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FLUCTUATION DIAMAGNETISM OF ALUMINUM AND
ALUMINUM ALLOYS ABOVE THE SUPERCONDUCTING
TRANSITION TEMPERATURE

by

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ABSTRACT

Thermodynamic fluctuations in the order parameter ψ have been shown to produce a small diamagnetic response at temperatures above the superconducting transition temperature T_c . Gollub, Beasley and Tinkham (GBT) have measured this effect for Pb and In, both pure and with impurities. They observed that the variable $M'(T)/(\sqrt{H} T)$ is a function only of scaled field and temperature variables H/H_s and $(T-T_c)(dH_{c2}/dT)/H$. Here M' is the magnetization ascribed to fluctuations and H_s is a scaling field obtained empirically for each material.

The functional behavior and values of H_s observed by GBT could not be explained satisfactorily with any theory based on the Ginzburg-Landau formulation. A microscopic calculation obtained independently by Kurkijarvi, Ambegoakar, and Eilenberger; and Lee and Payne, has been shown to be in rather good agreement with the experimental results for pure Pb and In. For the alloys measured by GBT, however, the dependence of the scaling field on ξ_0/ℓ (ξ_0 is the BCS coherence length, ℓ is the electron mean free path) is not completely consistent. All of these alloys, moreover, fail to meet a condition for the validity of the microscopic theory that

$$\xi_0/\ell \ll 0.18 \theta_D/T_c.$$

We have measured this effect in both pure Al and Al alloys of solute concentration 0.05 and 0.15 at.% Ag and 0.1, 0.3, 0.5, and 0.8 at.% Si. The apparatus used for these measurements included a SQUID magnetometer in a configuration similar to that of GBT which allowed a resolution in sample magnetization of $\sim 2 \times 10^{-9}$ Gauss. The fluctuation magnetization was separated from other contributions by the fact that it is temperature dependent and is completely quenched in sufficiently high fields or temperatures. The apparatus could operate in fields $H > 100$ Oe and allowed the sample temperature to be raised as high as 5 K.

The alloy specimens were polycrystals, and comprised a range of values for ξ_0/ℓ from 2 to 17; these are all within the range of validity of the microscopic theory, since for Al one finds that $0.18 \theta_D/T_c \sim 60$. We concentrated on measurements of the field dependence of $M'(T_c)$ for these specimens, since this is of primary interest in current theories. It was found that for the samples with $\xi_0/\ell \leq 8$, the shape of $M'(T_c)/(\sqrt{H} T_c)$ vs. $\log H$ was reasonably close to the theoretical one, except in the low field regime, where M' is larger than expected. It is believed that this deviation is at least partly due to a lack of complete homogenization of the solute. The more concentrated Si alloys ($\xi_0/\ell \approx 10$ and 17) had a shape somewhat different in detail from the "universal" one.

The scaling fields for all the alloys fell considerably below the predicted dependence $H_g = 0.018(\phi_0/\xi_0^2)(1 + 0.88\xi_0/\ell)^2$, and in fact were somewhat better represented by the results of a calculation by Maki and Takayama which predicts a dependence on mean free path $\sim \xi_0/\ell$. Some technical details of this calculation have, however, been disputed by the authors of the microscopic theorys.

CHAPTER I: INTRODUCTION

The superconducting transition in zero field is probably the closest nature has come to providing us with an "ideal" second-order transition- ie, one in which there is a sharp discontinuity in the specific heat. Most other transitions which are of higher than first order (eg, ferromagnets, antiferromagnets, λ -transition in He^4 , order-disorder) generally display rather broad transitions, which can be attributed to the effect of fluctuations. That is, as the transition temperature is approached the difference in free energy between the ordered and disordered phase vanishes, and the system wavers between them, taking on some of the properties of both. As we shall see, a superconductor is saved from this fate (except in an unobservably small temperature range) by virtue of its very large correlation range. The observed width of its transition (as small as 10^{-5}K) can be ascribed exclusively to inhomogeneities, etc.

