature and then allow the film to warm in stages up to room temperature. For thin film experiments this method has the advantage of a constant thickness with the capability of varying the defect concentration by annealing.

ii. Description of the Experimental Cryostat and Auxiliary Equipment.

The essential part of the experimental arrangement is a liquid helium cryostat with demountable tail section, shown in Figure 4. The upper section consists of an outer Dewar containing liquid nitrogen, and an inner liquid helium container with a hollow copper finger extending into the tail. The tail section was constructed in the W.S.U. Physics Department Instrument Shop originally for Hall voltage work, and a rotating vacuum tight flange was added for the present angular dependence measurements.

The tail section consists of the liquid helium finger, a substrate holder mounted in a track which allows its vertical position to be changed, and an oven. The substrate holder is a 24mm x 29mm x 6mm copper block which slides in the track from a position opposite the oven to the center of the magnet pole faces. The track is made from the same piece of copper as the finger to assure the highest thermal conductivity possible. Thermal contact between the substrate holder and the helium bath is maintained by several

Figure 4. Experimental Cryostat - Tail Section.

Note: Substrate and track are rotated 90° from actual position opposite oven for clarity; nylon string connecting substrate holder to pulley and wires maintaining thermal contact between bath and substrate holder not shown.

hundred tinned copper wires of 0.003" diameter.

The track was necessitated by the fact that the 2.5" gap of the magnet would not allow sufficient space for the oven. Thus the oven was moved upward to just clear the pole face. The oven itself contains a tungsten filament to which the sample is fused and a shutter to control the opening to the substrate. The substrate - filament distance is 5cm. The interior region of the tail section is shielded from outside heat radiation by two concentric copper cans fastened to the two baths. Cut into each can are small ports to allow the metal vapor from the oven to quench on the substrate, and to prevent vapor from hitting other interior parts.

The lowering of the substrate holder after film formation is effected by means of a nylon string and pulley rotated externally using a small screwdriver through an 'O' ring vacuum seal. The lowering is accompanied by an increase in the temperature of the substrate of approximately 1°K, due to its increased distance from the helium bath.

The cryostat is continually pumped by a CVC 175 watt oil diffusion pump backed by a Welch 1405B

forepump. The pressure as measured by an NRC Type 710 ionization gauge located in the pump line is 10^{-5} Torr. before cooling, and is estimated to be less than 10^{-6} Torr. at the substrate before evaporation.

The helium bath pressure is regulated by a manostat designed originally by Sommers (49), with the pumping provided by a Beach-Russ 135D high capacity pump.

The magnetic field was produced by a Varian V-3400 rotatable magnet with 9" pole faces and 2.5" gap. The field strength was calibrated periodically with a rotating coil gaussmeter checked against an NMR probe, and had a maximum value of 11.2 kilogauss.

Figure 5 shows a more detailed sketch of the sample configuration. A single crystal of quartz, cut perpendicular to the c axis and polished, was used as the substrate. The 17mm x 20mm x 1mm quartz plate was held against the copper substrate holder by six copper pressure plates, which also pressed 0.002" platinum foil electrodes into the predeposited gold electrodes. The platinum electrodes were electrically insulated from the copper by thin strips of mica, and electrical contact to the foil was made by fusing

Figure 5. Details of the Substrate Holder and Electrical Contacts.

Note: Small contacts (C, D, E, F) are similar to A and B but are omitted for clarity.

platinum wires into the foil.

The two large contacts (A,B) cover the width of the film and were designed to provide a uniform current. Contacts C and D were used to measure the resistive transition, whereas the transverse contacts E and F, originally used for Hall voltage measurements (50), were held as spares.

The relative orientations of the current, magnetic field, and film plane are shown in Figure 6. The magnetic field is always perpendicular to the current. To eliminate current dependent effects, the value of the current was chosen to be 0.80 mA for all the films with the exception of Film 102, in which case a current of 46 mA was required to obtain a measurable voltage upon transition into the normal state. The measured curves for Film 102 do not differ appreciably from those for the other lead films, so that it is thought that the higher current used did not have a measurable effect on the results.

