MULTIPLE-TRANSITION EFFECTS IN

SUPERCONDUCTING FILAMENTARY CRYSTALS

OF TIN

Thesis by

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In Partial Fulfillment of the requirements

For the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

1965

From 1 July 1960 until 30 June 1961, this work was supported in part through a grant from the Sloan Foundation.

From 1 July 1961 until 12 June 1964, this work was supported in part through funds granted by the National Science Foundation.

ABSTRACT

This paper reports some interesting effects involving stepped transitions from the superconducting to the normal state, and vice versa in filamentary crystals (whiskers). The problem, as conceived when the experiments were undertaken, was to study the behavior of critical-field curves and the hysteresis effect, in a broader region of temperature and field than previously reported, and to compare results with calculations made according to the Ginzburg-Landau theory. The crystals were produced by extrusion under high pressure from plates of tin, and mounted on glass; the transitions were observed by measuring voltage across the samples, as they passed through the transition induced by varying the temperature in a constant external magnetic field.

Contrary to what had been expected, the resistance was observed to change from zero to normal, and vice versa, in discrete steps. In each particular stage of the transition, the resistance was apparently constant even though the temperature was continuously changing. The new effect was most prominently evinced when the sample axis was inclined slightly to the field. The effect was found only in the first-order transition region.

The conjectured interpretation proceeds along the lines of work of Little and Parks, who first found evidence of quantized Abrikosov vortex lines in the intermediate state of filamentary samples. In further corroboration of this hypothesis, the dependence of the new effect on angular orientation was investigated. The data regarding the upper limit of transition regions are consistent with predictions of Tinkham, calculated on a vortex-line model. The lower limit of transition regions was found

to be irregular and not very sensitive to field orientation. If the proposed interpretation is correct, then we have a more clear-cut verification of quantized vorticity than what has been previously reported—first, because the observed jumps are sharp; secondly, because they are observed (generally) throughout the intermediate state, not merely in the limit where R/R_N is small.

CONTENTS

CHAPTER I: INTRODUCTION

A. Why Study Superconductivity of Whisker Crystals?

"Whiskers" are microscopic filamentary crystals grown by extrusion from plates of various metals under high pressure. They are excellent specimens for experiments in superconductivity. Their superconducting properties are especially interesting for several reasons:

(1) They are usually single crystals. Therefore, their superconducting properties are quite sharply defined. Ordinary polycrystalline specimens, on the other hand, are apt to have the transition spread out or blurred due to the presence of strains, irregular crystal boundaries, dislocations, and inhomogeneities of the composition. Whiskers, being such ideal crystals, generally exhibit a sharp transition, whose fine structure can be pinpointed reproducibly to within a millidegree. Thus, when a specific theoretical prediction can be made concerning the temperature dependence or other properties of the transition curve, it is possible to make a really discriminating test.

(2) Their diameter is of the order of one or two microns; it is therefore comparable to the correlation distance, a length that is of fundamental importance in the modern theoretical understanding of the superconducting state. This means that the interesting small-sample effects begin to show up prominently in samples of such dimensions. However, practically all other investigations of small-sample effects have been made on thin plane films. Whisker specimens, being small along two of their three dimensions, often exhibit a more conspicuous departure from bulk-sample behavior than do the films, under comparable conditions.

(3) Their geometrical symmetry often facilitates the mathematical analysis (as also in the case of the thin films), thus making it possible to calculate exactly the predictions of the appropriate theory. A whisker crystal was formerly believed to be a true circular cylinder, with a spiral dislocation extending along the cylindrical axis; growth of the crystal was supposed to take place progressively around the cylindrical axis, with successive rows of atoms being laid down like steps in a spiral staircase. It is now known, however, that the whiskers are polygonal in cross section, the sides being formed by crystallographic planes.[1] Still, the approximation by a circular cylinder is very convenient; and it gives quantitatively accurate, calculable results. The reason for this is that small-sample effects are essentially those due to having the collective wave function limited by a finite boundary and having the magnetic-field penetration throughout the sample. What matters is the dimension of the boundary, not its detailed shape.

B. Previous Work by Lutes and Its limitations

Despite these advantages, there has not been much work on the superconducting properties of whisker crystals. In fact, the only such studies that are known to the writer were done by Olin S. Lutes, circa 1955.[2] He examined the critical-field curves for whisker specimens of tin, in a parallel field only, and at temperatures down to about 2^{o}K. He concluded that the observed data were definitely inconsistent with

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1. Filamentary crystals grown by sublimation from the metallic vapor onto a cooled substrate do have the spiral-dislocation configuration. (These are also called whiskers by some authors.)

2. Olin S. Lutes: Physical Review, vol. 105, p. 1451 (1957).

the simple London equation; but other than that, the results were not very conclusive. He considered that some of his results were in satisfactory agreement with predicted behavior, according to the Ginzburg-Landau theory,[3] which is a generalization of the London equation taking into account the magnetic-field dependence of the characteristic penetration distance. In particular, he verified that the transitions become second-order in a temperature range close to T_c, and (for most of his samples) that the function $H_c(T)$ descends to zero with a vertical slope at $T = T_c$, as required by G-L. He did not attempt to interpret his data in the region of first-order transitions, probably because the G-L theory was at that time assumed to be inapplicable to such cases.

The probable reason for the reluctance of experimenters to make greater use of whisker crystals for studies in small-sample superconductivity is the difficulty, and especially the time required for the growth and mounting of good usable specimens. Although the specimens grow rapidly during the first few days, the maximum length that is obtainable from the initial growth is a half millimeter or so. To grow longer specimens, as we shall explain in Chapter 3, requires a couple of years or so.

In the present case, I have "inherited" some tin whisker specimens already grown. Some of them had been growing for as long as five years, thereby reaching lengths of two to three millimeters. These had been originally produced by Marvin Chester, who was formerly associated

3. The Ginzburg-Landau theory, as subsequently reinterpreted by Abrikosov and Gor'kov (called GLAG in the literature), which is fundamental to nearly everything treated in this paper, will be discussed in more detail in the following chapter and in Appendix 1.

with this laboratory, and who spent a considerable amount of time and effort before inducing them to grow well. Having finally obtained a copious supply of whisker specimens, Dr. Chester subsequently became interested in another project, not related to superconductivity, and so the crystal-growing clamps, with the specimens still growing, were laid aside. About that time, I became interested in the study of the small-sample effects in superconductivity, and I was informed that I might have all of these specimens and do whatever I pleased with them.

CHAPTER II: THEORETICAL TOPICS

A. Summary of the Modern Theory of Superconductivity

1. BCS Theory. The modern period in the understanding of the phenomenon of superconductivity dates from 1957, with the advent of the microscopic theory of Bardeen, Cooper, and Schrieffer. For reference, in what is to follow, here is a summary of the main ideas of the BCS theory:

(i) The fundamental fact of the superconducting state is an energy gap: that is, there is a minimum energy necessary for the raising of any electron out of the coherent ground state of the system.

(ii) As demonstrated by Cooper in 1956, the electrons in the neighborhood of the Fermi surface in a metal may form a system of bound pairs, in the presence of a net attractive two-body interaction, no matter how weak. The pairing involves mainly electrons whose Bloch momenta lie at opposite sides of the Fermi surface. The two electrons in such a pair have necessarily a large momentum relative to each other, and they are accordingly excused from the usual restriction imposed by the uncertainty principle; the pairing takes place even though the attractive potential is so weak that no bound state could exist if the particles were free. The "energy gap" is, in fact, the binding energy of a Cooper pair.

(iii) The condensation into a superconducting wave function is due to an attractive interaction (the Fröhlich interaction), which produces an effective two-body potential mediated by the exchange of phonons (i.e. lattice-vibrational quanta) between the two particles concerned.

(iv) The superconducting wave function is a sort of Bose condensation among these pairs; the effective unit of charge per particle is 2e.

(v) The wave function is characterized by long-range phase coherence, for there can be no incoherent scattering, involving either single electrons or bound pairs, without incurring a cost in energy comparable to the size of the energy gap, $\approx kT_c$.

(vi) The theory gives a natural interpretation to the Pippard correlation distance ξ. About 10 years ago Pippard concluded, on the basis of experimental evidence, that the London equation $\Lambda cJ = -A$ should be modified when distances of 10^{-4} cm or less are involved, and should be replaced by an expression of the form

$$-\mathbf{J} = \frac{3}{4\pi\Lambda c\xi} \int \frac{\mathbf{R}\mathbf{R}\cdot\mathbf{A}(\mathbf{r}_0)\, e^{-R/\xi}}{R^4}\, d^3\mathbf{r}_0 , \quad \mathbf{R} = \mathbf{r} - \mathbf{r}_0$$

This merely states that the current J evaluated at some point r is proportional to a weighted average of $-$ A in the neighborhood of the point r, extending for a distance of the order of ξ. The weighting function $e^{-R/\xi}$ was suggested by analogy with Chambers's equation for the anomalous skin effect. Upon combining this expression for J with the usual one that determines A in terms of a current source, one obtains a homogeneous integral equation which expresses the degree of field penetration (i.e., the Meissner effect), as follows:

$$\nabla^2\mathbf{A} = \frac{3}{c\Lambda\xi} \int \frac{\mathbf{R}\mathbf{R}\cdot\mathbf{A}(\mathbf{r}_0)\, e^{-R/\xi}}{R^4}\, d^3\mathbf{r}_0$$

It turns out that the BCS theory has effectively corroborated Pippard's conjecture, by developing from first principles an integral equation of exactly this form; only the kernel function $e^{-R/\xi}$ is replaced by a different function of R/ξ having, in fact, the same exponential behavior.

(vii) The density of energy levels in the superconducting state is roughly given by: $N(E)\,dE = \frac{|E|\,N_f\,dE}{\sqrt{E^2 - \Delta^2}}$, where the energy E is measured up or down from the Fermi surface, N_f is the normal density of states at the Fermi surface, and Δ represents the energy gap. This density function has been strikingly well verified by tunnelling experiments, where the current passed through a non-superconducting barrier serves to measure the product of densities of electron energy states on both sides.

(viii) The electronic specific heat in the superconducting state tends to zero like $e^{-\Delta/kT}$, in agreement with experiment and in disagreement with calculations based on any system of Fermions without an energy gap. A model of this latter type always yields a linear specific heat.

2. Ginzburg-Landau. Although the BCS theory is now recognized as the correct explanation of superconductivity from a fundamental point of view, for purposes of calculations involving the penetration of a magnetic field into a thin superconductor, most investigators prefer to use the Ginzburg-Landau equations[1] (which are differential equations involving only two field variables, and can be more conveniently used for numerical calculations in realistic problems), and we shall do so also in the present paper. Before proceeding further, it is desirable to make a few comments as to why the G-L phenomenological description is in fact correct. The G-L theory postulates that the behavior and field penetration are determined by these two coupled equations:

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1. As an example, consider the following verbatim quotation, from a recent paper: "This article in its most abstract form, might simply summarize the solutions of the Ginzburg-Landau equations..." [B. B. Goodman: Rev. Modern Physics, vol. 36, p. 12 (1964)] Quite a few other recent papers consist of nothing but calculations of solutions to the G-L equations with some particular boundary conditions.

$$\frac{\hbar^2 c^2}{(2e)^2}\nabla^2\psi - \frac{A^2}{\lambda^2}\psi + 2H_c^2(\psi - \psi^3) = 0 \; ; \quad \nabla^2 \mathbb{A} - \frac{\psi^2}{\lambda^2}\mathbb{A} = 0$$

The scalar function Ψ is a parameter of the theory, originally assumed to represent a collective wave function for the single energy state into which all the superconducting electrons are condensed. Shortly after the BCS theory became widely known, Landau's colleague L. P. Gor'kov was able to demonstrate[2] that the G-L equations may be derived from the more fundamental BCS theory, thereby explaining in part the reason why they work so well. What he did was to calculate the thermodynamic Green's function—i.e., the solution of the equation

$$\left[\frac{\partial}{\partial\beta} - \mathcal{H}_{BCS}\right] G(r,r';\,\beta-\beta') = \delta(r - r')\,\delta(\beta - \beta')$$

where β, as usual, stands for the reciprocal temperature. In an elegant mathematical treatment, Gor'kov finds two coupled non-linear differential equations, in which the desired Green's function is paired with a second function F^+, defined on the same space, and which comes naturally out of the analysis. He then finds that the cut-off in the BCS integral equation (as is necessary, in order to obtain finite results with the Fröhlich interaction) requires that the auxilliary function $F^+(r,r')$ be non-vanishing over a distance corresponding to $r - r' \approx \xi_0$, the correlation distance. So, he defines Δ, which is eventually to be identified with the energy gap, to be the on-diagonal value of F^+, and investigates the behavior of Δ in the limit of $\beta \approx \beta_c$. In this limit, certain terms of the equations become small, and the remaining equation for Δ is just the Ginzburg-Landau equation for Ψ/λ. In this way, the G-L theory is

2. L. P. Gor'kov: "Soviet Physics—JETP," vol. 9, p. 1364 (1959); also ibid., vol. 7, p. 505 (1957).

shown to follow mathematically from the presumably correct BCS theory. The G-L theory, therefore, is in a sense more advanced than BCS, despite the fact that G-L was proposed (phenomenologically) several years sooner. Ginzburg and Landau were calculating the energy gap, but did not know it.

Gor'kov's proof shows that the G-L theory is rigorously true (provided the BCS theory is), in the limit of $T \approx T_c$; more recently, it has been found that the range of validity of G-L may be extended to substantially the entire H-T plane, albeit with somewhat less mathematical precision. As is indicated in more detail in equation (3), Appendix 1, the G-L theory is based on a certain assumed functional form of the free energy, as determined by the configuration of the two field variables, A and ψ. Two of the four terms appearing in the functional are already implied by the London equation. The other two are more interesting: the condensation energy, and the "surface energy." These we shall now discuss briefly.

The condensation energy term, which is negative when the system is in the superconducting state, is an essentially phenomenological way of representing the fact that the superconducting state, with an energy gap, is thermodynamically preferred to the normal state. As explained in greater detail in Appendix 1, the assumed functional dependence of this condensation energy on ψ, i.e., on a parameter proportional to the energy gap, is obtained from a power-series expansion, rigorously valid only in the limit of small ψ. But now, experimental evidence reported by Tinkham,[3] and extensive numerical calculations[4] made directly from

3. M. Tinkham: IBM Journal of Research and Development, Jan. 1962 p.49

4. John Bardeen: Rev. Modern Physics, Vol. 34, p. 667 (1962)

the BCS integral equation, determining the energy gap, have shown that the behavior of the condensation energy as a function of Δ is rather well represented by the G-L assumption; $F_s = (\Delta/\Delta_o)^2 \, [2 - (\Delta/\Delta_o)^2] \, H_c^2$; this holds even in the high-field region, where T is nowhere near T_c.

The way in which the surface-energy term relates to the empirically verified Pippard-type integral equation, and thus—on the basis of our subsequent knowledge—to the BCS theory, had been discussed by Pippard himself, shortly after the appearance of the G-L theory. The surface-energy term may be written in the form $(\varphi^2/\lambda^2)(\nabla\psi)^2$ where φ is the notation adopted in this paper for the celebrated London Quantum of flux: $\varphi = \hbar c/2e = 3.29 \times 10^{-8}$ Maxwell.[5] This term being essentially positive, it always tends to offset the gain in free energy due to the condensation-energy term; accordingly, the superconducting state will be preferred until the ratio of the magnitudes of these two terms is about unity. If the functional is written in terms of appropriate reduced variables, the implication of the gradient term is that the parameters of the system cannot change much over a characteristic distance $\sqrt{\frac{N_s \hbar}{m \, H_c}}$ —which distance is about the same as the Pippard correlation distance ξ_o. So, there exists implicitly in the surface-energy term a sort of representation of Pippard's empirical postulate, requiring that London's relation between current and A be smoothed out, due to an averaging over a distance ξ_o. Pippard, of course, in calling attention to this interesting connection between his work and the G-L theory, re-

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5. NB: The value of the flux quantum, as defined and used herein, is different by a factor of 2π from the usage of many other writers, based on London's original, but less convenient, definition of hc/e.

garded the latter as providing confirmation of his postulated equation; now, since the Pippard-type integral equation has received a very firm theoretical foundation through the BCS theory, we may turn the argument around and consider Pippard's equation as providing a theoretical basis for one of the terms in the G-L theory. As Gor'kov's proof shows, the connection between the two theories becomes rigorous and exact in the limit of $T \approx T_c$.

In summary: It now appears that the G-L theory is a very useful, semiquantitatively accurate description of the behavior of real superconductors throughout the H-T plane: its range of validity extends far beyond what was assumed at the time when it was originally proposed. Herein lies the reason behind many recent applied-mathematical papers on superconductivity, based exclusively on the G-L model rather than on the BCS theory—which is known to be physically fundamental, but is in general less tractable for calculations.

B. What We Expected to Observe

The central problem, as it was conceived when these experiments were getting under way, was neat and unambiguous: namely, to check out the behavior of whisker specimens, as described by the G-L model, in a much broader region than that which Lutes studied. This would have entailed observation of upper and lower critical-field curves in temperature ranges down to about $1^{\circ}K$, with particular attention to the low=temperature, high-field region. We also wanted to obtain data for various angular orientations of the field; this latter variation is a sensitive test of the applicability of the G-L theory; for in effect, it allows one to vary the coefficient of the term involving $\int [H_o - H]^2 \, dV$ in the G-L model, while holding everything else constant.

The predictions of the theory will be briefly summarized here, although there is no point in describing in fine detail something that we didn't observe. In what follows, we use this notation:

$\lambda = \lambda(T)$ = London penetration distance (for a vanishingly small field)

α = angular orientation of field with sample axis

H_o = external field

H_c = bulk-sample critical field

a = radius of the sample

The proofs of the following statements are outlined in Appendix I. According to the Ginzburg-Landau theory with constant-ϕ assumption:

1. When $\lambda > a/\sqrt{3}$ the transition is second-order, there is no hysteresis, and the critical field (upper or lower) is given by $H_o/H_c = 4\lambda/a$ if the field is parallel to the sample axis. Since this formula is of interest in the region of T near to T_c, we may conveniently represent $\lambda(T)$ by the empirical Gorter-Casimir expression, which is known to be very accurate in that region,

$$\lambda(T) = \frac{\lambda(0)}{\sqrt{1 - (T/T_c)^4}} \quad \text{and } H_c(T) = H_{c0}(1 - T^2/T_c^2), \text{ giving}$$

$$H_{o\,crit.} = \frac{4\lambda_o}{a} H_{co} \sqrt{\frac{1 - (T/T_c)^2}{1 + (T/T_c)^2}}$$

and showing that the critical-field curve has a vertical slope at $T = T_c$. Lutes verified this behavior rather well for all but one of his samples; the anomalous one seemed to prefer a linear descent of $H_{crit.}$ for temperatures near T_c.

2. When $\lambda < a/\sqrt{3}$ there is hysteresis, and the transition is

first-order. Lutes also observed this fact, but gave no quantitative interpretation of his data on the hysteretic behavior. As a matter of fact, both the upper and the lower $H_{crit.}$ for a cylindrical sample can be calculated exactly (again see Appendix I), within the limitation of the G-L model and the constant-ϕ assumption; so the extent of the hysteresis provides a sensitive test of the theory. Lutes did not carry out the calculations, probably because the G-L theory was not then believed to be applicable to the low-temperature, high-field behavior.