This does not mean that fluctuation effects are absent in superconductors-only that they are rather small. The primary concern experimentally has usually been to enhance these effects enough to make them observable by examining samples of reduced dimensionality or small correlation lengths. However with the development of very sensitive superconducting magnetometry, it has become possible to observe bulk fluctuation effects in the magnetic susceptibility of pure superconductors above T_c . It is observed that the perfect diamagnetism of the material in its superconducting state is anticipated by a much smaller diamagnetic signal which grows as $T \rightarrow T_c$ from above.

The goal of the work reported in this thesis was to measure these effects in aluminum and some of its dilute alloys.

In the second chapter we will review the work that has been done to date on this subject. This includes a veritable flood of theoretical efforts; in order to provide physical insight, we discuss in some detail the mean field approach to this problem (i.e., the Ginzburg-Landau theory). As it turns out, this theory is of little utility for solving the problem, and recently more powerful theoretical ammunition has been brought to bear with rather more success.

We report in addition on the excellent pioneering experimental work that was done by Gollub, Beasley, and Tinkham. Their measurements on Pb and In stimulated considerable theoretical research, which resulted finally in a theory which satisfactorily accounted for their data for pure materials. They have also obtained results for dilute alloys, but we express doubts about the applicability of current theories to these measurements. We consider finally the advantages that are provided by Al and Al alloys with respect to a comparison to these theories.

In Chapter III the details of the experimental apparatus that was used are discussed. Because of the extreme sensitivity to sample magnetization that was required, we devote a good deal of space to a discussion of the practical considerations that are involved in state of the art utilization of SQUID magnetometers. In addition, possibly useful details of our experiences with the more standard problems of temperature measurement and control, resistivity measurements, and sample preparation are included.

This experiment had its standard share of anomalies, unforeseen diffi-

culties, etc. These are discussed, along with other necessary preliminary observations, in Chap. IV. In particular, we note a curiously broad transition that occurred only for pure single crystals, and discuss the problems in obtaining homogeneous alloys in Al, as well as various diagnostics.

The heart of this work is reached in Chap. V, where the results of measurements on fluctuation-induced diamagnetism are reported, for both pure Al and a variety of alloys. We also note a discrepancy between our results on pure Al and those reported by other workers, and give various arguments supporting the trustworthiness of our measurements.

Finally, in Chap. VII we summarize the results that have been obtained both here and elsewhere and compare them with the relevant theories.

Some of the more technical considerations from Chap. III have been placed in two appendices; one is an analysis of the feedback arrangement involved in temperature control, which is quite straight-forward. The other contains calculations and discussion relating to the problem of optimizing the efficiency of the "flux transformer" configuration. This subject has been touched on in various places in the literature, but never seriously examined-particularly with reference to practical experimental limitations.

Chapter II

REVIEW OF THE SUBJECT

A. Theory

It is well known that many of the equilibrium properties of superconductors in the vicinity of the transition temperature T_c are described by the Ginzburg-Landau (GL) equations:

$$\begin{aligned} [\alpha(T) + \beta|\psi|^2 + \frac{\hbar^2}{2m} (-i\nabla - \frac{2\pi}{\phi_0} A)^2] \psi(r) &= 0 \\ j &= \frac{e\hbar i}{m} (\psi^* \nabla \psi - \psi \nabla \psi^*) - \frac{4e^2}{mc} |\psi|^2 A \end{aligned} \quad (1)$$