All of the measurements were made with the field increasing in strength, thus driving the sample film from the superconducting state to the normal state. The reason for this choice is the fact that flux can

Figure 6. Orientation of Film, Field, and Current.

be trapped as the field is lowered and thus result in a reduced value of field at which superconductivity will take place, described as "supercooling" in Section II B.

To change the field direction with respect to the film plane the magnet was rotated about a vertical axis. Since the oven extends several inches from the tail section (it is tangent to the tail section) it was necessary to simultaneously rotate the outermost part of the lower half of the tail section which contained the oven. Reference to Figure 4 will show the rotating flange inserted in the tail section to effect this.

For temperature measurement a carbon resistor was fastened on the rear of the copper block, and was calibrated using the equation of Clement and Quinzel (51). The temperature was continually recorded using a Leeds & Northrup multiple point recorder, which also monitored the longitudinal film voltage when field sweeps were not being made.

Recording of the voltage versus field relation for the film was done with the use of an Electro Instruments Model 500 X-Y recorder, where the X axis voltage

was obtained from the magnet power supply and was proportional to the field strength. Maximum Y sensitivity was 0.5 mV per inch. In Figure 7 a schematic diagram of the electrical circuitry for the measurements is given.

Figure 7. Schematic Diagram of the Film Measuring Circuitry.

iii. Experimental procedure.

The perpendicular cut quartz single crystal substrate was chosen because of its long standing satisfactory performance in low temperature film work. Such a substrate was used in 1938 by Shalnikov (52), and subsequently by investigators at the University of Gottingen.

The most important question to ask about the substrate is its influence on the growth and recrystallization of the quenched film. As far as film formation is concerned, the atoms of the metal have a very low surface mobility at such low substrate temperatures, and we expect little effect. At most, the first one or two layers of atoms could be influenced by the substrate, but for films of 1000 - 2000 Å this would be unnoticed.

Experiments have substantiated the fact that this type of quartz substrate does not influence the recrystallization. Buckel and Hilsch (53) used this substrate in making electrical resistivity measurements on Bi and other metals. Bulow (48) used collodium films as substrates in his electron diffraction work

on the same metals and found that the changes in structure occurred at the same temperature for his films as did the changes in the electrical properties as measured by Buckel and Hilsch.

In a subsequent series of experiments Bulow (54) simultaneously formed films of Bi-Sn alloys on quartz and collodium attached to the same substrate holder and made both electrical measurements and electron diffraction patterns, observing again that the changes in measured properties occur for both films at the same temperatures.

On this basis we do not anticipate any influence of the substrate on the growth and recrystallization of our films.

For our experiments the substrate was chemically cleaned in the usual manner*, and was then moved to

*The procedure was as follows: the quartz was cleaned in acetone to remove any oils present from handling, allowed to dry, and then boiled in concentrated chromic acid for 15-30 minutes; this was followed by several rinses with distilled water, at which time the success of the cleaning would be evident if the water completely wet the surface; the substrate would then be rinsed with reagent grade alcohol and allowed to air dry; this drying procedure provided the quickest and best method of removing the water from the quartz surface; the film was then ready for the gold plating.

an evaporating station where the gold electrodes were deposited from the vapor through a mask. The substrate was then mounted on the sample block in the manner described earlier and pictured in Figure 5, and a copper mask was added to provide the proper film shape. The sample metals used are listed in Table 2, and were fused to the tungsten filament of the oven in the auxiliary evaporating station before the oven was inserted in the tail section. The fused sample was allowed atmospheric exposure only for the time required to switch the oven from the evaporating station to the tail section, which was then immediately pumped. Surface contamination would then be held to a minimum, and to further insure a good film the oven was provided with a shutter which would not be opened during the film evaporation until after the surface "dirt" was boiled away.

When the cryostat pressure was sufficiently low (less than 2×10^{-5} Torr.), cooling of the cryostat and sample would begin and evaporation of the sample followed immediately after thermal equilibrium was reached. The rate of evaporation was 250 - 350 Å/sec.