3. When the field is oblique, the behavior in both first- and second-order transitions is the same as in the parallel-field case—only, the applied field H_o behaves like an effective field given by: $H_{o\alpha} = H_o \sqrt{1 + \sin^2 \alpha}$. The increase in effectiveness of the field is due to the extra energy required to partially expel the flux passing around the boundary of the sample.

Prediction 1 was pretty well verified by Lutes's experiments—although the anomalous sample suggests that there is still something not quite understood about the behavior in the second-order region. Prediction 2 is interesting in that it bears directly on the extension of the G-L theory to the low-temperature behavior, as is now believed to be correct. Prediction 3 is perhaps the most interesting of all; it does not seem to have been commented on prior to the present paper. It would be a striking success of the G-L theory if, e.g., one could compare the temperature-dependent behavior of the sample, in a constant parallel field H_o, with the corresponding effects in a perpendicular field $H_o/\sqrt{2}$, and were to find the transitions (upper, lower, and second-order) occurring at like temperatures in these two cases, even for arbitrary values of H_o.

Another way in which the theory could be brought to bear on the low-temperature behavior is in the matter of the dependence of λ on temperature. The empirical formula of Gorter and Casimir, mentioned above, is now usually replaced, in the lower temperature region, by a more complicated but calculable function, which is based directly on the BCS theory. Since λ, in the dimensionless form a/λ, enters as a parameter into all of the critical-field calculations, the self-consistency of the observed data would provide an opportunity to check this rather definite prediction of the BCS theory.

CHAPTER III: PRODUCTION AND HANDLING OF WHISKER CRYSTALS

The appearance of whisker crystals spontaneously on certain metals kept in a dry place over a period of years has been known for about 100 years. The acceleration of the growth process by compressive stress was demonstrated by Fisher et al.[1] The method of production is to take thin sheets of steel, plated with the metal (tin, in the present experiments, as also in theirs), to be used, and clamp them tightly between stainless= steel blocks. The side of the sandwich arrangement must be ground flat and highly polished, so that the edge of the plating is accurately coextensive with the squeezing blocks; this is important because it is the gradient of the pressure which induces such large-scale mass transport, as is necessary for crystal extrusion. Apparently the process involves a repetitive back-and-forth movement of an edge dislocation at the base of the emanating whisker, depositing a new layer of atoms over the whole cross section of the whisker with each cycle.[2] If this is so, then such a cycle must be completed in a surprisingly short time, during the early phase of rapid growth. For, some of the samples attain a length of 0.5 mm., in one day after tightening of the clamp. Assuming an interatomic distance of, say, 2 Å, this means that the migrating-dislocation mechanism must be capable of laying down a crystal lattice at the rate of some 50 atom layers per second. After the initial rapid growth period, which lasts two or three days, the growth continues at a much slower rate, and terminates after several months or a year. In order to get good, useful

1. R. M. Fisher, L. S. Darken, and K. G. Carroll: Acta Metallurgica, vol. 2, p. 368 (1954).

2. George Sines: Journal of the Physical Society of Japan, Vol. 15, p. 1199 (1960)

data on superconducting transitions of the specimens, they must be long enough to have an appreciable normal resistance at $4^{o}K$. Therefore, it is necessary to wait for long specimens to grow. The minimum useful length for observation of a transition is about one millimeter; samples of two to three millimeters length are even more desirable, although if the length exceeds two millimeters, the specimen is difficult to mount.

The first, and probably the most difficult, part of the experimental project was to learn how to handle and mount the whisker specimens. The writer required about a year of practice in order to become proficient at this art. The details of unsuccessful trials need not be recorded; but for the edification and guidance of others, who may be desirous of undertaking or continuing such experiments, here are some comments on what has been found to be the best technique.

Before starting operations, one needs to have a heater prepared. This consists of a platinum or tungsten wire, a few millimeters long, mounted on two heavy copper leads buried in porcelain. The one I have been using is .005" in diameter, but that is not critical provided that careful control is maintained over the current. What is critical is the temperature reached by the heater. To supply current for it, it is convenient to use a filament transformer with the primary circuit plugged into a Variac, so as to provide a variable output of some two volts or so, and up to five amperes. The heater and its holder are to be clamped in a micromanipulator, and positioned so that the wire loop is visible in the field of view of the microscope. Sticking the specimen onto the loop is accomplished using diphenyl carbazide (DPC), an organic crystalline material with a low melting temperature and which becomes extremely sticky when it is melted. It is necessary to adjust the heater current carefully, so the stuff is just melted and no more; if it gets hot enough to vaporize, it will not stay on the heater. It is also important not to use too much of the DPC, as I have found out to my sorrow, by losing more than one beautiful specimen. If there is enough of it to form a visible drop, the whisker will get swallowed up as soon as it touches the surface of melted DPC.

All operations, from the time when the desiccating jar (in which the crystal-growing clamps are stored) is opened, until the whisker is safely stuck down onto the glass slide, are conducted while breathing through a plastic tube. The end of it is under the table, well away from the scene of operations; this precaution is necessary, to prevent loss of the specimen by blowing it away. The crystal-growing clamp is supported under the microscope by a large portable vise, which helps to prevent jarring and also makes it easy to get at the growing area from a convenient oblique angle. Using a magnification of 25X and a strong side illumination, one may observe the whiskers waving in the air near the growing slot. After deciding which specimen is going to be taken, the delicate operation of transferring it onto the glass is begun. Bringing the heater wire little by little nearer to the free end of the whisker, one finds that there is a noticeable attraction. This force, presumably of electrostatic origin, is rather useful for getting the whisker into contact with the heater wire; with a bit of practice, one can make contact at the very end of the specimen. A current pulse of about one second duration is sufficient to melt the DPC and get the specimen well stuck. Pulling the specimen away from the grower is a difficult and sometimes disappointing operation. It is best done by using the fine control on the micro-manipulator, and pulling the whisker in the same direction as that in which it is growing. Usually, the whisker breaks off at its base, and that does it. Fortunately, if it breaks elsewhere, it is most likely to break at the point where it enters the DPC, in which case nothing is lost except a bit off the end of the whisker. So, one has to start over again with the same or another specimen.

After getting the specimen attached by one end to the heater, the next step is to mount it on the glass slide. This is a piece cut out of an ordinary microscope slide. In preparation of the glass slide for the mounting, the first thing to do is to abrade the upper surface by grinding it with 600-mesh carborundum grit. This roughening of the surface of the glass is for the purpose of making the silver paint stick better. Then the two electrical contacts are formed on the surface, by painting parallel strips of colloidal gold about a millimeter apart. The glass is then baked at about 1150 $^{\circ}F$ for a half hour, in which time the gold becomes permanently diffused into the surface of the glass, which can now be scrubbed clean with acetone without affecting the gold contacts. The glass is placed under the end of the heater, which is then lowered gradually while keeping the microscope view focused on the surface of the glass. When the free end of the specimen drags on the surface, it may be moved if necessary to the exact position where it will be tied down to the gold strip. In choosing the position, it is necessary, of course, to consider the direction in which the specimen will eventually lie, extending from one of the strips to the other. When the free end is in the desired position, it is stuck down with a small drop of silver paint, applied with the end of a needle. After waiting ten minutes or so, so that the silver paint is hard, the heater is turned on. Moving the heater very slowly in a horizontal direction away from the end that is stuck down, one finds that the whisker will slide right off the heater wire, and will lay itself out in a straight line on the glass. All that remains to be done is to stick the other end of the specimen onto its gold-film contact, using another blob of silver paint; the job is then complete. The silver paint must be allowed to harden and cure thoroughly (even though it already appears perfectly dry) by placing it under artificial heat for about 48 hours. It is then ready for use.

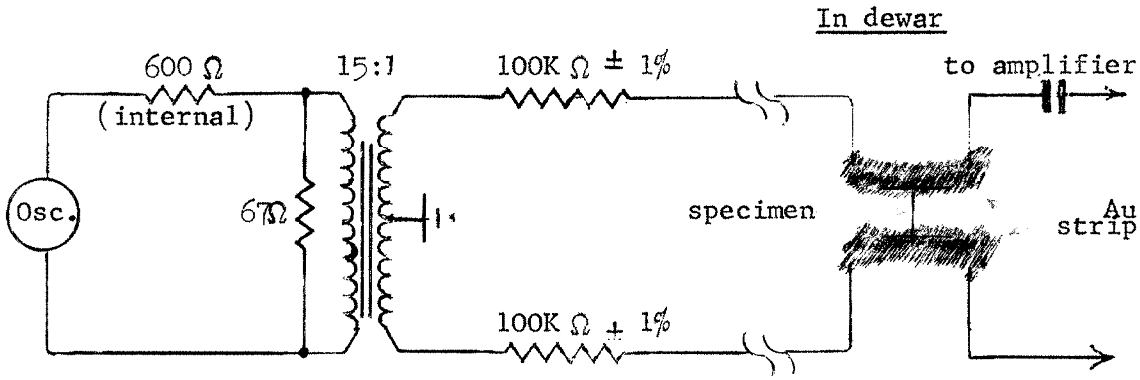
Many of the earlier experiments were plagued by failure, in which the silver paint came unstuck from the glass, upon cooling down to liquid-helium temperature. This was presumably a result of the shearing strain induced by differential thermal contraction between the silver paint and the glass. In order to cope with the problem, two measures were developed: First, as already mentioned, making the surface of the glass rough facilitated tight adhesion of the silver paint; second, the use of very small blobs of paint reduced the total differential thermal contraction, which is, of course, proportional to the diameter of the drop. With practice, one learns how to apply a drop which is about as big as the curved point of the needle, with which it is applied.

Electrical contact to the gold strips is made by attaching four copper leads (#38 wire), by indium solder, one contact at each end of each gold strip. Two of the wires serve to provide the measuring current, and the other two pick up the signal voltage. Since indium itself is a superconductor, care must be taken to make the indium connections small, and to keep them well away from the sample. This is in order to avoid distortion of the uniform magnetic field as seen by the specimen.

CHAPTER IV: EXPERIMENTAL DETAILS

A. Detection of the Transitions

The superconducting transitions in the present work were observed as resistive transitions, by measurement of the voltage across a specimen carrying a fixed current. The arrangement is shown schematically here:



The measurements were made mostly at a frequency of about 9 Kc; this frequency was chosen merely because amplification and detection of the signal is easy at such moderately low frequency, and so it has no fundamental significance. The signal was generated by a Hewlett Packard oscillator at about 6 volts, then attenuated by a shunt resistance and a step-down transformer, to a value of about 40 mV; with a load resistance of 200K Ω, the measuring current was therefore limited to about 2 microamp. The arrangement of the transformer with 67 Ω across the primary has the effect of a very low apparent impedance, as seen from the specimen's side; and so the pickup of 60-cycle voltage through the sample is effectively short circuited. The two sides of the transformer secondary circuit were carefully matched, and the resistors balanced, so as to reduce through mutual cancellation the effect of radiatively or inductively coupled signals getting into the detector circuit. As mentioned previously, separate contacts were used to pick up the voltage signal across the sample. The blócking capacitor serves to eliminate the DC surrent component, which invariably arises due to thermoelectric effects, and which otherwise might have been strong enough to damage the specimen. The signal from the specimen was introduced, via an impedance-matching transformer, into a cascode amplifier.[1] The output from the amplifier was detected using a General Radio wave analyzer tuned to the oscillator frequency. The amplitude of the detected signal was typically in the range of 100 to 300 millivolts. As it turned out, a substantial part of the detected signal was found to be due to a spurious background resistance, presumably contact resistance at the many junctions between tiny silver grains (in the paint blobs) and the surface of the sample. In Lutes's paper[2] the same difficulty is mentioned, with the same explanation; there appears to be no satisfactory solution to this problem.[3] However, the contact resistance is not always fatal to the observation of a transition. Under favorable conditions, the total change in resistance upon going from normal to superconducting is of the order of 20% to 30%; the spurious signal, although larger than the genuine signal, is stable throughout the experiment and is independent of temperature in the range of interest. In the earlier

1. For further details on the electronics and a diagram of the cascode amplifier, see Appendix 2.

2. Lutes, op. cit.

3. An attempt was made to bypass the contact resistance, by laying two other whiskers on top of the sample, to serve as pickoff contacts. The correct positioning of the auxilliary whiskers, however, is very difficult without damaging the sample already laid down.

experiments, the wave-analyzer output, which is proportional to the resistance being measured, was fed into a Varian strip recorder, and thus the transitions could be observed graphically with time as the abscissa. Later on, when it became desirable to compare the detailed structure of transitions in different field orientations, the output was recorded by using a two channel "X-Y" chart recorder, making the ordinate vary with the resistance signal, the abscissa with the temperature. All of these experiments were done by allowing the temperature to vary slowly (up or down), the magnetic field being held constant, rather than vice versa[4]; this procedure was necessitated by the face that the large magnet has no means for varying the field in a narrowly controllable way. As it turned out, this particular experimental exigency was a lucky circumstance: the effects to be described in the next chapter and which are the central subject of this paper would have been difficult or impossible to observe, if the transitions had been produced by varying field.

B. Magnetic-Field Measurements

In the earlier experiments, the source of the magnetic field was a large water-cooled electromagnet, powered by a 20-kW motor-generator combination with a rheostat-regulated exciting field. This made it possible to set the current through the magnet at a certain value and hold it constant for extended periods of time. The dewar apparatus was set up on a movable carriage running along a track, so that it could be put into or slid out of the magnetic field while in the course of an exper-

4. The Lutes experiments, like many other investigations of the small= sample effects in a magnetic field, were done by varying the field at a constant temperature.

iment, and in all cases the position of the sample was reproducible to within a millimeter. Two operating procedures were used in the recording of the magnetic field.

(1) In some of the experiments, the position of the sample in the field between the pole faces was marked, by sighting on it with a telescope. The dewar system has a window, as is common in low-temperature research, through which it is possible to observe apparatus mounted inside. Of course, the visual resolution, when sighting through four layers of curved glass, is not good enough to enable one to see the whisker in the telescope, but there was no problem in aligning the cross hairs on the two silver-paint blobs which marked the place where it was stuck down. And then, moving the dewar out of the way, one can simply put the probe coil of the gaussmeter in the same spatial position by sighting on it through the telescope, which of course has not been moved. Thus: the line of sight of the telescope, intersecting the common horizontal plane in which the whisker and the probe coil are constrained to lie, uniquely determines that the probe shall measure the field at the same point in space where the sample had been previously.[5]

(2) In some of the experiments a simpler and faster method was employed. Since the current through the magnet was at all times monitored by an ammeter, the field could be recorded in terms of current, instead of gauss. Then, after the experiment was finished, it was possible to calibrate the field, as a function of current, by placing the probe in the position of the sample as described above. In this way, the current

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5. The dewar track and all apparatus ancillary to the experiment were constructed out of non-magnetic materials; so, the field configuration was not sensibly altered by moving the dewar system within the field.

data were all converted to gauss in one operation. This alternative procedure has another advantage, in that it eliminates any possible uncertainty in the sample position due to the index of refraction of the liquid nitrogen and helium baths; the calibration was actually done after all the nitrogen and helium were evaporated, and the system warmed up.

The actual measurement of the magnetic field was made using a commercial gaussmeter built by Alpha Scientific Laboratories, Inc. This device utilizes a mechanical[6] pickup coil to sense the H field intensity. The coil, located in the tip of the probe, is rotated at a high speed, producing a voltage proportional to the field; the signal is then amplified and detected by solid-state electronic apparatus incorporated into the device. The accuracy is within 0.3%, according to the manufacturer.

It is clear that, with either of these two procedures, the crucial assumption is that the field remains constant for a period of time, once the generator rheostat has been set. There are two ways of checking this point. In the first place, using procedure (1), the field was measured both at the beginning and at the end of each transition; the time lapse involved was some twenty or thirty minutes. Moreover, when calibrating the field alone, as in procedure (2), it is possible to leave the probe stationary in the field and watch for any random or systematic variation in the indicated H. Evidently this is also a way of checking for variations in the sensitivity of the gaussmeter. It was found in this way

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6. Originally, we considered using a proton-NMR type gaussmeter. These are also available commercially, and extremely high accuracy, which is obtainable with such a device, certainly made it very appealing for our purposes. Unfortunately, consultation with the manufacturer of these devices has convinced us that they do not function reliably in such a low= field range (zero to 300 gauss) as is characteristic of the present experiments.

that the magnet required a few minutes to stabilize, following any change in current; but thereafter, the field was indeed constant to within the smallest conveniently readable division on the meter.[7] It is therefore believed that the magnetic-field data are accurate and constant to $\approx 1\%$.

The large magnet described earlier had been handed down to us from some other laboratory, and appears to have been previously used in β-ray spectroscopy experiments. For that purpose, the pole-pieces were provided with longitudinal slots which, as I found out during the course of the investigation, caused the field to be rather annoyingly inhomogeneous. This was no crushing disadvantage, as long as I was studying only the behavior of the sample at a particular orientation with respect to the field; for, as described above, the magnetic-field measurements were always made at the position of the sample. But then, when the strange, unexpected effects turned up, it became desirable to investigate carefully the variation of these effects with different field orientations. The rotation of the sample was effected by simply rotating the dewar cap —but it then became impossible to keep the sample confined to a certain point in space. So, it was imperative to continue the experiments using a magnet capable of providing a more homogeneous field. The magnet used for the last series of experiments was an old hand-wound relic, of which the early history is unknown to us. The power was provided by a storage battery. The results were quite successful: homogeneous fields up to 300 gauss were obtainable. The field was also more stable and more easily controllable than that obtained with the larger magnet had been.

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7. In accordance with the manufacturer's instructions, for best accuracy, the gaussmeter was allowed to warm up and stabilize for ten minutes before taking any readings.

C. Temperature Measurements

The usual specification of the temperature scale in the liquid-He range is, of course, by means of the vapor pressure of the helium bath, when it is in equilibrium with gaseous helium. However, in the present experiments, the direct measurement of the temperature as indicated by the vapor pressure was impractical, for three reasons: (1) It is difficult to read the manometer height, when it is continuously changing. (2) The pressure-head correction must be applied to all readings, since the sample is submerged in liquid helium to a depth of several inches. To do this for each data point greatly increases the amount of tedious labor involved in the run. (3) Most importantly, when readings are being taken in ascending temperature, the helium bath is not in an equilibrium state, for the warming takes place chiefly at the upper surface of the liquid. This is because the principal heat leaks are due to radiation off the dewar cap (at room temperature), and to heat conduction down the sides of the dewar. The time lag required for heat to diffuse down from the liquid-helium surface is often as long as thirty minutes. Indeed, it is commonplace to see the gaseous helium bubbling off at one atmosphere,[8] while deep in the interior of the bath, the temperature is still well below 3°K.