Here $\psi(r)$ is the order parameter; roughly speaking, it can be regarded as a wave function describing the collective motion of the superconducting electrons, where $|\psi|^2$ is the density of such electrons. α and β are parameters characteristic of the particular metal, m is the electron mass, A is the vector potential, and $\phi_0 = \frac{hc}{2e}$ is the "flux quantum". Among the predictions of this theory are: a second order phase transition in zero magnetic field, the exclusion (in type I superconductors) of magnetic fields for temperatures less than

$$T_c(H) = T_c - H \left(\frac{\beta}{4\pi} \right)^{1/2} \frac{1}{d|\alpha|/dT},$$

the existence of a coherence length and penetration depth which both diverge as $|T - T_c|^{-1/2}$ around T_c , etc. The solutions of the GL equations which lead to these results are the functions $\psi(r)$, $A(r)$ which minimize the "GL free energy functional:"

$$F_{GL}(\psi) = \int d^3r \left\{ \alpha |\psi|^2 + \frac{\beta}{2} |\psi|^4 + \xi^2(T) \left| \left(\nabla - \frac{2\pi i}{\phi_0} A \right) \psi \right|^2 \right\} \quad (2)$$

where the sign of the first term is that of $\alpha \sim (T - T_c)$, and the temperature dependent coherence length is defined by $\xi^2(T) = \hbar^2 / (2m|\alpha|)$.

The time averaged value of $\psi(r)$ is expected to be that which minimizes

F_{GL} ; at finite temperatures, however, we expect that there will be local thermodynamic fluctuations of ψ away from $\langle\psi\rangle$. The probability of such a fluctuation is proportional to $\exp(-\delta F_{GL})$, where $\delta F_{GL} = F_{GL}(\langle\psi\rangle + \delta\psi) - F_{GL}(\langle\psi\rangle)$. Hence the typical amplitude and spatial extent of a fluctuation $\delta\psi$ can be estimated with reference to the GL functional. In particular, we see that a minimum size is implied by the gradient term, while the powers of $|\psi|$ limit the amplitude. It is instructive to estimate the fluctuations in ψ for $T > T_c$ in the absence of magnetic fields: Since $\langle\psi\rangle = 0$ and the amplitude of the fluctuations is assumed to be small, the quartic term can be ignored. Then $F_{GL}(\psi)$ is a linear operator, and spatial fluctuations of the form $\psi = \psi_q e^{iqx}$ represent independent modes, each with an energy $F_{GL}(q) = V|\alpha|(1+q^2\xi^2)\psi_q^2$ where V is the volume of the system. The average value of ψ_q^2 is obtained by setting $F_{GL}(q) = kT$, which gives

$$\langle\psi_q^2\rangle = \frac{2mkT}{V\hbar^2} \frac{1}{[q^2 + (1/\xi^2)]} \quad (3)$$

We see that in the long wavelength limit the amplitude for fluctuations is constant, and becomes attenuated for wavelengths $< \xi(T)$. In fact, various considerations suggest that it should be cut off more dramatically than suggested by Eq. 3. We have $\langle\psi(r)^2\rangle = \sum_q \langle\psi_q^2\rangle$, which in three dimensions becomes $V/(2\pi)^3 \int d^3q \langle\psi_q^2\rangle$; if Eq. 3 is used, this expression is divergent, which implies that a cutoff wave vector q_{max} must be introduced. As suggested above, this is usually taken to be $^{(2)} q_{max} = 1/\xi(T)$, which gives finally

$$\langle|\psi(r)|^2\rangle \approx \frac{mkT}{\pi^2\hbar^2} \frac{1}{\xi(T)} \sim |T - T_c|^{-\frac{1}{2}} \quad (4)$$

It may seem unsettling that this vanishes at $T = T_c$; however, it turns out

that most observable fluctuation phenomena diverge in some fashion about T_c , which is intuitively reasonable.