TABLE 2

SOURCE AND PURITY OF MATERIALS

Metal	Source	Purity
Pb	American Smelting and Refining Company, South Plainfield, New Jersey.	99.999+ %
Sn	Belmont Smelting and Refining Works, Inc., 330 Belmont Ave., Brooklyn, New York 10007.	99.9999 % [<1 ppm]
In	The Indium Corporation of America, Utica, New York.	99.9999 %

During evaporation the temperature of the substrate block never rose above 6.3°K as measured by the thermoresistor on the rear face of the block. It may be argued that the film itself is at a much higher temperature, but this can be disproved by the following arguments. First, that the film did not go above 15°K can be shown in the following way. In work on thin bismuth films, Buckel (55) showed using a similar geometry that an amorphous film is deposited if the film and substrate do not go above 15°K , at which temperature a recrystallization takes place. The bismuth film is superconducting with $T_c = 6^{\circ}\text{K}$ in the first form, but it is no longer superconducting after the recrystallization takes place. We have made such films of bismuth (50) and have not encountered any problems keeping the film below 15°K on the substrate during evaporation.

A second and much more conclusive argument may be made by referring to work of Buckel and Hilsch (56). In their experiments on many substrates, including quartz, Cu_2O , and Al_2O_3 , and others, using similar geometry, they found that if the substrate temperature was lowered 3°K below the transition temperature of the material which they were using, then

during formation the film would always be superconducting. This implies the film temperature is at most 3°K above the measured substrate temperature.

Thirdly, we know that the response time lag of our thermoresistor is very short when compared with the duration of the evaporation. The time lag of the thermoresistor was found by passing a very high current through the film so that Joule heating would take place, and when this was done it was found that the thermoresistor responded with a time lag $\Delta t \ll 1 \text{ sec.}$ Since the film evaporations averaged five seconds duration, this is more than sufficient time for any large increase in temperature to be recorded.

Thus we might expect that our measured substrate temperatures during film formation will be lower than the actual temperature of the film, but still within a few degrees.

The substrate block and film, after evaporation, would be lowered as previously described, and field sweeps begun. When all measurements had been made, the remaining liquid helium would be allowed to boil off to a recovery station. After the sample had warmed to the desired annealing temperature a retransfer

of liquid helium would be initiated, thus resulting in an anneal between liquid helium and liquid nitrogen temperatures. Measurements would again be made at approximately liquid helium temperature, the exact temperature depending on the rate of pumping over the bath. The remaining anneals are then accomplished in a similar manner, with all measurements taking place at liquid helium temperatures.

Upon completion of this phase of the experiment the films are removed and using the technique of Stern (57) the film thickness is measured. His interference technique consists in taking a silvered lens and placing it over a channel cut into the film. (The film and channel are overlaid with a $\approx 1000 \text{ \AA}$ evaporated silver film to improve reflection before this is done.) The resultant interference pattern when viewed in reflection is a series of dark rings against a bright background, modified Newton's rings. The step in the film causes a shift in the radii of the rings from which the thickness is calculated.

III B

Presentation and Analysis of the Experimental Results*

i. Angular Dependence of the Transition Field.

In defining the critical field, H_c , we choose that field at which one-half of the normal residual resistivity has been restored. This definition of H_c has been used by other investigators of resistive transitions using wire samples, e.g., Seraphim (23), and Luders (58), although it is not the one used by Tinkhan to compare experimental data with his theory.

In a preliminary study performed by H. Bulow and this author (59) it was shown that analysis using the definition for H_c given above yields a decrease in H_c with increasing annealing temperature, i.e., with decreasing defect density. This is what one would expect on physical grounds, and is also the behavior found by Luders in his experiments on deformed lead wires. Our results are shown in Figure 8, which

*A portion of this work was presented at the January 1968 meeting of the American Physical Society in Chicago, and abstracted in Bull. Amer. Phys. Soc. 13, 77 (1968).

Figure 8. Critical Field versus Annealing Temperature - Results of our Preliminary Study of Lead.

Solid circles ($\bullet$) are our experimental points; Open circles ($\circ$) are the critical field values reported by Luders (58) on deformed lead wires; Squares ($\square$) are the critical field values read from our field sweeps using Tinkham's (6) definition of the critical field.

points out the fact that if one used Tinkham's criterion for determining H_c the critical field would not change as a function of annealing temperature, that is, H_c would not change with defect concentration in contrast to the experimental results of Luders. It has since been communicated to this author (60) by one of Tinkham's assistants that they no longer consider their definition of H_c valid.