It was decided early in this project that the best method of temperature measurement, for our purposes, was a resistance-sensing method. The familiar ceramic-enclosed graphite resistors, used in the building of electronic devices, are convenient for this purpose, because graphite, a semiconductor, exhibits a drastic variation in its resistance as

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8. A vapor pressure of 1 Atm in equilibrium corresponds to about 4.2°K.

a function of temperature when the latter is in the liquid-helium range. Provided that the resistance-vs.-T characteristic remains stable, it is necessary to obtain the calibration only once, for all the experiments. Moreover, the sensing resistor is placed as near as possible to the location of the sample—and by all means, at the same level as the sample—therefore sensing the actual temperature in which we are interested, irrespectively of the temperature elsewhere in the helium bath.

A considerable amount of time and experimentation were devoted to checking out the reliability and the potential accuracy of this method. Experiments reported by Clement[9] have shown that these commercial graphite resistors have reproducible R(T) functions in the liquid-helium region, to within about 0.5% even after being warmed up repetitively from liquid helium to room temperature. After a few such temperature cycles, the resistance stability improves still more. So, as Clement concluded, it is practical to use them as accurate temperature-sensing devices. In the present experiments, two Allen-Bradley 1/4-watt resistors were used, with nominal values of 150 Ω and 220 Ω. The resistances at 3°K were respectively 3K Ω and 5K Ω. The resistors were calibrated before and after the series of experiments, and found to have remained stable within a few parts in 10^3. The data of the second calibration, which is thought to have attained greater precision, were used in all cases to reduce the resistance readings to temperature, for the purpose of plotting the data included herein. The 150 Ω resistor was used in all the runs made using the strip recorder, and the 220 Ω resistor was used in connection with

9. J. R. Clement, and E. H. Quinnel: Rev. Scientific Instruments, vol. 23, p. 213 (1952)

the two-channel recorder. This latter arrangement involved making the $220\ \Omega$ resistor one arm of a DC Wheatstone bridge; the input to the recorder was connected across the bridge in place of a galvanometer. The other resistances in the bridge were chosen so that it balanced with the recorder pen near the middle of the chart. So, with the gain of the recorder set at a rather high value, e.g. 2 mV/inch, a full-scale motion of the recording pen represented a temperature interval of merely a few hundredths of a degree. Thus (and this is important), since the sensing resistor, as used in any particular run, has to range over only a small temperature interval, the response of the recording system becomes substantially linear: with suitable calibration, the pen traces out actual temperature as one coordinate.

The calibration of the temperature-sensing resistor was done with somewhat more precision than what was strictly necessary for the purpose of the experiment. This was in keeping with our original intent, namely, to obtain a high-precision measurement of the upper and lower critical=field curves, $H_{c1}(T)$ and $H_{c2}(T)$. The technique of calibration will be summarized here. The resistor was not calibrated in terms of its exact resistance, but rather, by comparison with a decadic resistance box of the sort commonly found in undergraduate laboratories. Since the same standard resistance box was used in converting back to temperature after each experiment, the temperature measurements were just as accurate as the calibration. The actual resistance measurements were made with a GR impedance bridge. This device operates at a frequency of about one Kc/sec, and uses a high-gain transistor amplifier to improve the precision of the null. To get a still more sensitive null, a variable capacitance was inserted in parallel with one arm of the impedance bridge, opposite to that of the sensing resistor; this served to balance out the inevitable capacitance of the resistor and the wires leading into it. The temperature, as it was being measured in the calibration run, was made to decrease continuously by a clockwork attached to the Foxboro pressure controller; hence, since vapor bubbles were free to form in the liquid helium, the problem of non-thermal-equilibrium conditions, as previously mentioned, did not occur. The manometer pressure data were carefully corrected for the liquid-helium pressure head at the depth of the resistor, and also were corrected to mm. Hg at standard gravity and $0^{o}C$, according to Table VII of the NBS "1958 He Temperature Scale" pamphlet, and the tables therein provided the conversion from pressure to temperature.

In measuring each datum point for the calibration, the following standard technique was used: Using an appropriate compensating capacitance in the GR bridge, I would balance the bridge to the best obtainable null with the sensing resistor in the circuit. Then, moving the dial slightly off balance (actually, this means at the next higher wire in the potentiometer), I would wait, and watch the needle of the detector descending toward the previous null. This it must do, for the measured resistance was slowly increasing. When the null was reached, I would call out "now" and my assistant would simultaneously read the manometer. The manometer data could then be recorded in more leisurely manner. Finally, the null would be duplicated, as nearly as possible, using the decadic resistance box; then the measured resistance would be recorded off the box.

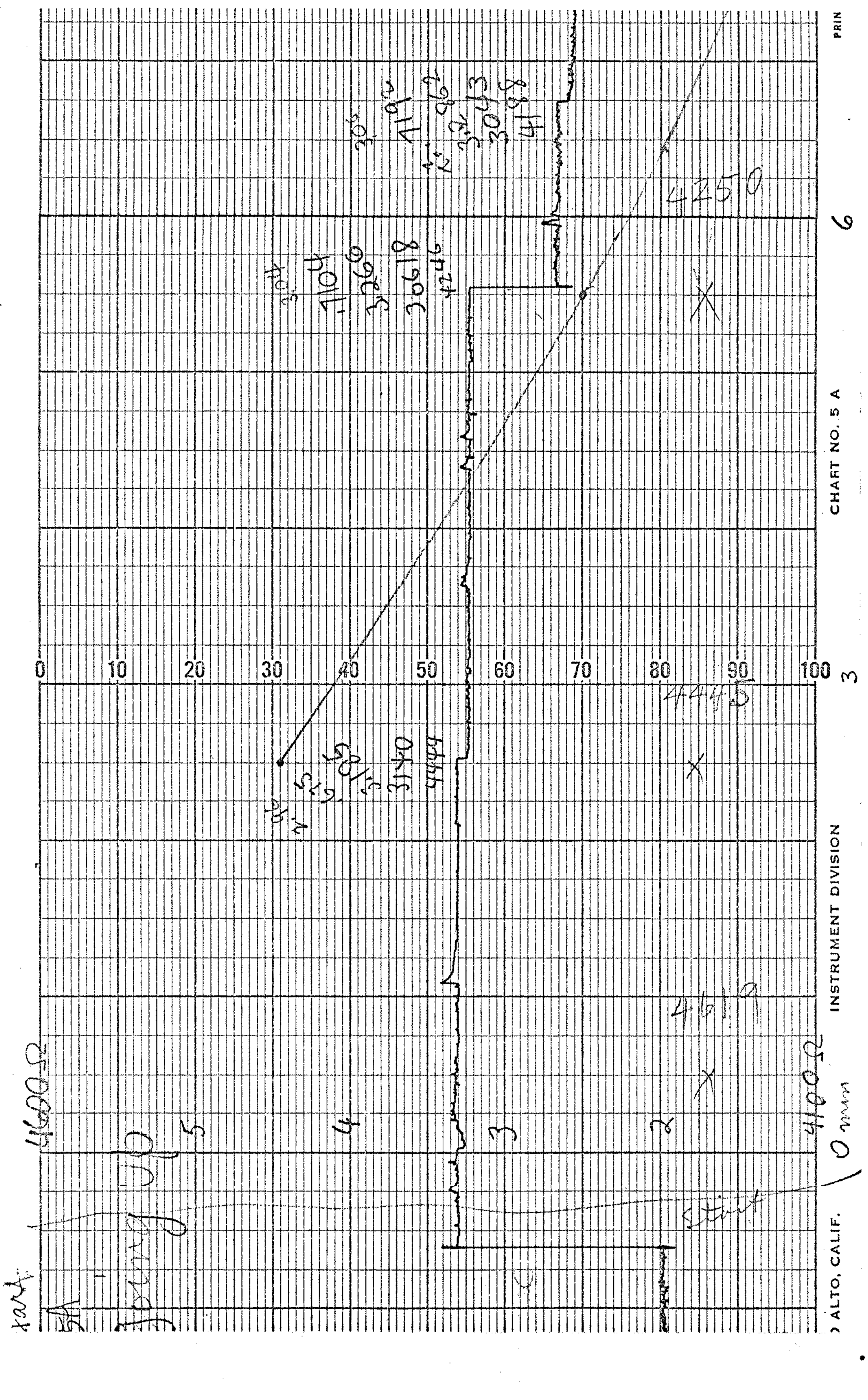
The resistance data were plotted on a logarithmic scale with T^{-1} as the abscissa. Then, provided that a graphite resistor behaves like an ideal semiconductor, the data points all fall along a straight line. By plotting the best-fit line through the data points, any random error (due to the discrete values in the comparison resistance box) was statistically eliminated. Overall, it is believed that these temperature measurements were accurate to within a few parts in 10^4.

D. Typical Procedure During a Run

The most discouraging time in the whole course of an experiment was often the cooling-down period, for it was then that a large number of failures, of the sample or of the silver paint, occurred. For this reason, the cooling was done very slowly, with the inside of the dewar evacuated, the process generally requiring six hours or more. The oscillator and the wave analyzer were meanwhile turned on, allowing both to stabilize in frequency before the experiment was begun.

If all went well, a closed circuit was maintained and the liquid He poured in. The amplifier and auxilliary equipment were made ready, but the final connection to the sample leads was not made until we had assured ourselves that the grounds were in place and the amplifier had become stabilized. This latter precaution was in hopes of forstalling any transient voltage pulse from coming backward out of the amplifier. In fact, we lost several samples, apparently due to such back-talk out of the amplifier, before becoming aware of this particular problem.

With the amplifier duly connected, and the big magnet turned on, the experiment was under way. A sample of the raw data, in the form of


0
10
20
30
40
50
60
70
80
90
100
CHART NO. 5 A
INSTRUMENT DIVISION
ALTO, CALIF.

a Varian strip chart, is appended herewith (Figure 1). Examination of the specimen chart will make the method of plotting temperature clear. Since the chart moves at a constant speed, the whisker's resistance is in effect plotted versus time. In order to make these data meaningful for the purpose of the experiment, it was necessary to convert the abscissa to temperature. This we did, by synchronizing a pencil mark to each measured value of the temperature-sensing resistance: these marks are the pencilled x's appearing regularly along the chart. The correlation of temperature-sensing resistance with time was accomplished by having one person observe the GR resistance bridge, while another, at the instant when the bridge indicated a balance, would mark an "x" at the appropriate place on the strip chart. Afterwards, during the following minute or so, the resistance was read off the bridge, using the comparison method, and recorded adjacent to the most recent mark.[10]

Ascending transitions were observed by shutting off the pumping valve, so that the dewar and the helium bath were permitted to warm up at their own natural rate as determined by the residual heat leak. An artificial heat source was not used, for such a source would have made it impossible to keep the sensing resistor in thermal equilibrium with its surroundings. The time required to pass through an ascending transition ranged from five to thirty minutes, the shorter warmup time being associated with the lowest temperature range, where the specific heat of liquid helium becomes very small. The time scale used in the

10. All this involved procedure for temperature measuring was necessary only for measurements in the range above the λ point, of course; below the λ point, no thermal gradient can exist at all in the helium. In the few instances when we had occasion to work in this region, the ordinary vapor-pressure method (with an oil manometer) was used.

sample strip chart is one inch/minute, so it is clear that the temperature scale is much expanded and shows the transitions in fine detail. For some experiments, even longer time scales were used, by opening the valve into the long 4" pumping pipe, while having the pump itself shut off from the pipe. Then, the rate of warmup was governed by evaporation into a large reservoir, consisting of a sixty-feet-by-four-inch diameter pipeline.

Descending transitions were produced by means of the clock-actuated input to the Foxboro controller, just as described earlier in connection with the calibration of the temperature-sensing resistor. The controller is a feedback device, which senses barometrically the pressure existing inside the dewar system and opens or closes a valve in the pumping pipe, as required to maintain a constant pressure. It was found convenient to drive the controlled pressure down at a rate of about 3 mm Hg/minute; in a large portion of the temperature range of interest, this cooling rate corresponds to about the same dT/dt as does the natural warmup rate.

As may be seen from the sample strip chart, this same chart served as a coordinate paper on which to plot the temperature-resistance versus time; any value of the temperature-sensing resistance at which an interesting event took place was therefore very easy to read directly. Conversion to temperature data was made according to the R-vs.-T^{-1} plot obtained previously and described in section 4C.

CHAPTER V: EXPERIMENTAL RESULTS AND THEIR INTERPRETATION

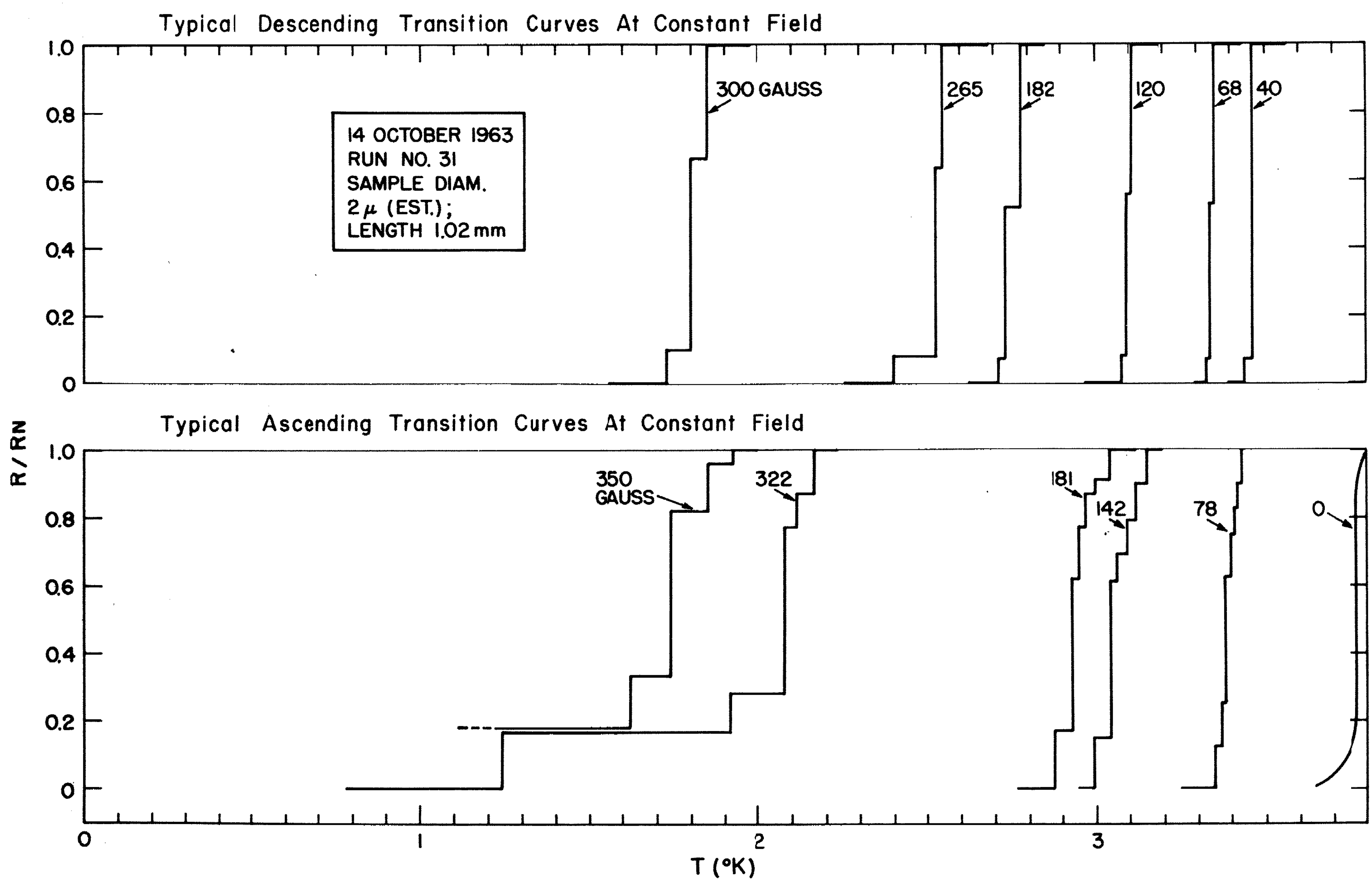
A. Multiple Transitions

When this study of critical-field transitions of Sn whiskers was undertaken, our guideline was an intention to make a more thorough investigation of the hysteresis effect, in the light of the present-day views on the applicability of the G-L theory over a wider range of conditions than had been previously acknowledged. Not long after the multifarious experimental problems had been overcome, and we began to observe transitions, a puzzling new effect was evinced. It is the principal subject of this chapter.

(1) Exhibition of typical ascending and descending transitions. The transition curves of the whiskers showed the upper and lower H_c to be ambiguous; for the change in resistance from zero to normal, or vice versa, was found to take place in several discrete steps. Figure 2, which is plotted from one of the best observations, shows some characteristics of the new effect. Although our intention was to obtain H_{c1} and H_{c2} as functions of temperature, for various angles and specimen diameters, it is clear that these curves are not so meaningful when, instead of one transition, there are several. So, our attention was perforce diverted from the original aim.

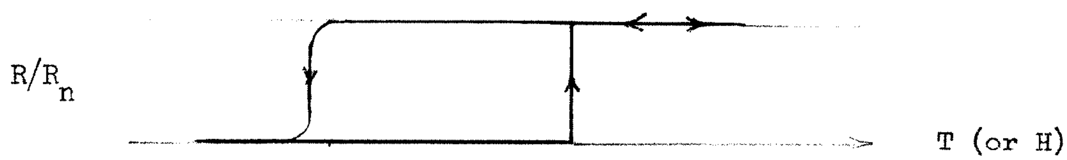
The jumps are best observed by varying the temperature at a constant (external) field, rather than vice versa. This observation suggests that a jump represents a rearrangement of the two field variables (A and ϕ) to a new configuration that has become more stable, owing to the changing temperature, than the previous one. Naturally, if there

Figure 2


Typical Descending Transition Curves At Constant Field
14 OCTOBER 1963
RUN NO. 31
SAMPLE DIAM.
2 μ (EST.);
LENGTH 1.02 mm
300 GAUSS
265
182
120
68
40
Typical Ascending Transition Curves At Constant Field
350
GAUSS
322
181
142
78
0
R / RN
T (°K)
0
0.2
0.4
0.6
0.8
1.0
1
2
3

is nearly complete field penetration, the thermodynamically preferred configuration for a given field will be chiefly determined by the current configuration, and will be therefore less sensitive to the temperature than to changes in the applied field. This point of view will be amplified in the following section, as we consider the problem of an appropriate model for describing the system.