Eq. 4 can be obtained in a more intuitive manner by the following approach: We see from the form of F_{GL} that spatial variations of ψ on a scale smaller than $\xi(T)$ are energetically expensive, so that most fluctuations will be coherent over distances of this magnitude. To simulate this, we imagine that the specimen is divided into regions $\sim \xi^3$ in volume, and that within each such volume ψ is uniform and uncorrelated with adjacent volumes. The amplitude of ψ^2 within any volume is obtained by setting $kT = (\text{vol}) \times |\alpha| \langle \psi^2 \rangle = \xi^3 [\hbar^2 / (2m\xi^2)] \langle \psi^2 \rangle$, which leads immediately to Eq. 4 (to within the accuracy we are talking about). This argument can be applied to samples of "reduced dimensionality" - i.e. where one or more of the sample dimensions is less than the coherence length; we have simply to replace the fluctuation volume ξ^3 with $\xi^d L^{3-d}$, where d is the dimensionality of the sample and L is the size of the reduced dimension(s). We then find $\langle \psi^2 \rangle \propto \xi^{2-d} / L^{3-d}$, and clearly the fluctuations are enhanced for $d < 3$. Originally it was thought that fluctuation effects could only be observed for such cases, or possibly in bulk samples with extremely small coherence length. Indeed, fluctuation effects have been observed in specimens whose dimensionality is zero⁽³⁾, one⁽⁴⁾, and two⁽⁵⁾.

At this point we feel that it is important to distinguish between two conceptions of a "fluctuation effect". The first arises when one considers what is the range of validity of a mean field theory (e.g. the GL theory)⁽⁶⁾. It is generally believed that once the fluctuations in ψ predicted by the GL functional become too large, the theory itself breaks down completely; at this point, one is in the "critical region", for

which at present no real theory can be said to exist. The criterion for what constitutes fluctuations that are "too large" has been discussed by Hohenberg⁽⁷⁾. He concludes that for superconductors a criterion first proposed by Ginsberg⁽⁸⁾ is appropriate: that the fluctuations from the "equilibrium" value of ψ should be small enough that the corresponding variation in F_{GL} contain no significant terms of higher order in $\delta\psi$ than quadratic. Another way of saying this is that the fluctuation modes should be essentially independent. It is easy to show that both above and below T_c this leads to the requirement $\langle |\delta\psi(r)|^2 \rangle \ll |\alpha|/\beta$. Since the r.h.s. of this expression approaches zero near T_c faster ($\sim |T-T_c|$) than the l.h.s. ($\sim |T-T_c|^{\frac{1}{2}}$), there is necessarily a range of temperatures around T_c where this condition is not satisfied. For a pure bulk superconductor, it turns out this happens for $|\Delta T|/T_c < \sim 10^{-16}$ - i.e., the critical regime is for all practical purposes experimentally inaccessible. In samples of reduced dimensionality, this temperature region is enhanced, and for "zero-dimensional" samples may be experimentally accessible⁽³⁾.

Nevertheless, when we speak in general of fluctuation phenomena in superconductors, we are not referring to the critical region discussed above. Rather, we are considering possible deviations in the equilibrium properties of superconductors from those predicted by the minimization condition on F_{GL} ; these are due to fluctuations in ψ which in principle can themselves be adequately represented by mean field theory. This means that it is not quite correct to represent F_{GL} as the free energy; the exact free energy F (or rather that part of the free energy due to the interaction that leads to superconductivity) is generally taken to be

$$F = -kT \ln \left\{ \int \delta\psi \exp[-F_{GL}(\psi)/kT] \right\}, \quad (4)$$

where the integral refers to a "functional integral" over all possible functions $\psi(r)$. We note that if F_{GL} has a sharp minimum in ψ -space then the integral is dominated by a small region about ψ_{min} , and minimization of F is almost equivalent to minimization of F_{GL} .