The critical temperatures of quenched thin films are not necessarily those of the bulk material. This has been pointed out by Buckel and Hilsch (56), and by Bulow (48), and for reference Table 3 is included listing the values of T_c for the metals we used and for some additional metals for comparison. The change in T_c is an effect undergoing considerable study in other laboratories in an effort to find materials with higher critical temperatures, but is not of interest in this investigation.

The data as recorded for a Typical Sn film are shown in Figures 9, 10, and 11 in the order of increasing annealing temperature. Similar curves are given for In in Figures 12, 13, 14, and 15. The curves for Pb and Sn are similar with respect to broadening

TABLE 3

CRITICAL TEMPERATURE

Element	T_c (bulk)	T_c (film quenched at liq. He temp.)
Sn	3.71°K	4.6°K
Pb	7.22	7.2
In	3.37	4.1
Al	1.20	2.6
Hg	4.15	3.9
Tl	2.38	2.6
Zn	0.90	1.4

Figure 9. Representative Field Sweeps as Taken by the X-Y Recorder for Tin Film 107 - Annealing Temperature = 11°K .

Figure 10. Representative Field Sweeps as Taken by the X-Y Recorder for
Tin Film 107 - Annealing Temperature = 77°K .

Figure 11. Representative Field Sweeps as Taken by the X-Y Recorder for Tin Film 107 - Annealing Temperature - 300°K .

Figure 12. Representative Field Sweeps as Taken by the X-Y Recorder for Indium Film 110 - Annealing Temperature = 6°K .

Figure 13. Representative Field Sweeps as Taken by the X-Y Recorder for Indium Film 110 - Annealing Temperature = 38°K .

Figure 14. Representative Field Sweeps as Taken by the X-Y Recorder for Indium Film 110 - Annealing Temperature = 77°K .

Figure 15. Representative Field Sweeps as Taken by the X-Y Recorder for Indium Film 110 - Annealing Temperature = 300°K .

and shape, and the Pb curves are not reproduced here for that reason.

There are several features of the curves that should be pointed out. As is evident from all of the curves, the transitions are broad when compared with those of the bulk material, for which typical widths would be measured in gauss. For our films the widths are usually over one kilogauss and often an order of magnitude larger, especially in indium.

It is found that the maximum height (proportional to residual resistance) is constant for Pb and In for any given annealing temperature. This is most evident from the 300°K annealing temperature curves, where H_c is low enough that for all angles the maximum is reached. Use was made of this fact for measurements when θ was near zero, for in some cases our field strength was not high enough to drive the sample completely normal. Thus knowing the maximum height from a $\theta = 90^\circ$ curve, where the full residual resistivity was always reached, would allow us to extend our range of measurements considerably. The slow onset of normal resistance did not hamper us as long as half of the maximum height was reached before 11.2 kG.

For each annealing temperature, the transition curves for several angles have been included. It should be noted that the transitions shift toward lower fields as θ approaches 90° . In Figures 12-15 we see that the shift toward lower field transitions is very rapid in indium as θ is increased from 0° ; that there is little change at all for θ from 45° to 90° will be shown in later figures. (Figures 21,22)

Looking again at the series of figures we also note a decrease in maximum height with increasing annealing temperature. These changes were used to determine the variation in the resistivity of the film.

As mentioned in the preceeding theoretical discussion, the films are very sensitive to small perpendicular components of the applied magnetic field. Use of this fact was made to determine the zero point for angular measurements by sweeping angles near parallel while the applied magnetic field was sufficiently strong to restore some resistance. The angle at which the maximum signal was observed was taken as the zero reference.

We can now check the agreement of our measured

$H_c(\theta)$ values with those predicted by Equation (IIC-13). Figures 16-20 show the experimentally observed values of H_c as a function of angle versus angle for Pb and Sn. In each figure are contained the results for several annealing temperatures for a given film. Each experimental point represents a critical field value determined from a curve similar to those shown in Figures 9-15. The solid curves are the theoretical predictions of Tinkham's theory, obtained by substituting in Equation (IIC-13) the observed values of $H_{c\perp}$ and $H_{c\parallel}$ and then computing the values of $H_c(\theta)$ for intermediate angles.