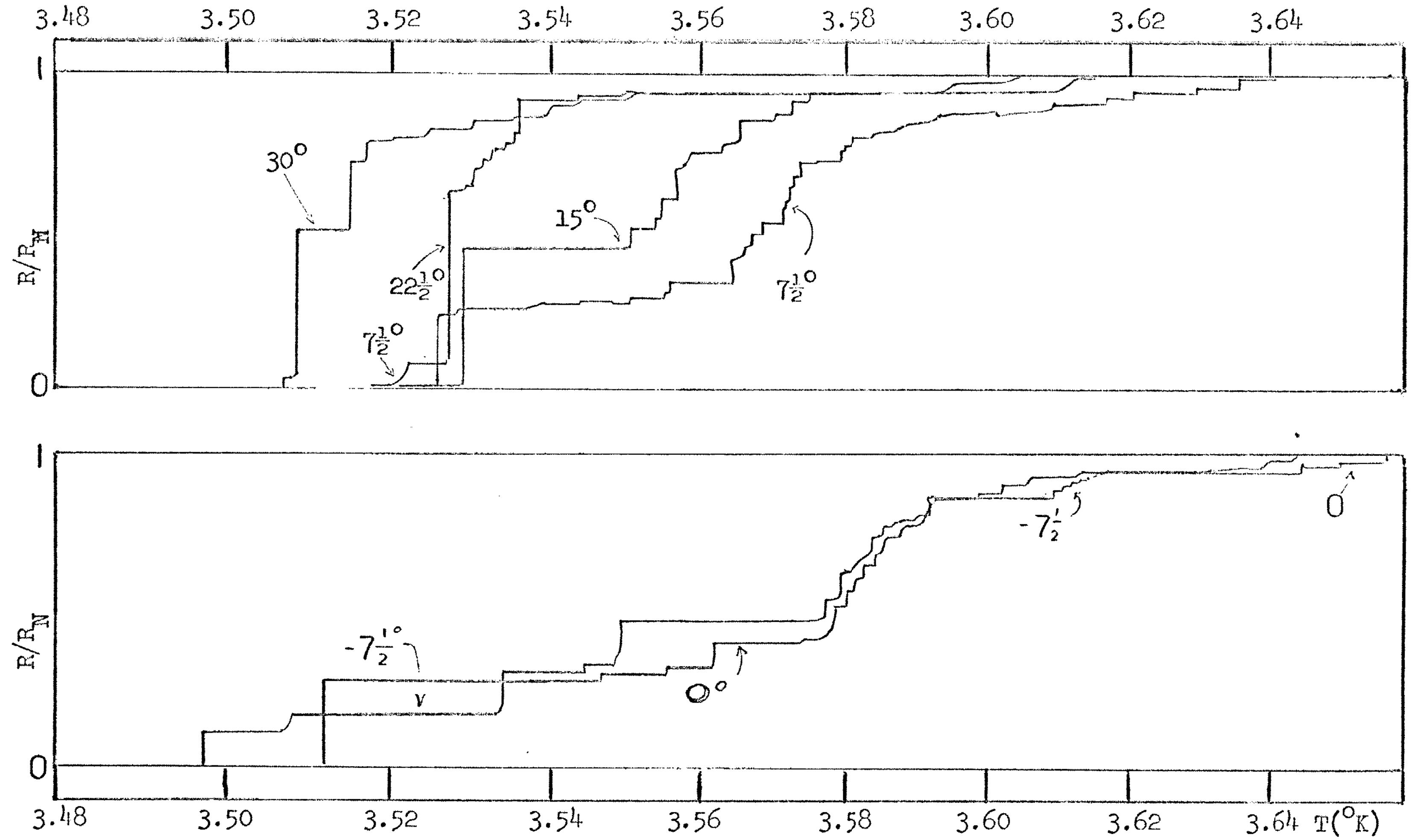
The theory suggested that there should be a clean, nearly rectangular hysteresis curve like this,



with the interval of hysteresis becoming narrower toward the upper limit of the first-order transition region. Examination of the observed transitions does show such a behavior, provided one interprets the "interval of hysteresis" to be the temperature difference between corresponding abscissae on the ascending and descending curves, compared at equal field intensity as shown.

(2) Angular Dependence. The theory also suggested that the interval of hysteresis should become much narrower as the field orientation angle is increased, and the demagnetization term thus becomes dominant. Accordingly, it was decided next to investigate the way in which the new effect depends on field orientation, with respect to the sample axis. Typical results are shown in the next set of curves (Figure 3). As regards the hysteresis interval, and also the general dependence of the upper limit of these transitions on the field angle, the results are in qualitative agreement with calculations made by Tinkham, for the thin=

Figure 3: Angular dependence. H = 38.0 Gauss; angular orientation, as indicated.
All these curves were traced directly from the X-Y recorder chart.



film geometry.[1] Nevertheless, we do not consider this agreement to be a sensitive test or verification of Tinkham's model; for clearly, any model which properly takes into account the demagnetization term will predict the same qualitative dependence, because, as we have already mentioned, this term is generally the dominant one in the thermodynamics.

(3) Why was the effect not previously observed? We suspect that the jumps represent abrupt rearrangements in the configuration of Abrikosov vortex lines. Presumably, a discontinuous increase in the intermediate state resistance occurs when each vortex sheds one or more flux units into the interstitial region. As Tinkham's calculations suggest, the total free energy of the system is only weakly dependent on the number of flux quanta in each vortex,[2] so much so that he was unable to determine, on the basis of his rough trial function, which number of quanta should be thermodynamically preferred. Thus, the equilibrium configuration is probably a rather delicately balanced one, and a slight change in temperature might easily shift the preferred quantum state. Of course, if the applied field H_o is changed, many flux quanta will be involved, and thus the jumps will be so close together that the resulting transition will be

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1. We became aware of Tinkham's calculations [Physical Review, vol. 129, p. 2413 (1963)] after the experiments were well under way. His model is an adaptation of the Abrikosov solution, involving a regular rectangular array of vortex lines. On the basis of a somewhat rough evaluation of the energy, he predicts $(H_{oc}/H_1) \sin\alpha + (H_{oc}/H_2)^2 \cos^2\alpha = 1$; here H_1 and H_2 are the upper critical-field values for a perpendicular and a parallel field, respectively. His upper critical field represents, of course, the limit of stability of the model. Our attempt to interpret these data by means of Tinkham's calculations was only qualitatively successful; but then, this was before we realized that the presence of the vortex lines themselves may play an important role in the resistive transition.

2. M. Tinkham: Ibid. [Physical Review, vol. 129, p. 2413 (1963)]; see, in particular, eqq. 20 and 21 and the discussion following.

essentially continuous. Herein lies the probable reason why the effect was not previously observed: Other experimenters proceeded by variation of the field, while carefully holding the temperature constant.

Nevertheless, it appears that one isolated instance of a multiple transition, produced by varying the field, was observed in the Lutes experiments.[3] There is no comment, in the text of his article, concerning this highly anomalous phenomenon; my conclusion is that, if he noticed it at all, he must have considered the effect to be due to some peculiarity of that particular specimen.

Another possible reason for the other experimenters' having overlooked the effect is that it is most easily observed when the sample is inclined at a small angle to the field. Other investigations have been made using either a parallel field, as e.g. Lutes did,[4] or a transverse field.[5] Indeed, if our interpretation of the underlying mechanism of the effect is correct, then the jumps should not be observable at all in an exactly parallel field. This is because the condition for stability of the vortex-array solution to the G-L equations is that the ordinary London-type solution, with most of the field excluded, require a higher energy; this condition cannot be satisfied in a type-I superconductor, unless the geometry of the London-type solution forces the sample to ex-

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3. Olin S. Lutes: Op. cit. [Physical Review, vol. 105, p. 1451], fig. 3, showing two jumps in one of the curves plotted there.

4. He went to considerable effort, using a telescope and machine-screw mechanism, to align the specimens with optical precision, so as to have a strictly parallel field.

5. As far as I know, no previous experiments involving whiskers have been done in any transverse-field configuration. Quite closely related work, using thin films, has been reported: e.g., Douglass: IBM Journal of Research and Development, January 1962, page 44.

pel the field from a spatial region exterior to its own boundary.[6] On the other hand, the effect would be difficult to observe in a perpendicular field, because the jumps in that case are small and close together. As for our own observation of the effect, perhaps we owe its discovery to sloppiness in the matter of aligning the sample parallel to the field. When the effect first showed up, we were chiefly interested in checking out the technique for detection of the transitions; the sample was set up roughly parallel (in order to be reasonably sure of seeing hysteresis), but no great pains were taken on this account.

(4) Repetitive Transitions; Apparently Metastable Configurations. In our earlier observations of the stepped transitions, it was quickly concluded that the jumps are accurately reproducible for a given sample if the applied field is not changed. This point was one of the first things that we checked, after the initial observation, for we naturally suspected some sort of instrumental defect as the cause of the anomaly. The following table exhibits the data we recorded on the effect, when

13 September 1963. H = 210 Gauss. Angular orientation not recorded; probable about 5 degrees. Jumps occurred at two characteristic points.

	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Av.
T_1 ($R/R_n = 0.7$)	1.879°K	1.875	1.90	1.89	1.896	1.888
T_2 ($R/R_n = 1.0$)	1.933°K	1.92	1.94	1.96	1.94	1.938

it was observed for the first time. The temperature measurements were made, in this instance, with an oil manometer, and the conditions were such that the temperature was rising rather rapidly. We were willing

6. As a practical matter, when one is working with whiskers, it is a difficult if not impossible task, to mount a sample in such a perfectly straight line, that all parts of it could be simultaneously parallel to the field (with such accuracy as to exclude the vortex-line solution).

to accept at least tentatively the assumption that the variation of these temperature data was due to a statistical error in reading the manometer.

Much later, after the characteristics of the new effect had become a bit better understood, it was decided to investigate this question of reproducibility further. The specimen chosen was one of the best that I ever mounted, about 2.5 mm long and between 2 and 3 microns in diameter. The specimen was made to go through the transition many times, under as nearly identical conditions as possible, and the results were plotted in parallel graphs using the two-channel recorder. The graphs are reproduced in Figure 4. We find that there do exist significant differences in the pattern of the jumps. In the first place, not all the jumps show up on every trial. Secondly, jumps which are apparently correlated do not occur necessarily at the same temperature. Both of these circumstances—which, incidentally, seem to be quite generally observed, on all of the larger specimens—may be interpreted if we assume that the specimen has several or many stable configurations in any particular external field, each of which is characterized by a definite apparent[7] resistance. Each of these states is thermodynamically metastable: it has a local minimum in free energy relative to states for which the system parameters differ by infinitesimal amounts. The instant at which the jump occurs to a new state is only roughly determined by the temperature, because some random impulse such as stray inductive pickup provides the nudge that triggers

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7. In saying "apparent" resistance, I am deliberately hedging slightly, for what is literally observed is a voltage, that is proportional to the current through the sample. According to one possible model (see section B3), this voltage may be interpreted, not as an IR voltage drop at all, but as an induced voltage associated with the transverse motion of flux bundles across a Josephson barrier.

the jump. (At times, we found that we could induce a resistance jump by switching on or off some electrical apparatus not even connected to the detector.) The idea is somewhat analogous to a superheated or a supercooled substance which, on the basis of minimum free energy, would prefer to exist in a different phase—but nevertheless remains in this non=equilibrium state, until some outside disturbance causes equilibrium to be suddenly restored. The implication of these observations is that not too much significance should be attached to the precise temperature data points at which the discontinuous jumps take place. Broadly, these data points may be taken as marking the temperatures at which a new configuration becomes more stable, but the exact temperatures may be variable.

The next plot (Figure 4a) serves to illustrate the same idea in a slightly different way. This was made by holding the field and angular orientation constant, while the same transition was recorded in both ascending and descending temperature. It is to be noted here that many of the intermediate resistance states observed in the descending curve are absent in the ascending curve. This is typical, when we are operating well inside of the region where the ascending transition is first-order. Presumably, the necessity for transfer of a quantity of latent heat in the ascending transition, involving of course much more energy than that involved in shifting from one intermediate resistance state to another, gives the necessary nudge to send the sample through most or all of the transition at one jump. However, it should be noted that this pattern was not invariably observed; occasionally, a sample got itself into an intermediate metastable state and stayed there with remarkable tenacity.

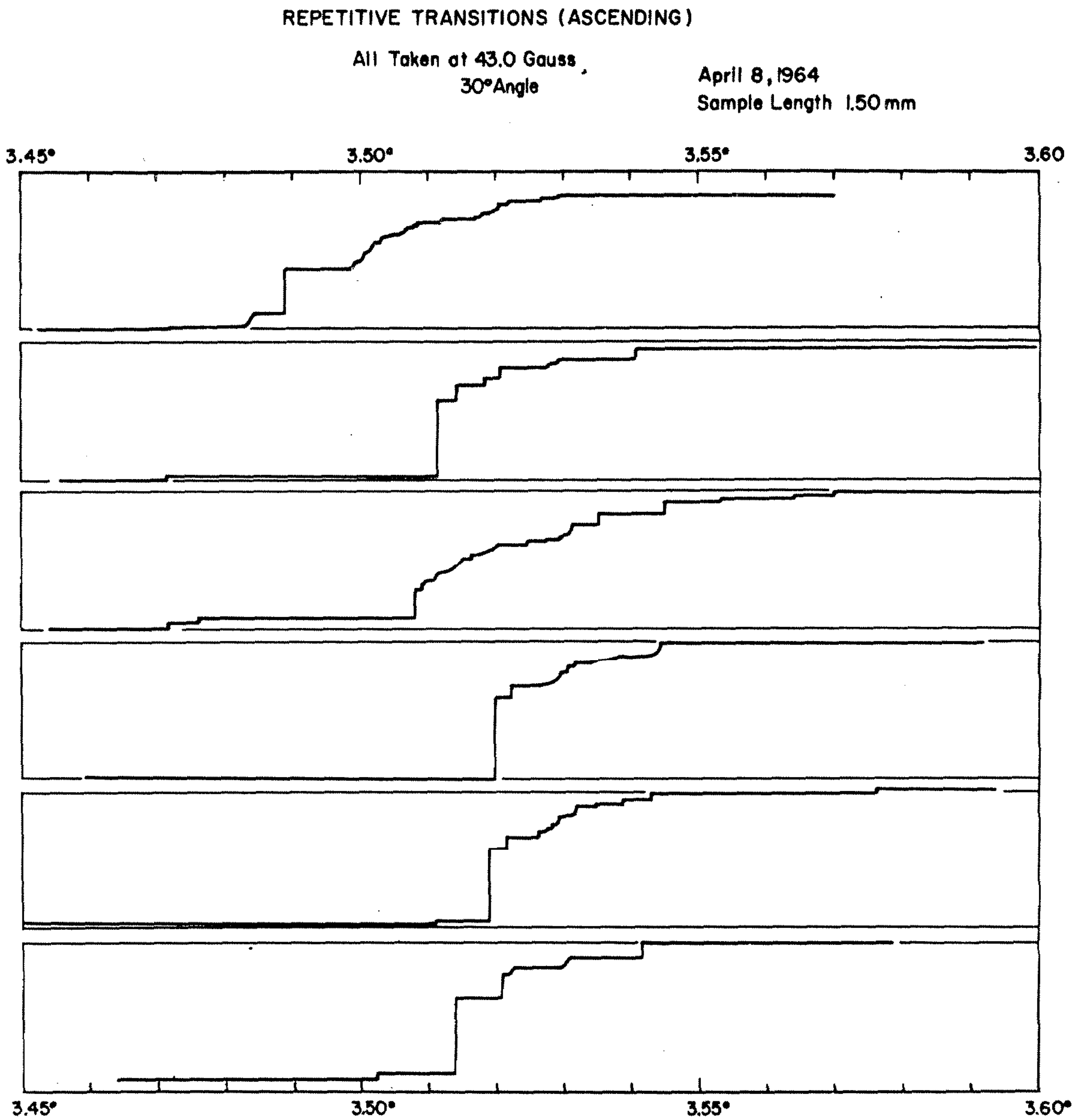
REPETITIVE TRANSITIONS (ASCENDING)
All Taken at 43.0 Gauss,
30° Angle
April 8, 1964
Sample Length 1.50 mm
3.45°
3.50°
3.55°
3.60
3.45°
3.50°
3.55°
3.60°

Figure 4

8 April 1964. Sample-field orientation: 30°; Field: 40.0 Gauss

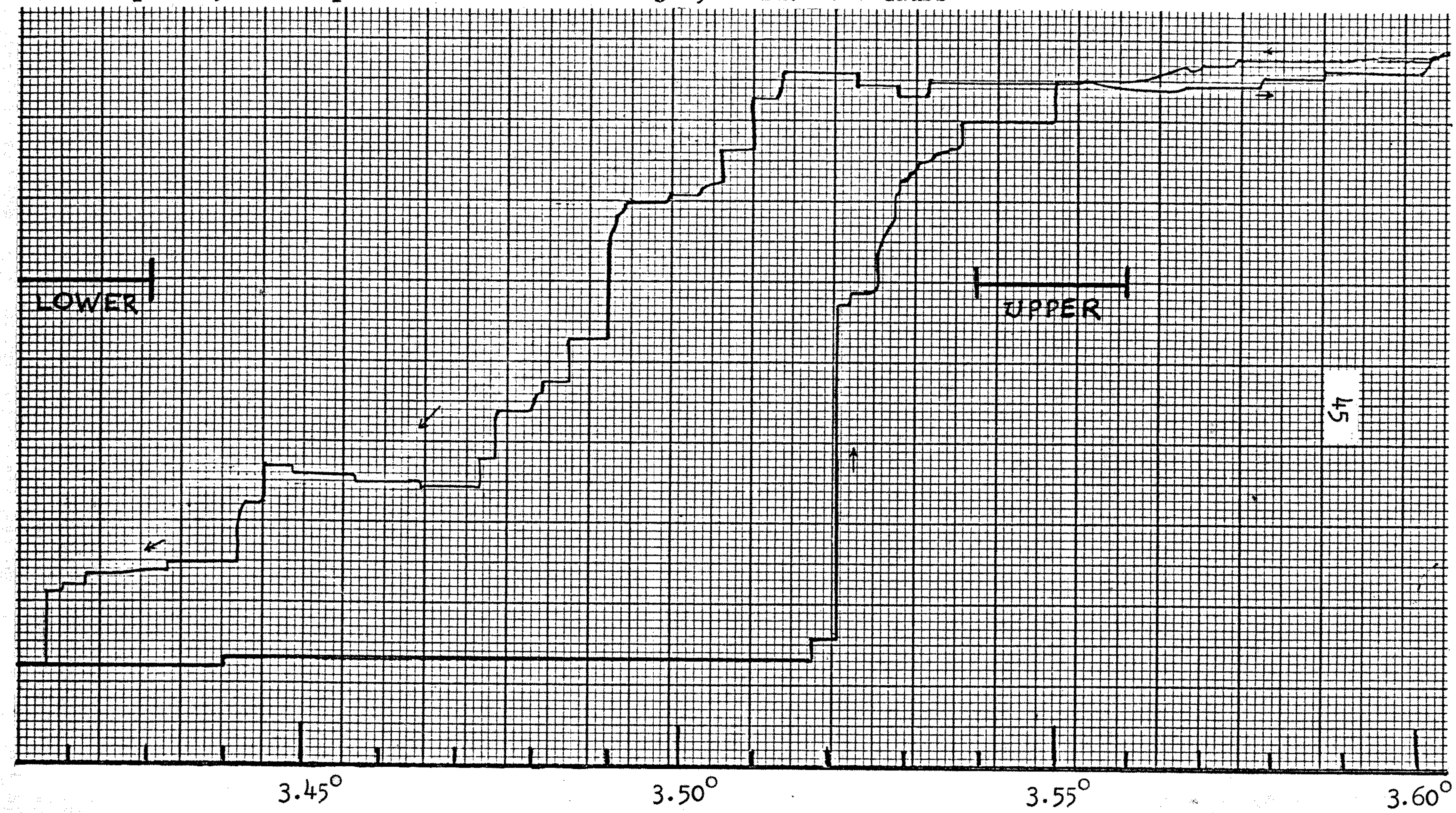

Figure 4a: Cyclic transition. Also shown are the expected upper and lower transition temperatures as calculated according to Ginzburg-Landau (see Appendix 1, sec. B). The indicated spread of the calculated transitions does not imply that they are supposed to extend over any appreciable temperature intervals, but rather, it reflects the uncertainty due to the lack of accurate knowledge of the sample diameter.