In the region above T_c and outside the critical region, Schmid⁽⁹⁾ indicated the procedure to follow in order to perform this integral: We can construct any function $\psi(r)$ as a linear combination of the set of independent fluctuation modes ψ_i (which are just the solutions of the Schrodinger equation for a particle of mass m , charge $2e$). The corresponding $F_{GL}(\psi)$ is given by $\sum_i |C_i|^2 E_i$, where C_i is the coefficient of ψ_i and $E_i = F_{GL}(\psi_i)$. If we insert this expression for $F_{GL}(\psi)$ into Eq. 4 and integrate each C_i over all real and imaginary values, the prescribed integration over all possible $\psi(r)$ will have been accomplished. The result is:

$$F = -kT \sum_i \ln\left(-\frac{kT}{E_i}\right) . \quad (5)$$

Our concern in this thesis is fluctuation effects in the magnetization of a superconductor above T_c — in the mean field approximation, this is exactly zero. To obtain a correction to this result, we use the "exact" free energy functional as is given above, where $M = -(1/V)(\partial F/\partial B)$. Still following Schmid, we note that in a magnetic field the energies E_i become

$$E_{q,n} = \frac{\hbar^2}{2m} [q^2 + \frac{1}{\xi^2(T)} + \frac{2\pi B}{\phi_0} (2n+1)] .$$

corresponding to the orbits of a free charged particle in a field; here q represents the motion parallel to the field and n is related to the radius of the orbit. Taking proper account of degeneracies, we find

$$\sum_i \ln\left(\frac{\pi kT}{E_i}\right) \rightarrow V \frac{eB}{\pi \hbar c} \sum_n \int \frac{dq}{2\pi} \ln\left(\frac{\pi kT}{E_{n,q}}\right) . \quad (6)$$

Schmid was able to solve the resulting expression in the limit $B \ll \phi_0/2\xi^2(T)$, obtaining

$$M' = -\frac{\pi}{6} \frac{kT}{\phi_0^2} \xi(T) B \quad (7)$$

where the prime distinguishes this source of magnetization from other processes not involving superconductivity. Other authors⁽¹⁰⁾⁽¹¹⁾ obtained essentially the same result with different techniques; the basic physics that went into these calculations is presumably the same.

The restriction on B that is required for this to be valid is experimentally prohibitive for pure superconductors; nevertheless, some general conclusions about the nature of fluctuation-induced magnetization that might be drawn from this result are: (a) It diverges, as expected, near T_c (as opposed to $\langle\psi^2\rangle$). (b) The temperature dependence is rather slow - $\sim (T-T_c)^{-\frac{1}{2}}$. (c) The magnitude of the effect is $\chi \sim 10^{-7} |T_c/(T-T_c)|^{\frac{1}{2}}$; in small magnetic fields (~ 1 Oe) it cannot be observed by conventional techniques. (d) The effect appears to be largest for materials with large coherence length - again different from the behavior of $\langle\psi^2\rangle$. This last conclusion, as we shall see, is quite misleading.

An exact solution for M' using the expression of Schmid for the free energy was later obtained by Prange⁽¹²⁾; he found that

$$-M' \propto \sqrt{B} T f(x) \quad (8)$$

where x contains the temperature dependence:

$$x = \frac{mc}{e\hbar} \frac{\alpha(T)}{B} = \frac{(T-T_c)}{B} \frac{dH_{c2}}{dT}$$

The most important difference between this result and that of Schmid is that the divergence in M' occurs at $x = -1$, which corresponds to the temperature $T_{c2}(B) = T_c - B/(dH_{c2}/dT)$. Otherwise, the dependence of $f(x)$ is

not too different from $(1+x)^{-\frac{1}{2}}$, which corresponds to the Schmid temperature dependence $\sim \xi(T)$. The nonlinear dependence on B results from the fact that the origin for this $(\Delta T)^{-\frac{1}{2}}$ dependence is shifted downward as B increases. An apparently equivalent result was obtained by Tsuzuki and Koyanagi ⁽¹³⁾ in a microscopic calculation using the Ginsburg-Landau-Gorkov approximation.

The shift in the origin of the divergence in temperature is easily understood: By definition ⁽¹⁾ $T_{c_2}(B)$ is the highest temperature at which bulk superconductivity can coexist with a magnetic field B in the specimen; in a type I superconductor [$T_{c_2}(B) < T_c(B)$] it is the lowest temperature to which it can supercool, implying that the nucleation barrier against formation of superconducting regions vanishes as $T \rightarrow T_{c_2}$. It is quite reasonable then, that fluctuations should lead to a smooth approach of the susceptibility to the superconducting value $\chi = -1/4\pi$ as $T \rightarrow T_{c_2}(B)$. On the scale of sensitivity we are talking about, this is for all practical purposes a divergence.