For these films the experimental points and theoretically predicted curves are in agreement for all annealing temperatures. With the exception of Film 97, where the experimental points show considerable scatter, the deviations from the theoretical curve are all within 3%. For Film 97 the relatively large error bars associated with the experimental points indicate that the disagreement should not be unexpected. In figures where no error bars are shown, the error is smaller than the size of the symbol used for the experimental point.

Figure 16. Angular Dependence of the Critical Field.
Measuring Temperature = 5.7°K.

Figure 17. Angular Dependence of the Critical Field.
Measuring Temperature = 6.2°K.

Figure 18. Angular Dependence of the Critical Field.
Measuring Temperature = 6.2°K.

Figure 19. Angular Dependence of the Critical Field.
Measuring Temperature = 3.8°K.
Note: 300°K curve has been multiplied by factor of 4 to show detail on this scale.

Figure 20. Angular Dependence of the Critical Field.
Measuring Temperature = 4.1°K.

At this point we asked whether or not a preferred orientation for the film would lead to a disagreement between experiment and theory. A review of the electron diffraction experiments mentioned earlier showed that indium would be a good element to choose for this study, since it showed a preferred orientation for the majority of crystallites on annealing between 90°K and 180°K , and continued to grow with this preferred orientation until room temperature was reached. The growth is such that either the 202 or 220 planes are perpendicular to the surface of the substrate. Sixty per cent of the oriented crystallites will have the 202 plane perpendicular to the substrate with the remaining forty percent in the other mentioned orientation. An advantage of choosing indium would be the fact that for the first two anneals the film would be randomly oriented, and should agree with the theoretical predictions, whereas if there is going to be any deviation, it would be expected only for the higher temperature anneals.

The experimental results and the theoretical curve for indium are shown in Figures 21 and 22. It should be noted that for some of the anneals the critical field was beyond the measuring capability of the

Figure 21. Angular Dependence of the Critical Field.
Measuring Temperature = 3.7°K.

Figure 22. Angular Dependence of the Critical Field.
Measuring Temperature = 3.8°K.

equipment for angles near 0° , in which case the measured critical fields for the angles nearest zero which could be obtained were used to extrapolate a value for $H_{c\parallel}$, using Equation (IIC-13) and this value of $H_{c\parallel}$ would then be used to generate the entire curve. The end point determined in this way may be in error by a large amount, but the effect of such an error in the generation of the curve is relatively minor due to the fact that the first term predominates over such a large angular range. For example, if $H_{c\parallel}$ for the 6.0°K anneal curve for Film 109 is taken to be 20 kG rather than 17 kG, an increase of 18%, the resultant increase in the predicted value of H_c for $\theta = 10^\circ$ is only 3.6%.

This extrapolation did not have to be performed for the 300°K annealing temperature, since H_c was within our capability. This is an important point since it is the angular dependence for this annealing temperature which shows the greatest deviation from the theoretical predictions.

Returning to Figures 21 and 22, we note that as expected the experimental points and theoretical curve are in close agreement for the first two anneals.

At the room temperature anneal the deviation from the predicted angular dependence is evident. The maximum deviations are 32% for Film 109 and 12.3% for Film 110. These maximum deviations occur within 15° of 0° , and the deviation is very small for angles greater than 45° .

These results are interpreted in the light of the known preferred orientation of the crystallites on annealing as follows. For 0° the magnetic field "sees" a cross-sectional area of the film equal to the thickness of the film times the length. The orientation of the crystallites can not have a large effect, since so small an area is shown to the field (about 10^{-5}cm^2). As soon as θ is increased from 0° , however, the cross-sectional area presented to the magnetic field is enhanced by the oriented crystallites, and the larger area presented to the field causes a lower critical field value to be observed.*

*The basis for this statement is the same argument as presented in Section II C concerning the difference in magnitude in H_c for parallel and perpendicular fields.

Thus as θ is increased the experimental points will lie below the theoretical curve, until the projected area of the film surface normal to the field has masked out the effect of the orientation. This is what is expected and found.

For Film 109 the third anneal took place at 177°K. This anneal also shows a large deviation of the experimental points from the theoretical curve, and is in fact in the opposite direction from the observed deviation for the 300°K anneals. Here it is thought that there is some mechanism which has retarded the recrystallization until about 177°K, and this contention is supported by the behavior of the resistivity changes of this film, to be described later.