B. Probable Interpretation

(1) Parks's Experiments and Inferences Therefrom/ As we have already implied in several places, the conjectured interpretation of the stepped-transition effects is that they represent rearrangements of the flux bundles in an Abrikosov-type mixed state. This interpretation follows most closely, and indeed was originally suggested by, some work recently reported by Parks and Little.[8] They found evidence that the apparent resistance in the intermediate state (or more properly, the mixed state) is functionally related to the amount by which the free energy is forced out of balance, due to the quantum condition; moreover, this extra free energy is found to be a periodic function of the applied field. Our results are consistent with all these assumptions; and if the interpretation is correct, then our observations clearly exhibit a more prominent effect than they found. This is presumably because the effective diameter of a whisker crystal is only a few times larger than that of a vortex line; so, the number of discrete arrangements is more restricted, in the present case,[9] than where there is an extended thin film permitting lateral motion and unlimited variation in the diameter of the vor-

8. W. A. Little and R. D. Parks: Physical Review, Vol. 133, page A97 (1964); also, Physical Review Letters, Vol. 9, page 9 (1962). I should like to emphasize at this point that Little and Parks's own interpretation of their experimental results is presently a matter of some controversy; the vortex-line model, proposed by themselves and by Tinkham, and which we are considering here, is not by any means universally accepted. Anderson has proposed a possible alternative interpretation of their results [P. W. Anderson and A. H. Dayem: Physical Review Letters, Vol. 13 page 195 (1964)], relating these effects to the Josephson Effect.

9. This remark is true irrespectively of whether the rearrangement of vortices is assumed to mean an actual movement of their position or separation, or as we prefer to think, a change in the number of flux quanta per vortex, giving rise to an effective change in the vortex diameter.

tices. The Parks experiments showed measurable effects only in the incipient state of the transition, with $R/R_n = 1\%$ or so. This limitation, I suspect, is because their observations were made by varying the field; and, perhaps, that method breaks down as soon as the number of quanta in each vortex line becomes larger than a small integer. Our experiments, on the other hand, provide a situation wherein a change involving only a few quanta is spread out over the whole resistive transition. That is, we are inducing the changes in the flux quantum number by varying something to which it is rather insensitive.

(2) Speculation on the Model: i. Arrays of Vortices. The vortex lines in the Abrikosov model have cylindrical symmetry.[10] The lines are arranged in a square lattice; hence the field and other relevant functions are two-dimensionally periodic.

Indeed, this periodic behavior was deduced by Abrikosov in an interesting way, which we have not got the space to treat properly here; his demonstration can scarcely be given in any more concise and elegant form than it is in the original paper. Roughly, what he does is this: First, deleting the ϕ^3 term and assuming H = const., he obtains an unperturbed equation that is linear and homogeneous in ϕ, so that the requirement that ϕ be finite and single-valued leads, in a familiar way, to a set of eigenfunction solutions. Then he constructs a general solution out of these eigenfunctions, by the perturbation method, treating the rest of the equation as an inhomogeneous term; finally the result is

10. This statement is literally true only infinitesimally close to the vortex axis, of course; farther out, the current configuration for any one vortex is perturbed, due to the proximity of the others. Cf. the following paragraph.

a self-consistent representation for ϕ, as Fourier-transformed on the spatial coordinates x and y. He then shows that the condition of ϕ being single valued restricts one to a set of discrete points in the k – space: i.e., the representation becomes a Fourier series and implies ϕ must be periodic in spatial coordinates. Finally, he actually is able to derive an explicit representation for the function that this series defines, namely: $\phi = e^{-\frac{1}{2}y^2}\,\theta_3[\sqrt{2\pi}\,(x + iy)]$, in suitable normalized coordinates, where θ_3 is one of the well known elliptic theta functions. Along the "real" or x-axis, the function designated here is real-valued and periodic, consisting of a set of Gaussian peaks at integer values of the argument. When displaced by a unit distance in the y-direction, the function again reproduces itself, except that it is multiplied by a constant phase factor. Accordingly, we have $|\phi|$ two-dimensionally periodic, and the zeros of it mark the locations of the famous vortex lines. The magnetic field, with perturbation terms included, turns out to be: $H/H_o = 1 - |\phi|^2$; so, the field has maxima at the vortex locations.

Having thus predicted, and as a matter of fact, by now well verified experimentally, the existence of these vortex lines, it is preferable that we regard a vortex line as a known entity by itself, rather than dealing with the periodic solution in its full form; and that is what we shall do in this paper. The behavior of the field and order=parameter in the center of a vortex may be characterized as follows: The potential A is finite, and in a suitable gauge for the description of this model, is zero along the vortex axis. The order-parameter ϕ is complex-valued and tends to zero like $r\,e^{i\theta}$. The magnetic field everywhere is parallel to the vortex lines, and has a finite maximum along the axis. The quantity $\Lambda cJ + A$ becomes infinite to the order of $N\varphi/r$, where[11] N is integral and represents the number of units of fluxoid in the vortex. The line integral of $\Lambda cJ + A$ around any closed path, which is commonly called the fluxoid, is $2\pi N\varphi$ if the path encloses the origin, and zero otherwise. If $N \neq 0$, it is necessary that ΛJ become infinite, while $(\Lambda/2)J^2$, which is the kinetic-energy density, remains finite at the origin; moreover, under certain conditions regarding the parameters of the system, the integral of this kinetic energy, when combined with the other terms in the G-L model, gives a lower value than the alternative solution in which most of the field is expelled.

The vanishing of ϕ at $r = 0$, while the kinetic-energy does not go to zero, requires that the electron transport velocity tend to infinity there. (This latter velocity is interpreted as the c. m. velocity of a Cooper pair, much smaller than the intrinsic velocity of a single electron near the Fermi surface.) Herein lies the crux of the problem of understanding the relation between vortex lines and the onset of resistance in an Abrikosov mixed state. For, whenever the transport velocity exceeds a definite critical value, usually assumed to be the speed of sound, then the Fröhlich interaction becomes ineffective, as a pairing mechanism; in fact, the interaction is thought to become repulsive. So, the underlying mechanism of superconductivity breaks down. There is, of course, no provision for a critical velocity in the G-L theory, for it does not take into account explicitly the nature of the electron-electron interaction. What one must assume, then, is that the critical ve-

11. As before, φ stands for the flux quantum $\hbar c/2e = 3.29 \times 10^{-8}$ Maxwell.

locity represents a criterion for failure of that model. Since, in the vicinity of the vortex axis, A tends to zero, we must have $mv = -\Lambda qJ \approx N\varphi q/rc$, and we may estimate the critical radius to be $N\varphi q/mcv_c$, where $q = 2e$ and v_c is of the order of the speed of sound. This radius defines a core at the center of the vortex, inside of which the metal is in the normal state (even though its electronic wave function is coherent with that of the surrounding superconducting region). Experimental evidence for the existence of such a core has recently been reported.[12, 13]

To recapitulate: We assume the Abrikosov mixed state, and assume moreover that the velocity of the "super-electron" component which, according to that model, tends to infinity like r^{-1}, is limited in a real vortex by the onset of critical velocity. Then the appearance of dissipation—i.e., resistance—turns out to be a particular manifestation of the critical-current effect. Now the externally supplied current produces a uniform drift velocity, which is superimposed on the velocity-field of the vortex itself. And since (as we shall discuss presently) the measuring current is typically 1% of critical current, we may certainly assume that its interaction with the vortex current represents a very small perturbation on the latter. Only first-order effects being considered, accordingly, the current density on one side of the vortex core will be increased, due to the measuring current. Because the current density at the core is already critical, the minimum radius, out-

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12. Bruce Rosenblum and Manuel Cardona: Physical Review Letters, vol. 12, page 657 (1964).

13. A. R. Strnad, C. F. Hempstead and Y. B. Kim: Physical Review Letters, vol. 13, page 794 (1964). This includes a concise survey of the experimental facts concerning dissipative effects which are presumably associated with the vortex cores.

side of which a supercurrent can flow around the vortex, must increase. Since the total flux enclosed is fixed by the London quantum condition, the end effect is that the vortex swells. In case of a plane-film geometry, it is free to do so; but in such narrow samples as whiskers, any increase in the effective diameter of a vortex is impeded by the concentration of flux around the boundary. The vortex is then faced with the dilemma of having its current density go hypercritical if it remains the same size, or of running into an energy barrier if it tries to expand. There is available to the sample a source of additional energy, which is being supplied continuously in the form of a measuring current; so, the idea of our model is that the vortex does <u>not</u> expand, but instead dissipates energy continuously, through current which is being squeezed into the normal core. That, of course, is tantamount to saying that there is a resistance present. Evidence for the appearance of such a resistance, when measuring current is constrained to go through (or around) a vortex line and the latter is not allowed, owing to a constriction in the sample, to evade the hypercritical current by increasing its diameter, has been found in the course of the Parks experiments;[14] their interpretation of the effect was apparently rather similar to the ideas presented here. It must be emphasized that there exists at present no theory concerning the behavior of Abrikosov vortex lines in the presence of a uniform background current; so, these ideas must necessarily remain somewhat vague and speculative.

What is not so speculative, though, is the rather obvious corol-

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14. J. M. Mochel and R. D. Parks: American Physical Soc. <u>Bulletin</u>, vol. 9, No. 4, Abstract EF7 (1964).

lary (once we accept the notion that the interaction of vortices with a background current does somehow show up as a resistance), that a discontinuous rearrangement in the lines reflects a change in the apparent resistance. Conversely, only a change in the vortex quantum number, or in their arrangement, may reasonably be expected to alter the resistive effect. As the temperature goes up or down, while the system remains in a certain configuration, then $N_{s\ eq}$, which is proportional to $1/\lambda^2$, is accordingly changing; but in such a case, the velocity configuration must alter itself in such a way that the product ΛJ remains constant, as required by the quantum condition.

(3) Speculation on the Model: ii. Anderson's idea.[15] A rather different idea has been suggested to the author, as possibly germane to the problem that we have just been discussing: i.e., the relation between Vortex lines and the onset of an apparent resistance. Dr. P. W. Anderson, of the Bell Laboratories, has surmised that such effects are related to the existence of "free energy barriers to the transverse motion of vortices." If I understand this idea correctly, then his assumption means that the apparent resistance is really an induced voltage, produced by the transverse motion of the flux, which is being conveyed across the sample in the form of vortex lines. The "free-energy barrier" refers merely to the loss of condensation energy at the axis of a vortex: this energy must, of course, be supplied in order to generate new vortices at the boundary of the sample. In order to account for discrete jumps, such as those observed in the present experiments, he apparently assumes that the idiosyncratic properties of the sample

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13. Philip W. Anderson: Private correspondence, March 1964

may give rise to local free-energy minima, where this process of creation, migration and annihilation of vortices can take place more easily. Such irregularities could be, e.g., dislocations extending transversely across the sample. He further remarks that the existence of the energy barrier is related to the peculiar periodicity occurring in the current-voltage characteristic of the Josephson effect, for which the theoretical interpretation is now regarded as very satisfactory. If such an interpretation of our phenomena is to be accepted, one must hypothesize, in addition to the existence of dislocations or some other suitable imperfections in the crystals, that these imperfections are so prominent that they can create "bridges" of normal material extending all the way across. Then these narrow slices of normal metal could conceivably act as Josephson-Effect barriers.

C. The Resistance-Interpolation Procedure

Following out a suggestion due to Professor Pellam, I have succeeded in obtaining a very rough estimate of the size of the fluxoid-quanta involved (if such there are) in these discontinuous jumps, by interpolating a background resistance contour into the observed stepped-resistance curves. This is a smooth curve, and is drawn so as to come close to the center points of the several jumps, while retaining the general shape of the zero-field resistive transition. This hypothetical resistance curve, we assume, represents the thermodynamically preferred R-vs.-T transition, which the system would like to follow if it were not constrained to maintain the quantum condition. Using differentials as estimators of the discrete increments, we may obtain formally:

$$\Delta H \approx \frac{dH}{dR} \Delta R = \frac{dH/dT}{dR/dT} \Delta R$$

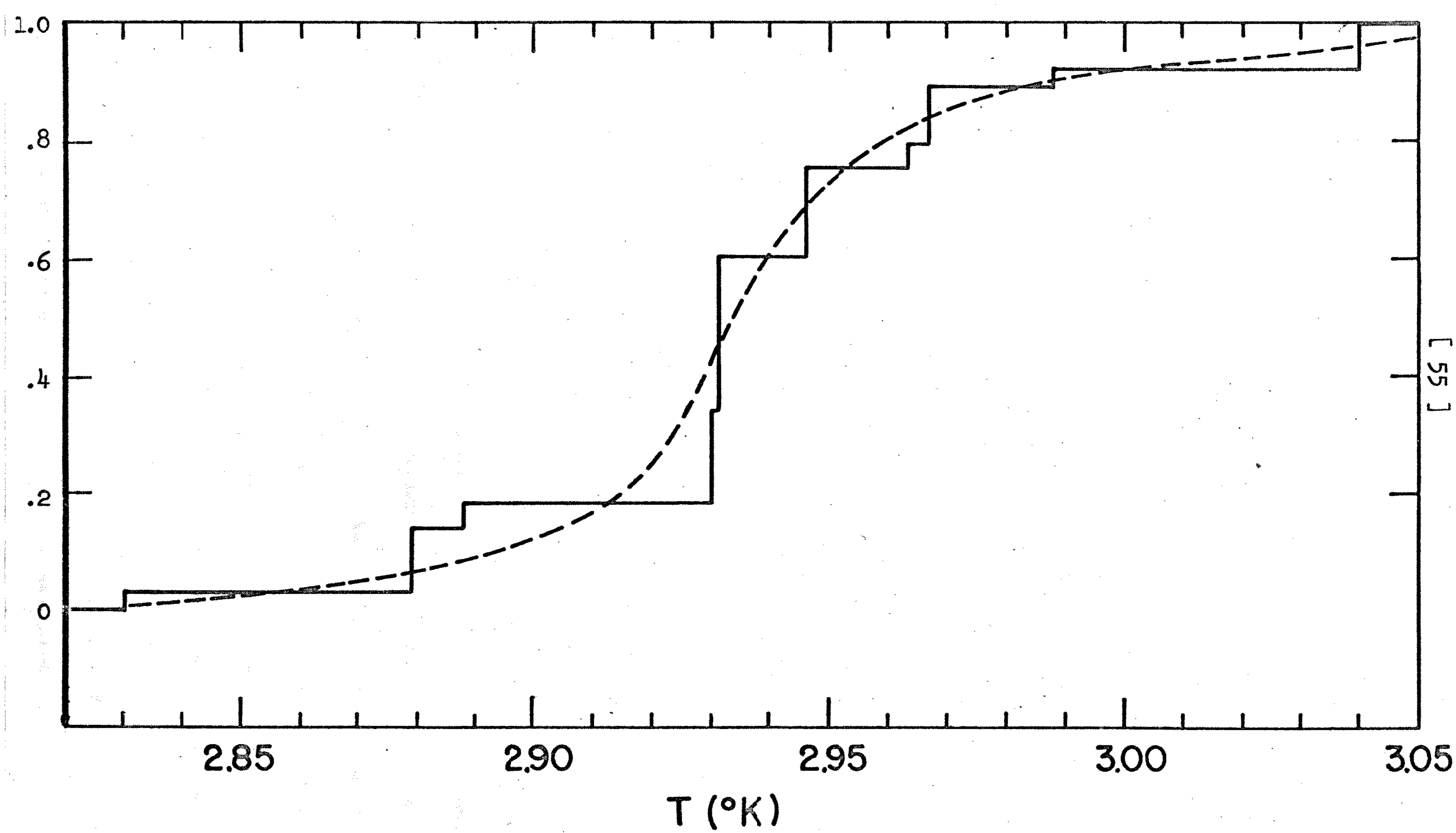
Now, dH/dT may be estimated from the critical-field curve; dR/dT is estimated from the assumed background resistance curve; for ΔR, one inserts the actual observed resistance jump, expressed as fractional part of R_N. Then, since the unit cells of Abrikosov's mixed state are square, and we believe the number of them that can be stably arranged abreast in a filamentary crystal is small (probably one), we can obtain by this method an estimate of the flux change $\Delta\varphi = H\, d^2$, where d is the effective diameter of the specimen. The answers have always been found to fall within the right power of 10. Usually they are inclined to be on the large side of the London flux quantum; this is all right, inasmuch as we may have more than one flux quantum involved in a jump. The method may be illustrated

H = 181 Gauss, T range as in Figure 5, orientation angle about 9^o

T, ^oK	dH/dT, G/deg.	dR/dT, %/deg.	$\Delta R\%$	$\frac{dH/dT}{dR/dT}$	x d^2
2.879	-122	21	10.5	61	2.3 x10^{-6}Maxwell
2.932	-128	240	26	22.5	1.0
2.947	-129	90	15.5	22	1.0
2.968	-130	38	10	34	1.5

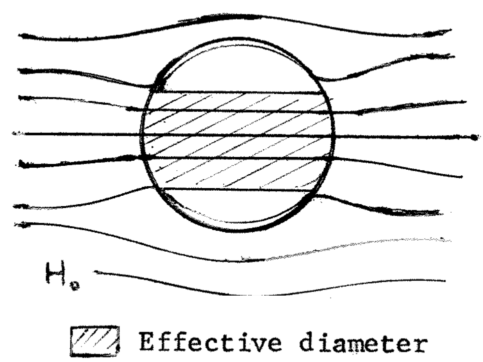
by an example. The above data are from Figure 5. The value in the last column may be compared with the accepted value of the London quantum φ_o, (= 2π times φ used in the present paper) = 2.06 x 10^{-7} Maxwell. Now, it appears, at first sight, that the disagreement is so large as to render this procedure meaningless. But then, the diameter of that portion of the sample which actually may be assumed to allow the flux penetration in the form of Abrikosov vortex lines must be smaller than the physical boundary of the sample. This we know, because a substantial part of the

Figure 5



Expanded view of one of the transitions from Figure 2, showing in addition the hypothetical background resistance curve.

flux passes around the sample, penetrating only to a depth of the order of λ, as required by the ordinary London solution to the field equation. By means of a rough, trial-function evaluation of the free energy in the G-L theory, and comparing the energy, for various mixed-state configurations, with that of the pure London configuration, it may be estimated that the thickness of the vortex-carrying section of the filamentary sample is about half of the true sample diameter. Accordingly, the values of the (assumed) quantum jumps in the last column of the table should be diminished by a factor of about 4. This brings the data into very satisfactory agreement with the accepted value; particularly notable is that the smallest value thus obtained—namely, 2.5 $\times 10^{-7}$ Maxwell, which is most likely to represent a single quantum jump—is in error by an amount that is easily ascribable to the uncertainty in the sample diameter (probably $\pm$ 50%).