The most likely cause of retarded growth would be an impurity or impurities of some kind, and the most suspect, for two reasons, is the presence of some water in the film. That this might be the cause is indicated by the fact that due to the presence of three rotating and two stationary 'O' ring seals the cryostat must be continually pumped. If any air should leak into the cryostat it would be frozen out on the coldest surface very quickly, and most likely would

not get to the vacuum pump. The coldest surfaces are those of the helium finger and attached track and substrate holder. Since there is water vapor in the air, we must consider its presence, and the fact that it could have contaminated this film.

The second reason for suggesting that water is the impurity is that in some of the electron diffraction patterns rings appeared at about 180°K which had the correct radii to correspond with ice. These rings disappeared upon further annealing, and as yet the reason for their disappearance is not known. It is our belief that this impurity would be the most likely to cause the behavior which we observe. Further investigation should shed more light on this point.

ii. Resistivity as a Function of Annealing Temperature

In Figure 23 the drop in resistivity as a function of annealing temperature is given for five of the films investigated. It graphically relates the reduction in defect concentration, where the steepest drop is seen to be between 20°K - 120°K . Sander and Mönch (61) measured the stored energy released by quenched thin Cu films during annealing from 20°K - 60°K . The value they found was in good agreement with stored energy measurements on neutron bombarded Cu. Thus their experiments show that the processes responsible are in both cases the same: crystallization with annihilation of simple atomic defects.

Here it should be mentioned that the behavior of the resistivity ratio of Film 109 is not like that of the other films investigated. Not only is the resistivity ratio very high right after film formation, it is still high at the 177°K anneal, in fact $2\frac{1}{2}$ -3 times that of the other films at the same annealing temperature. The resistivity ratio for Film 107 is also relatively high, but drops at 77°K to a value comparable with those of the other films. This is supporting evidence for the arguments presented earlier

Figure 23. Resistivity Ratio Versus Annealing Temperature. Measurements made at liq. He temp.; $\rho_{300^\circ\text{K}}$ is the resistivity at liq. He temp. after annealing at 300°K .

concerning the anomalous behavior of Film 109 for that annealing temperature.

iii. Relation of Transition Field with Changes in Defect Concentration, Crystallization, and Mean Free Path.

Figure 24 shows the perpendicular critical field as a function of annealing temperature, where the curves are seen to follow the trend of the $\rho/\rho_{300^\circ\text{K}}$ curves of the previous figure. We expect that this will occur, since the value of the critical field will depend on defect density as will the resistivity ratio. This result is similar to that reported by Iuders (58), in experiments where he plastically deformed lead wires at liquid helium temperatures and subsequently allowed the defects generated to anneal.

A second important result obtained from Tinkham's theory is the determination of the electronic mean free path from the measured values of H_{c1} . Following Equation (IIC-17), we calculated the electronic mean free path, ℓ , for all of our films and the results are presented in Figures 25-27. The values for λ_L and $H_{cb}(0)$ used in Equation (IIC-17) are contained in Table 1.

Also drawn in each of these figures are curves

Figure 24. Perpendicular Critical Field versus Annealing Temperature.

Note: Measuring temperatures are listed in Table 4, with Film 107 - 11°K value shifted to 3.75°K using (IIA - 1).

Figure 25. Electronic Mean Free Path and Nominal Crystallite Size (a) versus Annealing Temperature for Tin.

Figure 26. Electronic Mean Free Path and Nominal Crystallite Size (a) versus Annealing Temperature for Lead.

Figure 27. Electronic Mean Free Path and Nominal Crystallite Size (a) versus Annealing Temperature for Indium.

showing the change in nominal crystallite size with annealing temperature. The curves for lead and indium are from Bulow (48) and were calculated from the half-widths of the peaks in the photometric traces made from electron diffraction patterns for the two metals. His films were formed in the same manner as ours and the diffraction patterns were made as the films warmed. Buckel (62) has reported results for tin films, giving the photometric curves in his paper, from which we estimated the nominal crystallite sizes.

We note that for all films the calculated mean free paths follow the growth trend of the nominal crystallite sizes. For the tin films the proportionality between a and ℓ is constant over nearly the entire range of annealing temperatures. For the lead films this is true up to $\approx 170^\circ\text{K}$.* In this connection the results bear out the hypothesis made on the basis of our preliminary results (59). For the indium films the electron diffraction determined nominal crystallite sizes are known only up to $\approx 100^\circ\text{K}$ annealing temperature.

*For both tin and lead $a \approx 3 \times \ell$ for the temperature ranges mentioned. For Indium Film 110 $a \approx 1/3 \times \ell$ up to 100°K .

Beyond this point the increase in crystallite size is very rapid. Such a behavior is noted for Film 110, where in fact the ℓ values are greater than the a values given by Bulow, but a proportionality still exists. The fact that $\ell > a$ is not of great concern since the film was very thick ($1072\text{\AA}$) compared to the film used by Bulow ($\approx 100\text{\AA}$), and could have quenched with larger crystallites. This is even more likely with the knowledge that the heat of fusion of indium is the lowest of the materials which we investigated, and Bulow (48) has shown that the rate of increase in a on annealing is related to the heat of fusion.

The behavior of Film 109 again shows a reluctance to increase ℓ even at 300°K . It is not proportional to a , which was determined from a film without hindered growth, and this supports our belief that the behavior of Film 109 is a result of a retarding of the annealing of defects during warming.

To summarize our results, Table 4 presents some of the parameters measured and calculated for each of our films.

TABLE 4 - SUMMARY TABLE OF MEASURED AND COMPUTED QUANTITIES

Film	Metal	T_c [°K]	Thick. [Å]	Ann. Temp. [°K]	Meas. Temp. [°K]	$H_{c\perp}(T)$ [kG]	$H_{c\parallel}(T)$ [kG]	ℓ [Å]
97	Pb	7.2	1636	6	5.84	3.40	5.85	27.1
				37	5.85	3.20	5.40	28.5
				110	5.58	2.15	3.40	51.8
				300	5.37	0.73	1.51	174.
98	Pb	7.2	1130	6	6.30	2.00	3.40	29.6
				12	6.15	2.00	3.35	29.6
				125	6.30	1.35	3.00	51.6
102	Pb	7.2	1974	6	6.20	3.10	5.40	21.4
				28	6.20	2.90	5.20	22.8
				152	6.15	1.60	4.25	43.6
				300	5.88	0.80	2.17	111.
107	Sn	4.6	1309	11	4.05	3.75	17.50	11.2
				77	3.70	4.15	22.50	17.1
				300	3.78	0.37	1.38	174.
108	Sn	4.6	613	5	4.19	1.45	7.75	21.7
				34	4.16	1.28	7.40	26.0
				163	4.10	0.75	5.65	50.7
				300	3.85	0.30	7.90	195.
109	In	4.1	est. 1750	6	3.69	1.35	17.00	61.4
				25	3.69	1.00	16.00	83.0
				177	3.65	0.44	15.00	208.
				300	3.16	0.19	3.85	1059.
110	In	4.1	1072	6	3.83	2.68	28.	201.
				38	3.85	2.35	25.	211.
				77	3.18	1.75	23.	1123.
				300	3.37	0.28	8.60	6120.

IV

CONCLUSION

The good agreement of the angular dependence data with the theoretical predictions for tin and lead suggest that the nominal particle size and defect concentration do not greatly affect the angular dependence of the measured critical fields, since the theoretical and experimental points are in accord for several annealing temperatures for films with very different defect concentrations. The work with indium demonstrates that the orientation of the crystallites is important, however.

The experiments presented also show that the measured H_c values, used with Tinkham's theory, lead to very reasonable values for the electronic mean free path. The large increase in H_c right after the quenching follows from the high density of defects with consequent increase in the penetration depth and a correspondingly small mean free path. The decrease in H_c during the annealing of defects is coupled with a decrease in λ and an increase in ξ .

A comparison with electron diffraction results points out that changes in nominal crystallite size

and changes in the electron mean free path as determined from the measurements following each annealing are proportional and possess the same growth trend.

In summary, our experiments show that the theory of the behavior of the critical field of thin metal films as presented by M. Tinkham, based on the concept of flux quantization and vortices, provides a good description for such films, and is to be preferred to the filamentary theories mentioned at the conclusion of Section II B.

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