The trial-function calculations also indicated that the smallest sample diameter, for which <u>any</u> configuration involving vortex lines is stable, is of the order of 1 micron. Since most of our samples are only two or three times that large, the conjecture stated above, that there can be no more than one row of the vortices arrayed along the length of the sample, receives further corroboration from this source.

It should be commented further that the statement "dH/dT may be estimated from the critical-field curve," is a slight equivocation; for it is not obvious that dH/dT in the previous paragraph should be the derivative of the critical-field curve $H_c(T)$, as measured for the material in the bulk state. What the statement really means is that dH/dT is to be evaluated along the path taken by the system in the H-T plane, as it passes through the transition. Since all experiments reported here were done at constant field, with temperature as the only continuous variable, one might suppose that dH/dT = 0 is the correct value. But wait. The field H which is relevant to this discussion is not the externally supplied field, but the field actually existing in the interstitial region close to a vortex line, where the incipient resistance is supposed to be developing. This will in general be less than H_o, since some of the flux is being squeezed into the vortex lines. How is this internal field varying, as the sample is about to make a jump? Since the jumps are completely instantaneous, so far as we can ascertain, we must assume that they take place adiabatically, even though the sample is surrounded at all times by a liquid helium bath. So, before the jump can be made, the free energy must be out of balance far enough so that the sample itself can supply the required latent heat. Where is this extra energy stored? We submit that it can only be in the sample's own magnetization energy, and so the local field must be depressed as the sample approaches a transition. We therefore assert that dH/dT should be the slope along a contour of constant resistance in the H/T plane; it is known, in fact, from other evidence that the contours R = const. are, to a good approximation, parallel to the critical-field curve.[16]

In conclusion, we wish to suggest that even the rough agreement

16. Incidentally, this is demonstrated for our samples by noting that the temperature-width of the full transitions varies slowly as a function of H.

with the known value of the flux quantum is good justification for our increasing confidence that the interpretation of the stepped transitions as a quantum effect is basically correct. After all, if such a connection were not really there, it is hard to understand why, a priori, the answer might not just as probably be off by a factor of 10^6 instead of less than 2.

D. Critical Currents

The critical-current effect in superconductivity has, as we have already mentioned, a bearing on the ideas discussed in this paper. At this point, we wish to make a brief digression into this topic, insofar as it concerns the present experiments.

Critical current in superconductivity has been picturesquely described to the writer as a "solid-state analog of Cerenkov radiation."[17] The term is somewhat a misnomer; perhaps critical velocity is a better name for what is going on: the velocity in question is the joint velocity of the electron pairs which comprise the super-current component. Although this is an oversimplification of what is really involved, it is usual to assume that critical-velocity effects become prominent whenever the pair velocity approaches the local speed of sound. At any particular temperature, the super-current may be represented as $J = N_s(T)\ v_s$ (N_s should not be interpreted too literally) and so, intuitively, we expect the critical current to tend to zero like $1/\lambda^2$ as the temperature approaches T_c. Experimentally however, this behavior is not well corroborated; indeed, evidence has been reported indicating that critical=

17. Quoted from an informal discussion with Dr. James Mercereau.

current density does not even vary monotonically with temperature.

This writer's interest in critical currents stemmed from two considerations: First, before the experiments got under way, I decided to do preliminary experiments, so as to determine whether critical-current effects would seriously interfere with the desired measurements. If the minimum measuring current, necessary for clear observation of the transitions, should come close to the critical density for these filaments, then the samples might be driven normal by the measuring current rather than the field. Second, when the unexpected phenomena were discovered, we were naturally concerned as to whether the anomalous behavior was in some way connected with the critical-current effect.

The experiments, in which we searched for critical currents, were set up similarly to the resistance-measuring technique, already extensively described, except for one thing: The wave analyzer was carefully tuned to the third harmonic of the measuring-current frequency, rather than the latter frequency itself. Under such conditions, if the peak of the measuring current ever exceeds critical current for the sample, then twice in each cycle there will be a sudden burst of dissipation; and accordingly, a voltage signal will be evinced. This highly non-linear behavior evidently will give rise to harmonic distortion in the output (no even harmonics can be produced, inasmuch as the effect does not depend on the direction of the current); so detection of any signal by the wave analyzer marks the onset of critical current. A signal due to critical current can be easily distinguished from one which might be due to the sample's going completely normal, for the ohmic resistance which characterizes the normal state cannot give rise to harmonic generation.

Two interesting effects turned up and will be noted briefly here. The first third-harmonic signal that was detected was found to be not only non-linear, as expected, but even non-monotonic. As we increase the measuring current, we find that the third-harmonic signal appears; at first, it increases very gradually, passing through a maximum (see Figure 6); then it decreases through zero to negative values; finally, it increases rapidly and roughly linearly with measuring current. What is meant, by saying that the amplitude goes negative, is this: The 3rd harmonic voltage goes into an opposing phase, probably inverted by 180° with respect to the peak of the measuring current. The significance of such odd behavior is unknown to the writer, but in any case it is outside the scope of this paper and will not be discussed further.

The real critical current was subsequently found, by increasing the measuring current by a factor of 10 to 15 beyond what was necessary to produce the effect described in the previous paragraph. Its appearance is dramatic, and characterized by a really discontinuous jump in V_3, the third-harmonic amplitude. This change, by a factor of 1.5 to 2, takes place with a change in V_1 of, at most, a few parts in 10^4; I have tried unsuccessfully to obtain any intermediate points along the rise. The reason for having a discontinuous current-induced transition probably lies in the Joule heat, produced suddenly when the sample gets driven into the normal state. Such heat raises the temperature of the sample, as soon as the current goes through critical value, and then I_c immediately decreases, due to the rise in temperature. This means that the sample must stay normal over a sizable fraction of the current half cycle, if it goes normal at all.

Figure 6

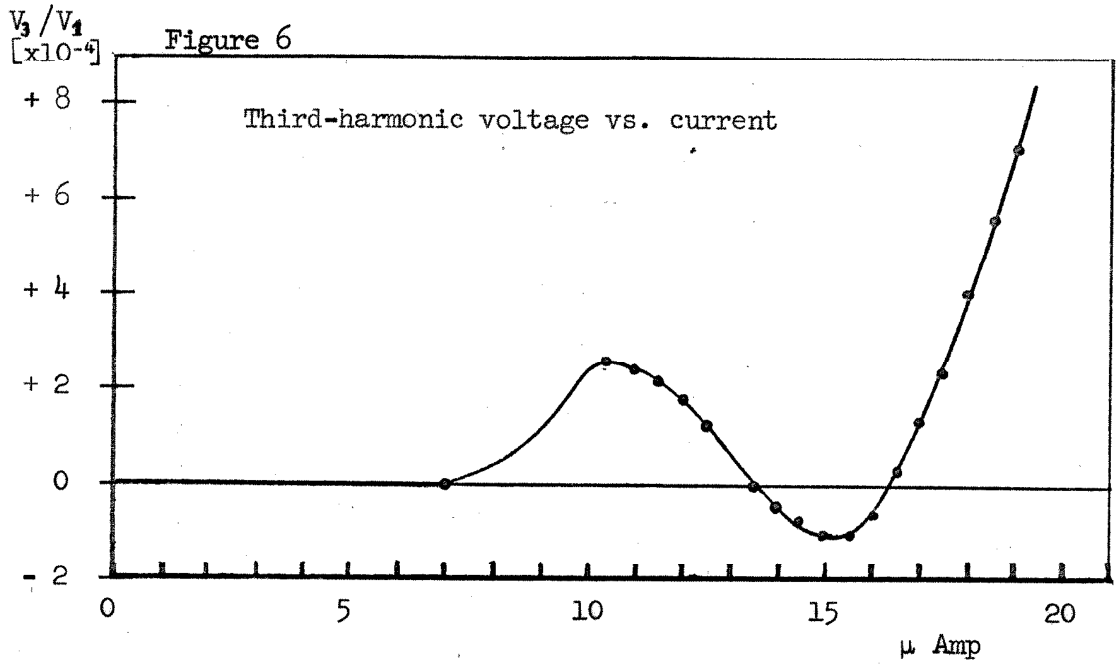
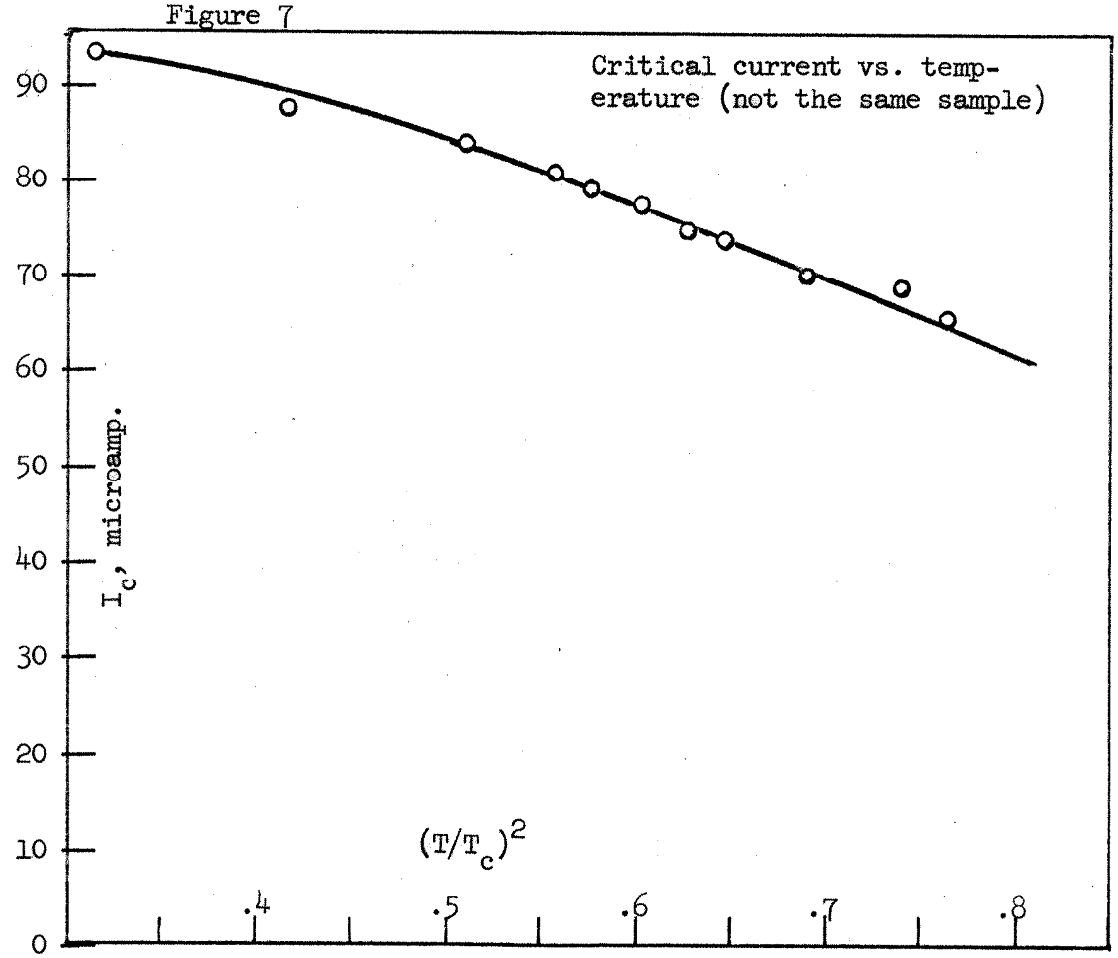


Figure 7



Having found this sensitive test for I_c, it was of course interesting to investigate the change in I_c (as defined by the discontinuous point) as a function of temperature. Typical data are shown in Figure 7. If we assume that the specimen has a diameter of 4 microns, and the current is confined to within a penetration depth, $\lambda \approx 10^{-5}$ cm., then the critical-current density works out to something like 150,000 Amp/cm^2; this appears to be in satisfactory agreement with values reported by other workers in critical-current experiments.

The principal significance of these data for the purpose of the present paper is a negative one: It shows that we have little to worry about as regards interference due to current-induced effects, with what we were measuring. As a matter of policy, it was found adequate, during most of the experiments, to keep the measuring current in the neighborhood of 1% of the critical current I_c. In a few instances, this was intentionally altered, and the measuring current was increased up to 10% of I_c, or more; this was only to verify that nothing startling would happen to our effect, and indeed nothing did. To forestall any misunderstanding, it should be recalled that the critical current does play a role in the conjectured model with which we are interpreting the data; but this critical current is produced by the sample itself, as an essential characteristic of the vortex lines, and is not related to the much larger measuring currents that we would have to have used, if any such effect were to be attributed to measuring-current-induced transitions.

E. Lalevic Experiments

After the preparation of this manuscript was substantially complete, it came to the attention of the author that some interesting experimental results, seemingly related to the phenomena reported here, were recently obtained by B. Lalevic.[18] The similarities between his results and ours are the following: (1) The resistance changes by discrete steps, for both directions of the transition. (2) The resistance is constant so long as the sample remains in a certain metastable configuration. (3) At the first onset of resistance, the steps are very small, while toward the middle of the transition, they become larger. (NB: So he states in the text of the article; nevertheless, the curves shown for tin appear to disagree with this statement.)

The ways in which his results disagree with ours are as follows: (1) His specimens were wires of about 0.1 mm diameter, whereas we were dealing with a much smaller specimen size, so that correlation effects are important in our samples but presumably not in his. (2) In his effect, there is a characteristic time interval between successive steps. In contrast, our experiments invariably showed no measurable time interval occupied in making the jump. The time duration of one of our jumps, as we observed it, was limited solely by the response time of the narrow-band wave analyzer, about 0.1 second. (3) The results for tin showed jumps of the order of 1% of the total resistance; our data usually indicated the jumps to be proportionally much larger. If his interpretation in terms of a domain structure were to be accepted, this discrepancy could perhaps be assumed to be a "scaling-down" effect, due to the difference in the sample size.

18. Boboliub Lalevic: "Metastable States in the Intermediate Region of Superconductors," Journal of Applied Physics, Vol. 35, page 1785. (1964)

It is obviously not possible for me to critically and objectively evaluate Lalevic's results within the scope of the present paper. He considers his results to be produced by the domain structure which, as is well known, is characteristic of large samples in the presence of a demagnetizing field. It may be pointed out, though, that his interpretation of his own data appears to be based on an obsolete theory, and so the agreement with predicted behavior may be more fortuitous than he realizes.

What I should like to concern myself with here are the reasons for doubting that Lalevic's interpretation of his results, whether correct for his own purpose or not, have a bearing on the correct interpretation of my own results. The two most crucial arguments in this connection are based on the time-lag phenomena and the difference in sample size, or so I think. The existence of a time lag between jumps in either direction is, as he would surely agree, essential to his explanation of the phenomena. According to the older (pre G-L) conception of the intermediate state, there exist large, completely superconducting regions interspersed with smaller, completely normal regions which convey flux through the body of the sample. As the field-induced transition proceeds, domains of one or the other kind disappear, one by one, until the whole sample is normal (or superconducting, as the case may be). This dissolution of a domain requires a non-zero time, due to the eddy current associated with the displacement of flux lines. From the measured time lag, the size of the domains may be computed, using this sort of model; Lalevic finds that they are prolate ellipsoids whose long axes are longer than even the diameters of his specimens. It is clear that the assumption of any such domain structure in samples the size of our whisker crystals is completely untenable. The thickness of the domain boundary, let alone the size of the domain itself, cannot be much less than a correlation distance; such a distance already occupies a sizable fraction of the sample size. As we now know, it makes no sense, in the light of the G-L theory to speak of domains of completely normal, or of completely superconducting material, when the sample size is of the order of a correlation distance.

CHAPTER VI: CONCLUSIONS

In this chapter, we shall first recapitulate, in outline form, what seem to be the significant new results obtained in this research project; then we shall indicate the lines along which further research is suggested.

A. Summary of Results

1. <u>The multiple-transition effect</u>. The chief objective, when this study of critical-field transitions was undertaken, was to make a more thorough investigation of the hysteresis effect. In the course of the project, an interesting and puzzling new effect has turned up, causing our attention to be diverted away from the original problem. The salient characteristics of the "Multiple-Transition Effect" are:

i. Under appropriate conditions, the resistance changes from zero to normal and vice versa in discrete steps.

ii. The steps are best observed by varying the temperature at a constant magnetic field.

iii. In the high-field, low-temperature region, the transition region extends over several tenths of a degree. It probably corresponds to the extent of the hysteresis.

iv. As long as the sample remains in a particular stage of the transition, its resistance is constant, even when the temperature is continuously varying.

v. The effect is most easily observed in a slightly oblique field. When the angle of inclination gets larger, the individual jumps get smaller.

vi. The effect is found only in the temperature region such that the transition is first-order.

vii. The temperature intervals between corresponding metastable stages get smaller as we go up in temperature (down in field), presumably going to zero at the point where the transition goes over to second-order.

viii. There appears to be no correlation between the jumps observed in ascending transitions and those observed at the same field in descending transitions.

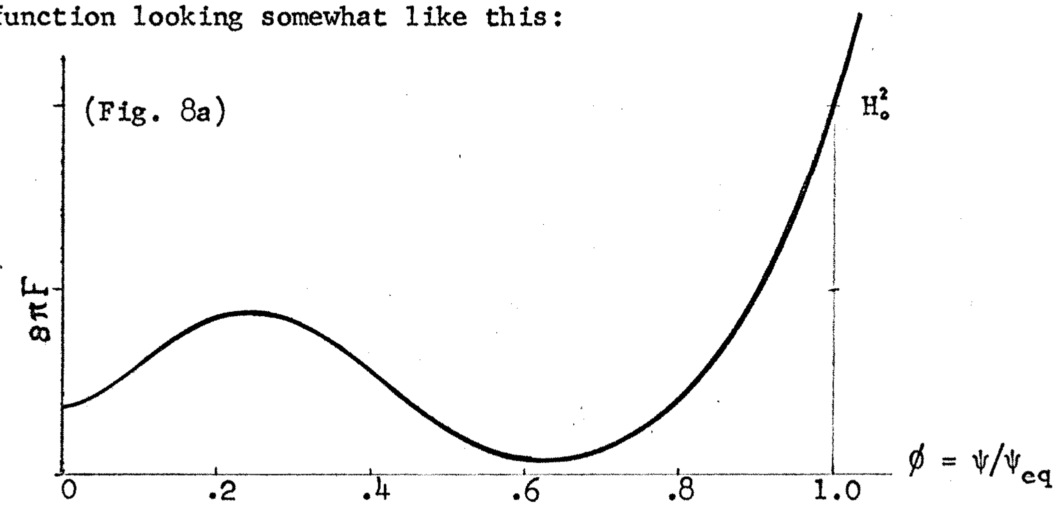
2. Probable Interpretation. Evidence discussed herein, and some apparently related effects reported recently by other experimenters, imply that the explanation of the multiple-transition effect is that the jumps represent rearrangements of the Abrikosov flux bundles, penetrating the sample in the mixed state. Once the vortices are in a certain configuration, they stay that way with considerable temperature stability, provided that the external field does not change. In this respect, filamentary samples differ from thin films, since the lateral movement of vortices is inhibited by the narrow boundary of the sample. The detailed mechanism whereby this inhibition of lateral movement gives rise to an apparent resistance, and changes in the configuration cause corresponding changes in the resistance, is not clear. It is probably related to the critical-current density near the centers of the vortices.

B. Suggestions for Further Research Projects

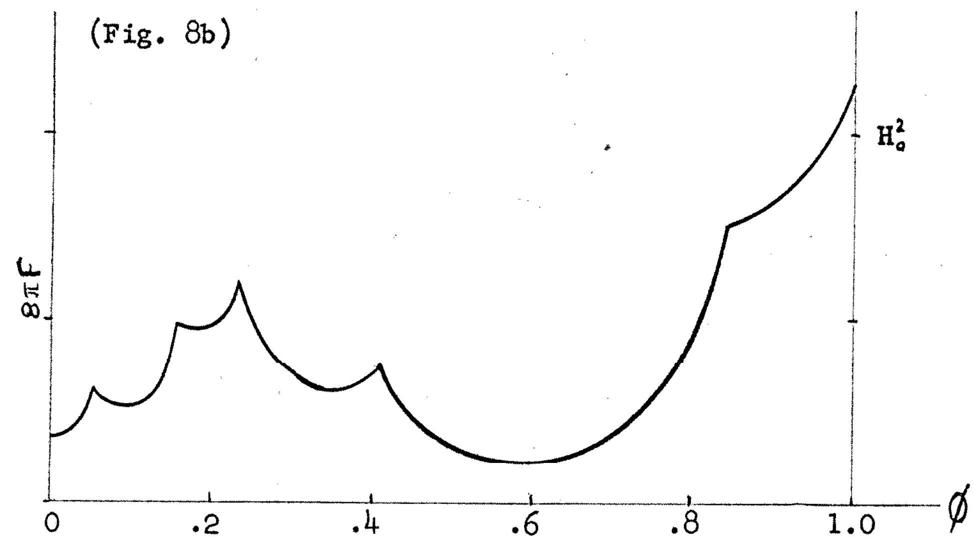
1. Study the Effect with Whiskers of Other Metals. It has been found that whisker crystals can be grown, by the pressure-acceleration procedure, out of many other metals than tin. It would seem, therefore, that superconductivity experiments on whiskers of other materials would be desirable. For the study of the phenomena described in the present

paper, whiskers of lead-indium alloy[1] would be especially interesting, because such alloys are, in some cases, "type II superconductors," in which the surface-energy term in the Ginzburg-Landau model is negative. Now, as we have indicated previously, in several places, this surface energy is really the basic fact underlying both the hysteresis effect and the behavior of the vortex lines. So, if the same type of experiment were performed, using filaments of a type II superconductor, then the similarities and differences between their behavior and the observations of the present study would, perhaps, shed further light on the basic unsolved problem of the nature of the interaction between a background measuring current and the Abrikosov vortices.

2. Calculations on the Model of Vortex Lines. As we have shown, from a simplified treatment based on the G-L equations, the calculated critical field is determined by the minimization of a free-energy-vs.-ϕ function looking somewhat like this:



1. The preparation of whiskers out of lead-indium alloys of various composition has been described in the article by Sines (see chapter 3, note 2). He was interested in comparing the alloy constitution of the whiskers with that of the parent material, and he found that there is no appreciable fractionation of the constituent metals, in the process of whisker extrusion.



Now, if a more sophisticated calculation were made, along the lines of the Tinkham calculation, and in which one assumed a particular configuration for the vortex lines, with the current density specified by some astutely chosen trial function—and most importantly, including the contribution to free energy due to the kinetic energy in the vortex current, necessary to maintain fluxoid quantization in the face of the continuously variable external field—then it appears intuitively clear that the curve 8a above would have a set of parabolas superimposed on it, rather like the curve in 8b. This means that there are a whole series of metastable minima in the free energy; these presumably represent the stepped transitions reported herein. Hence, it may be possible to predict the temperature at which the system would be just able to get over the cusp from one minimum to another. Such a method of calculation would be obviously much superior to the interpolation of an assumed "preferred" resistance curve, as has been done here. Such a calculation would not, of course, require any more fundamental or esoteric theoretical tool than the Ginzburg-Landau functional, and it probably would clarify the connection between the multiple-jump transitions and the hysteresis effect. After all, they are both manifestations of the same underlying model, and they are both found in the first-order transition region of small-sample superconductors. The inference that they are two facets of essentially the same phenomenon is hard to resist.

3. Look for non-linear effects. If we are correct, in assuming that the mechanism for translation of a given vortex configuration into a definite measured resistance involves critical-current density at the center of the vortex, then there should appear some sort of non-linear resistive behavior. For critical current is an essentially non-linear phenomenon. An interesting idea, albeit very difficult experimentally, would be to attempt to keep a sample in a certain intermediate resistance state, while varying the current over a wide range, so as to find out if the resistance is really non-ohmic. That no such effect was observed in the present experiments is of no significance, because the measuring current used was always much smaller than critical density; if the measuring current is only a small perturbation to the much bigger current which is locked into the vortex, it should produce a linear effect, no matter how the other currents may be arranged. Further confirming evidence would be interesting, if it were found that these assumed non-linear effects were strongly temperature dependent, even when the system is held in a certain configuration of the flux lines.

C. Acknowledgments

The author takes pleasure in acknowledging, first of all, a debt of gratitude to Professor J. R. Pellam, who has been his friend and advisor throughout the (unfortunately) many years during which this project, and the preliminary studies leading up to it, have been under way.

It is also fitting and appropriate at this point that the author express his appreciation for the financial support provided through the generous cooperation of the Sloan Foundation, and later on, the National Science Foundation. As one who attempted for several years to do without such subsidized assistance, this writer is in a position to know and appreciate the value of the assistance received through such grants, in enabling him to complete his graduate studies without distractions.

APPENDIX 1: CONCISE SUMMARY OF THE GINZBURG-LANDAU THEORY, WITH SPECIAL REFERENCE TO CYLINDRICAL SOLUTIONS

The Ginzburg-Landau theory is a descriptive theory of superconductors in a magnetic field. It gives a surprisingly accurate treatment of the field penetration, and of the critical-field enhancement in small samples, despite the fact that the underlying model is no longer believed to be realistic.

Soon after the development of the London equation for the penetration of a magnetic field, it was realized that a sizable bulk sample in the presence of a sufficiently large magnetic field must be unstable with respect to the formation of infinitesimally thin laminae of superconducting and normal material. Observation confirmed the existence of such alternating layers in the intermediate state, but indicated a definite lower limit, about 10^{-4} cm, on their thickness. To give a better understanding of the intermediate state, Ginzburg and Landau showed, in 1950, how a reasonable extension of the London equation can lead to the assignment of a positive surface energy in the field equations, at the boundary between superconducting and normal material, thereby curtailing the subdivision of the sample into arbitrarily thin layers. This was done by allowing the effective penetration distance, corresponding to London's λ, to vary spatially as a function of the local field.

In the G-L model, it is assumed that the density of superconducting electrons,"[1] N_s in the London theory, may be properly described by a one-parameter collective wave function ψ, the square of which is to

1. Let us emphasize, once for all, that the concept of "density of superconducting electrons" is at best a mental crutch. In the G-L formulation it is a useful one, nevertheless, in setting down the correct

be taken as proportional to N_s, and which accordingly goes to zero in the normal state. Then, proceeding along the familiar lines of quantum mechanics for a single particle, they assumed the quantum-mechanical contribution to the free energy to be:

$$F_1 = \frac{N_{so}}{2m} \psi^* [- i\hbar \nabla - (q/c)A]^2 \psi \qquad (1)$$

or, equivalently,[2]

$$F_1 = \frac{N_{so}}{2m} \left| - i\hbar \nabla\psi - (q/c)A\psi \right|^2 \qquad (1')$$

where, in the light of our present knowledge, the elementary unit of charge should be set equal to 2e. Let us now factor $(q/c)^2$ out of the expression (1'), and note further that $\hbar c/q$ is just the unit of quantized flux, herein called φ. Also, in anticipation of future developments, we define λ_o such that $1/\lambda_o^2 = 4\pi N_{so}(q^2/mc^2)$. Then the quantum-mechanical free energy becomes:

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free-energy functional; then, in the end, N_s disappears from the equations, because we can express everything in terms of the two empirical functions, $\lambda(T)$ and $H_c(T)$. To be sure, in the Bogoliubov formulation of the BCS theory, one may assign a meaning to N_s in terms of the unexcited quasi-particles; but that has no particular connection with N_s as used here. A bogoliubov excitation is a linear combination of an electron and a hole, and so its charge is not even a definite quantum number—certainly not 2e, as we assume in developing the G-L theory.

2. Strictly speaking, these expressions (1) and (1') are not exactly the same. The difference is a cross term, $2A\cdot\nabla\psi$ in the London gauge, and this can be shown to give zero contribution when integrated over all space, provided that one give proper attention to the delta function occurring in $\nabla\psi$ at the boundary of the sample (where the electron wave function is terminated). In all of the applications of G-L that we treat in this paper, the problem of what to do with $A\cdot\nabla\psi$ is evaded, by making sure that A is everywhere orthogonal to $\nabla\psi$. It is not really meaningful to ask which of these represents the actual energy <u>density</u> at a certain point in space.

$$8\pi F_1 = 1/\lambda_o^2 \mid i\varphi \nabla\psi - A\psi \mid^2 \qquad (1'')$$

So far, we have not said anything that is not already implicit in the London equation, if we admit that $N_s = N_{so} \psi^* \psi$ may be a function of position. But the ingenious part of the G-L theory lies in the phenomenological treatment of the condensation energy: i.e., that part of the gain in free energy F_3, which is specifically due to the rearrangement of electrons in a "condensed," or collective wave function. They assume F_3 is an analytic function of N_s, and hence also of ψ, and that it may be represented by a two-term algebraic series. The great success of the G-L theory rests chiefly on the fact that this bold guess has turned out to be much more accurate than they had any reasonable right to expect.

Summary of assumptions

(1) ψ is an "ordering" parameter, zero in the normal state.
(2) $F = \alpha \overset{*}{\psi} \psi + \beta (\overset{*}{\psi} \psi)^2$, with α and β to be determined.
(3) At equilibrium in zero field, $8\pi F = - H_c$, the critical field of the bulk material.
(4) $\overset{*}{\psi} \psi = N_s/N_{so} = \lambda_o^2/\lambda_T^2$ according to the London model.

At equilibrium in zero field, the condensation term is the only thing contributing to the free-energy difference. So, setting $\partial F_3/\partial\psi$ = 0 gives:

$$2\alpha\, \psi_{eq} + 4\beta\, \psi_{eq}^3 = 2\alpha\left(\frac{\lambda_o}{\lambda_T}\right) + 4\beta\left(\frac{\lambda_o}{\lambda_T}\right)^3 = 0$$

This equation, together with condition (3) determine the two constants α and β, and the free energy "ordering" term then becomes

$$\frac{1}{8\pi} H_c^2 \left[\left(\frac{\lambda}{\lambda_o}\right)^4 |\psi|^4 - 2\left(\frac{\lambda}{\lambda_o}\right)^2 |\psi|^2\right] = F_3(\psi) \qquad (2)$$

This must be true by construction whenever $\psi = 0$, or $\psi = \psi_{eq}$, or $\psi = 1$. So now we assume: (5) This expression holds even when $\psi \neq \psi_{eq}$ and there is field penetration into the specimen. Adding a constant term to complete the square makes the whole expression perspicuously positive, and hence makes more evident the existence of a minimum, to be found by the variational method.

The expression (1) or (1') is invariant under a gauge transformation: $A = A_o + \nabla\chi$; $\psi = \psi_o \exp(i\chi / \varphi)$, where φ again means the flux quantum. Therefore, the gauge may be uniquely specified, in any simply connected body, by requiring ψ to be real-valued.

In addition to the two terms considered so far, there is a contribution $F_2 = (1/8\pi)(H - H_o)^2$, where H_o is the applied external magnetic field, and H is the actual field inside the sample. This term, which is taken over directly from the London theory, merely represents the cost in free energy required to expel the applied field. Finally, it is convenient to take as a variable the ratio of ψ (now supposed to be real) to its equilibrium value λ_o/λ. Define $\phi = \psi/\psi_{eq}$; then we have the complete free-energy functional as follows:

$$8\pi F = \underbrace{\frac{\varphi^2}{\lambda^2}(\nabla\phi)^2}_{\text{"surface" energy}} + \underbrace{(H_o - \text{curl } A)^2}_{\text{magnetization energy}} + \underbrace{\frac{\phi^2 A^2}{\lambda^2}}_{\text{kinetic energy}} + \underbrace{H_c^2 (1 - \phi^2)^2}_{\text{condensation energy}} \qquad (3)$$

This form of the free-energy functional represents, quite literally, all that there is to the Ginzburg-Landau theory. To obtain the Ginzburg-Landau equations, the functional is to be varied simultaneously with respect to the two unknown functions, ϕ and A, so as to obtain a minimum: from here on, the problem is one of calculus of variations. The variational equations are:

$$\frac{\varphi^2}{\lambda^2}\nabla^2\phi - \frac{A^2}{\lambda^2}\phi = 2H_c^2\,\phi(1-\phi^2) \qquad (4)$$

$$\nabla^2 \mathbf{A} - \frac{\phi^2}{\lambda^2}\mathbf{A} = 0 \qquad (5)$$

Examination of equation (5) justifies our assumption that λ is to be identified with the London penetration distance, in the limit of weak field; for then, the solution of Eq. (4) is $\phi = 1$. Sometimes λ/ϕ is called the effective λ.

The appropriate boundary conditions, for an acceptable solution to the variational equations are: $\nabla\phi = 0$ at the boundary of the sample; A and curl A continuous across the boundary; outside the boundary, A satisfies $\nabla^2 A = 0$, while ϕ is undefined; curl A = H_o at infinity.

B. Solution for a Cylinder in a parallel Field

Exact solutions of the non-linear coupled equations (4) and (5) are difficult to obtain. Accordingly, it is preferable to work directly with the G-L free-energy functional, and try to minimize it with an astutely chosen trial function. A trial function that is convenient for the case of a thin cylindrical specimen, of radius a, in a field H_o parallel to the axis, is the following, with one adjustable parameter[3]:

$$\phi = \text{const.} \qquad A = A_\theta(r) = \frac{\lambda\, H_o\, I_1(\phi r/\lambda)}{\phi\, I_0(\phi a/\lambda)}$$

Since nothing depends on the longitudinal coordinate, the free energy

3. The assumption ϕ = const. linearizes Eq. (5), and the solution for A(r) leads automatically to the functional form given here. This type of trial function is quite accurate for specimens whose dimensions are of the order of the correlation distance, and remains rather good even for dimensions even up to several times that amount. The reason is, of

is to be evaluated per unit length and minimized. The results are:

$$\text{Average } 8\pi F = \frac{1}{\frac{1}{2}a^2} \int_0^a 8\pi F(r)\, r\, dr =$$

$$\frac{1}{\frac{1}{2}a^2}\int_0^a \left\{ H_o^2 \frac{I_1^2(\phi r/\lambda)}{I_0^2(\phi a/\lambda)} + H_o^2 \frac{\left[I_0(\phi a/\lambda) - I_0(\phi r/\lambda)\right]^2}{I_0^2(\phi a/\lambda)} + H_c^2(1 - \phi^2)^2 \right\} r\, dr$$

$$= H_o^2 \frac{I_2(\phi a/\lambda)}{I_0(\phi a/\lambda)} + H_c^2 (1 - \phi^2)^2 \qquad (6)$$

Now, differentiating this expression with respect to ϕ, we obtain

$$H_o^2 \frac{2 I_1^2(\frac{\phi a}{\lambda}) - 2 I_0(\frac{\phi a}{\lambda}) I_2(\frac{\phi a}{\lambda})}{\phi \; I_0^2(\frac{\phi a}{\lambda})} + H_c^2 (4\phi^3 - 4\phi) = 0$$

Or: $$\left(\frac{H_o}{H_c}\right)^2 = \frac{2\phi^2(1-\phi^2) \; I_0^2(\frac{\phi a}{\lambda})}{I_1^2 - I_0 I_2} \qquad (7)$$

Equation (7) is to be regarded as determining the equilibrium ϕ (i.e., ψ/ψ_{eq}) implicitly, there being given a known bulk-critical-field curve $H_c(T)$ and a known external parallel field H_o. But further investigation is required, to ascertain whether the said solution (if there is one) corresponds to a stable, metastable, or unstable equilibrium.

For a sufficiently large H_o, $\phi = 0$ is the only solution—stable or otherwise—of Eq. 7: that is to say, the sample goes normal if the

course, that if ϕ varies perceptibly over a correlation distance, then the gradient term constitutes the predominant contribution to the free energy. Note that this assumption does not imply that the unmodified London equation be applicable; for ϕ and hence Λ are allowed to vary as functions of H_o. All the essential non-linear characteristics of the Ginzburg-Landau theory are preserved in this simple trial function; in fact, calculations based on the constant-ϕ assumption were originally made by Ginzburg and Landau themselves.

magnetic field is large. To find more interesting solutions, we must study Eq. 7 to ascertain the range of values of H_o for which a stable solution other than $\phi = 0$ exists. First: If we assume ϕ is only infinitesimally > 0, then the Bessel functions may be replaced by their lowest-order power series expansions. We then obtain

$$\left(\frac{H_o}{H_c}\right)^2 = \frac{2\phi^2}{\frac{1}{8}\left(\frac{\phi a}{\lambda}\right)^2} \quad ; \qquad \frac{H_o}{H_c} = \frac{4\lambda}{a} \qquad (8)$$

So: $H_o = 4(\lambda/a)\, H_c \equiv H_{c1}$ is a solution for which ϕ tends to zero in a continuous manner, giving a second-order transition. Substituting this value into the free-energy functional, and expanding it in powers of ϕ, which is now assumed to be infinitesimally small, we get

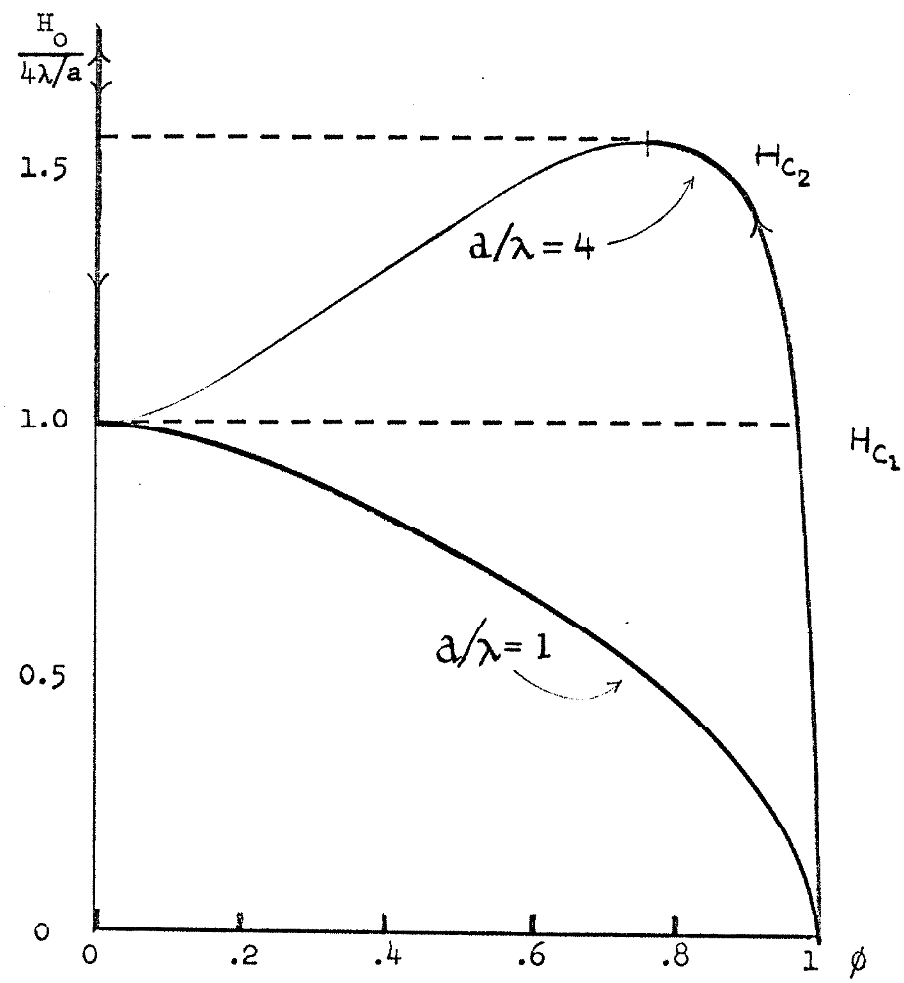
$$H_c^2\left(\frac{16\lambda^2}{a^2}\right)\left[\frac{1}{2}\left(\frac{\phi a}{2\lambda}\right)^2 - \frac{1}{3}\left(\frac{\phi a}{2\lambda}\right)^4 + \frac{11}{42}\left(\frac{\phi a}{2\lambda}\right)^6 - \cdots\right] + H_c^2\;(1-\phi^2)^2$$

If $a^2 < 3\lambda^2$, then the ϕ^4 term is positive and the solution is accordingly stable. This is the condition for the transition to be second= order,[4] and since $\lambda = \infty$ at $T = T_c$, this situation must actually obtain in some temperature range.

When the specimen is small,[5] but not <u>too</u> small, then we may have $a > \lambda\sqrt{3}$, and the situation is more complicated. In order to describe the onset of hysteresis, it is convenient to solve Equation 7 by graph-

4. This result was already obtained in 1951 by Silin, as quoted by O. S. Lutes (op. cit., Sec. IV). As I do not have access to the original paper, I am unable to know how much of the content of this section was anticipated by the Soviet workers, shortly after the advent of the G-L theory. At any rate, similar calculations were made for the thin-film geometry by J. P. Baldwin: Physics Letters, Vol. 3, page 223 (1963).

5. I. e., small enough so that the constant ϕ approximation holds.



A plot of the function defined by Eq. (7): The dark lines indicate stable equilibrium solutions; the light lines indicate unstable solutions; the dashed lines show the assumed jumps, involving a first-order transition, from superconducting to normal or vice versa.

ical means. Under appropriate conditions, there exist stable (or metastable) solutions for which ϕ is nearly unity, even though the applied field H_o may be considerably greater than $4H_c(\lambda/a)$. Consider first the plot shown for $a/\lambda = 4$. If we imagine H_o to increase continuously from zero to about 1.6 H_c, the equilibrium value of ϕ moves downward from 1 to about 0.74, at which point[6] the solution becomes imaginary and therefore unphysical; the system thereupon reverts to $\phi = 0$, the normal state which is always a solution. As we have seen, $\phi = 0$ remains a stable solution all the way down to $H_o = 4(\lambda/a)H_c$; so, the system may now remain at least metastably in the normal state while H_o decreases to that value. Below that point, $\phi = 0$ is still a solution; but now, unstable (i.e., it represents a local maximum in free energy), and so the system jumps discontinuously to the other side of the curve. For values of H_o between H_{c1} [$= 4(\lambda/a)H_c$] and H_{c2}, there is even a third solution—but this one turns out to be always unstable and therefore of no physical interest. By solving the equation graphically for H_{c2}, the locus of the maximum is obtained as a function of λ/a and is plotted roughly in the next figure. For large radii, we find H_{c2} increases proportionally to $a^{\frac{1}{2}}$, while H_{c1} decreases as $1/a$; but neither of these conclusions is realistic because, for large radii, the assumption of constant ϕ must break down; obviously both H_{c1} and H_{c2} approach H_c in the large-sample limit. Interestingly enough, however, it appears that H_{c1} may actually drop <u>below</u> H_c, if the conditions are right, and this may happen before the approximation of a constant ϕ breaks down. Lutes's data appear to indicate one such case.

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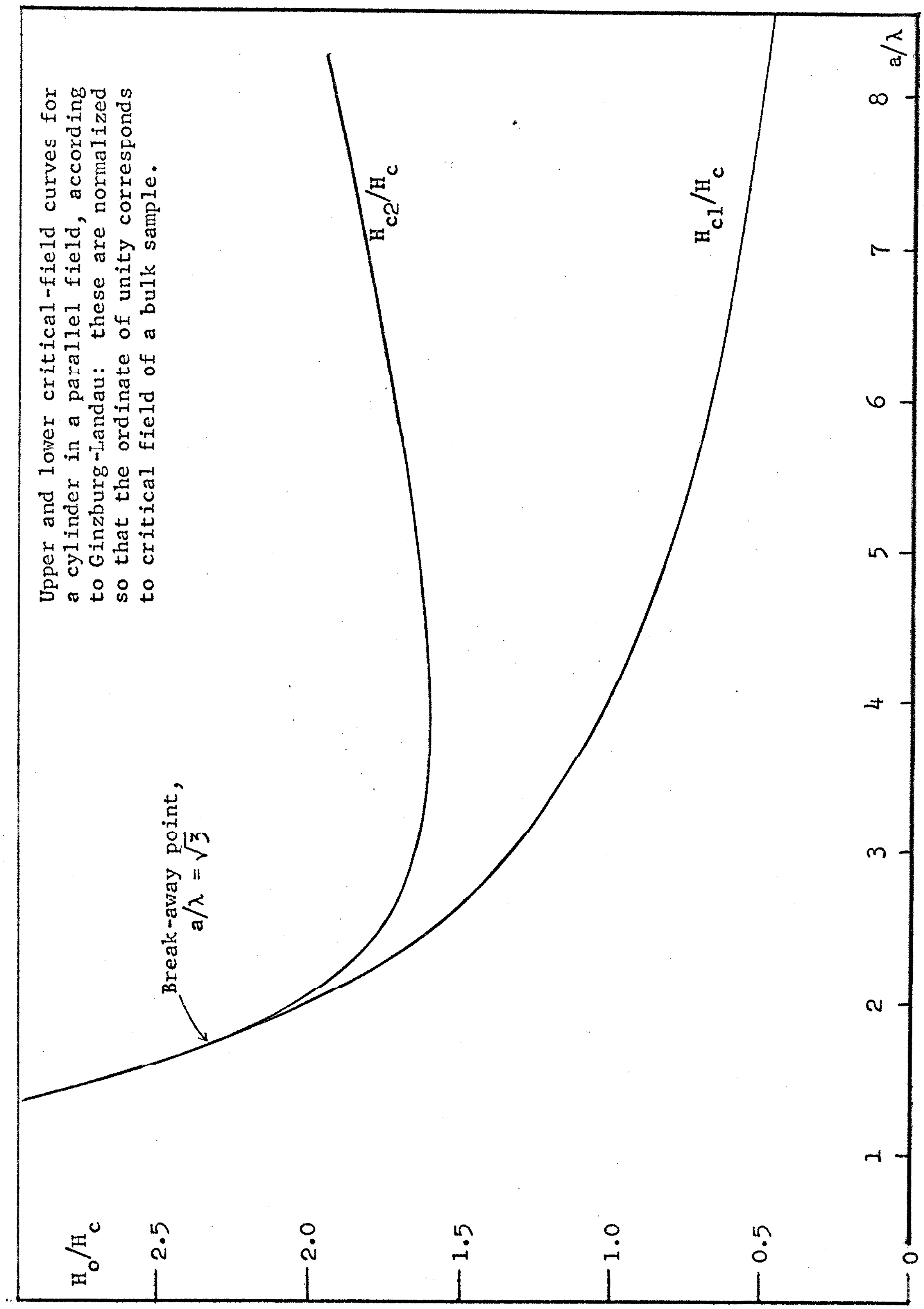
6. A more precise calculation shows that the peak of the curve occurs at $\phi = 0.7440$ and $H_o/H_c = 1.591$.

Figure 9.



Upper and lower critical-field curves for a cylinder in a parallel field, according to Ginzburg-Landau: these are normalized so that the ordinate of unity corresponds to critical field of a bulk sample.

C. Solution for a Cylinder in an Oblique Field

The solution of the G-L equations under the constant-ϕ assumption may be effected by the same method when the sample axis is not parallel to the field. To avoid unnecessary prolixity, we will not give details of the calculations here. Since all terms in the field are quadratic, the energy may be worked out by resolving the field into parallel and perpendicular components, which are orthogonal and thus may be treated separately. For the perpendicular field component, the field energy in space outside the sample, as well as inside, must be included. The result turns out to be

$$\frac{\phi^2 A^2}{\lambda^2} + (H_\theta - H)^2 \frac{r\,dr\,d\theta}{2\pi} = a^2 \frac{I_2(\phi a/\lambda)}{I_0(\phi a/\lambda)} H_o^2$$

that is, the perpendicular field requires just twice as much energy, to be excluded, as does the parallel field. For a field H_o at an angle α to the sample, the field contribution to the energy turns out to be

$\frac{1}{2}H^2 a^2 (1 + \sin^2 \alpha) \frac{I_2(\phi a/\lambda)}{I_0(\phi a/\lambda)}$. Thus, everything in the previous section carries over to the oblique-field case, if we make a rule that an oblique field H_o behaves like an effective parallel field of intensity $H_o (1 + \sin^2 \alpha)^{\frac{1}{2}}$. In particular, this suggests that the hysteresis effect should be found in transverse as well as parallel field, with both H_{c1} and H_{c2} being reduced by a factor $\sqrt{2}$ in a perpendicular field. This general conclusion is true independently of whether the constant-ϕ assumption holds exactly; provided, merely, that the behavior of ϕ is not itself influences by the angular orientation of the field. This we may safely assume, for the ability of ϕ to vary over the size of the sample is restricted mainly by the dimensions of the boundary.

D. The Abrikosov solution

We conclude this chapter with a few words about the Abrikosov flux bundles, or vortices. In the original form (1 or 1') of the quantum= mechanical contribution to F, there is one way in which ψ may be allowed to vary over a distance $\ll \xi$, without causing a large increase in energy. This is by making A also vary, in such a way that, when they are combined coherently as in (1'), the two singular parts cancel each other. Consider the following substitution:

$$\psi = \psi_o \exp(iN\Theta) \qquad A = A_\Theta = \mathfrak{A}(r) + \frac{N\varphi}{r} \tag{9}$$

Here Θ is the azimuthal coordinate; if N is an integer, ψ is evidently single valued. It may be easily verified that this "gauge transformation" formally reproduces the G-L free energy functional in the same form; the generalization to finite temperature by taking $\phi = \psi_o/\psi_{o(eq)}$ goes through just as previously. But, it may be quickly objected, what we have done here is not a legitimate gauge transformation; for, the term $\nabla\chi = N\varphi/r$, that generates it, is singular at $r = 0$. The interesting circumstance is, however, that solutions exist of Eq. (5) in which A, or $\mathfrak{A}$ as we now call it, behaves like $K_1(\phi r/\lambda)$ near the origin; and then, by appropriate choice of the constant in front of the gauge term, we may make the "real" A perfectly finite at the origin. We may consider the transformation (9(to be a mathematical artifice for classifying the types of solutions to the G-L equations. (Of course, it does represent the unique gauge transformation to a real ψ if considered in a simply connected region excluding the origin.) These solutions represent quantized flux bundles containing N quanta. Their existence was first pointed out in a famous paper by Abrikosov[7]; subsequently, ample experimental evidence has been found that they actually exist. To recapitulate: A flux bundle is a solution to the following coupled equations —

$$\varphi^2 \nabla^2 \phi - \mathcal{Q}^2 \phi = 2\lambda^2 H_c^2 \phi (1-\phi^2) \qquad (4')$$

$$\frac{1}{r}\frac{d}{dr} r\mathcal{Q}(r) - \frac{\phi^2}{\lambda^2}\mathcal{Q}(r) = 0 \qquad (5')$$

subject to the following boundary conditions:

$\nabla\phi \cdot \underline{n} = 0$ at the surface

$\frac{1}{r}\frac{d}{dr} r\,\mathcal{Q} = H_0$ at the surface, $\mathcal{Q} \to -\frac{N\varphi}{r}$ at $r = 0$

In an extended medium, the outer boundary may be regarded as an adjustable parameter to further reduce the average free energy. These conditions define an Abrikosov vortex; the solution discussed in the preceding section[8] may be considered as a special case, by setting N = 0. The remaining question is: Are these solutions stable; that is, can the system find a lower free energy by allowing the flux to penetrate in quantized bundles? If so, what value of the integer N is preferred? Abrikosov answered the first question by showing that the flux bundles are stable or unstable, according to the value of a certain parameter κ, the ratio of the condensation energy to the surface-energy term. If $\kappa < \sqrt{2}$, the flux bundles are unstable in a longitudinal field; if $\kappa > \sqrt{2}$, the flux-bundle solution becomes the more stable. In a trans-

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8. More correctly, the constant-ϕ solution is a close approximation to the correct solution for N = 0.

verse or oblique field, as Tinkham has shown,[9] the flux-bundle solution may be stable even when κ is small, for then the system is required to supply extra energy in order to exclude the field from spatial regions exterior to the sample. Moreover, investigating the question of what value of N is preferred under these circumstances, Tinkham found that the competition between different N may be rather close, and so it is not possible to say for certain which value may be preferred. Now, our experiments have provided further evidence along this direction, for we find that the equilibrium value of N may change several times as the temperature varies through the transition.

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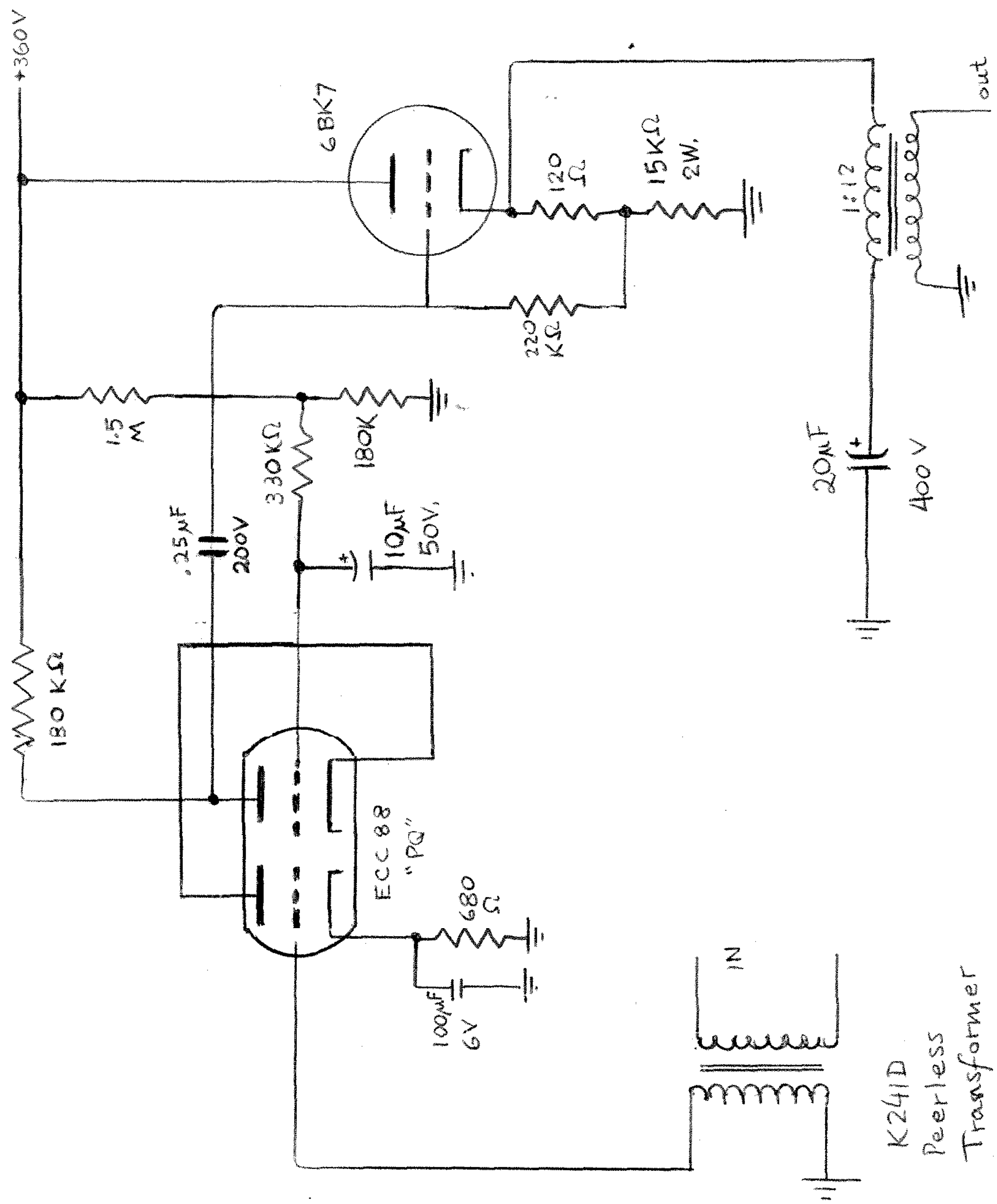
9. See Chapter V, note 1.

Appendix 2: Diagram of the Cascode Amplifier



This circuit is based on a low-noise amplifier designed by Dr. Jim Mercereau. Modifications introduced by the author include the addition of the output transformer, for better impedance matching into the wave analyzer, and changing several parameters of the circuit to obtain a high linearity at the expense of slightly increasing the noise figure. The cathode follower utilizes only half of the 6BK7 tube.

BIBLIOGRAPHY

A reasonably complete bibliography on superconductivity, even if it were restricted to the period of the modern (i.e., since 1957) understanding of the subject, would comprise many pages of references; the compilation of it would be a project of comparable scope to this entire paper. The much more modest list here is meant to include only sources that are really germane to the topics of the present paper; yet undoubtedly many equally good sources, notably those in the foreign literature, have been overlooked.

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John Bardeen, Leon N. Cooper, and J. R. Schrieffer: Physical Review, Vol. 108, p. 1175 (1957). This is the celebrated BCS Theory.

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