In the meantime, Patton, Ambegaokar and Wilkins (PAW) ⁽¹⁴⁾ concluded from general considerations that any calculation based on the GL functional is bound to fail at high fields or temperatures; this is based on the suggestion, which we have already mentioned, that the amplitude of short wavelength (high energy) fluctuations should fall off more rapidly than is predicted by Eq. 3. If we write the energy denominator in Eq. 6 as

$$E_{qn} = \frac{\hbar^2}{2m} \left\{ q^2 + \frac{1}{\xi(0)^2} \left[\frac{\Delta T}{T_c} + \frac{B}{H_{c_2}(0)} (2n+1) \right] \right\}$$

we note that if the quantity in [] is small, the result of the integral over q is primarily determined by a sharp maximum in the argument around

$q = 0$ - i.e. only the low-energy fluctuations contribute significantly to the results. On the other hand, if the temperature or field are "large" (on a scale of T_c and $H_{c2}(0)$, respectively) the suspect high energy terms contribute significantly. These authors therefore concluded that a correct theory in this regime could be derived only with reference to the microscopic (BCS) theory.

In fact, the microscopic theory has been cast into a functional integral form⁽¹⁵⁾. PAW observed that the free energy can be expressed in a form similar to Eq. 6, and that the argument of the logarithm can be easily calculated in the limits of sufficiently small or sufficiently large fluctuation energy: it is $\propto E_{qn}^{-1}$ for the former and ≈ 1 for the latter case. From this theory they concluded that the GL formulation is basically correct, provided the sums are somehow cut off for sufficiently large energies. The cutoff energy is related to the crossover region between the two limiting forms given above; PAW proposed to treat it as a parameter, rather than attempt to extract it from the murky details of the microscopic theory. To simulate the cutoff in a mathematically tractable form, they replaced the argument of the logarithm in Eq. 6 $[(\pi kT)/(E_{q,n})]$ with $[1 - \exp(-E_{n,q}/E)]^{-1}$ where E is the cutoff parameter. The result of their calculation is equivalent to that of Prange in the limit of small B and ΔT , independent of the choice of E ; at large fields or temperatures, however, the magnetization is strongly depressed from the Prange result. In this range the results are scaled by $H^* = (mcE)/(\hbar e)$ and $T^* = 2mE\xi(0)^2/\hbar^2$. An educated guess by PAW for the magnitude of E leads to a value of $H^* \geq H_{c2}(0)$, $T^* \geq T_c$.

The fact that a cutoff in the energy spectrum should lead to a depres-

sion in $|M'|$ can be easily understood: we note that the terms in Eq. 6 refer physically to the occasional appearance of a Cooper pair which moves in one of the Landau orbits identified by n, q . The motion in such an orbit is such that it tends to shield out the external field - i.e., produce a diamagnetic effect. Hence a reduction in the number of such fluctuations considered leads to a reduction in $|M'|$.

The results of Prange and PAW suggest that an appropriate variable for experimental consideration is $-M'(T)/(\sqrt{H} T)$; this is predicted by the former theory to be a function only of $(\Delta T/H) (dH_{c2}/dT)$, and in particular to take on the value $4.74 \times 10^{-7} \text{ G}/(0e \frac{1}{2}\text{-K})$ at $T = T_c$, independent of all material parameters. This number has come to be called the "Prange Limit". The PAW results are also appropriately plotted in these variables; in particular, a graph of the field dependence at $T = T_c$ shows a fall-off at high fields from the Prange result (which is field-independent). This is shown in Fig. 1.

Lee and Payne,⁽¹⁶⁾ starting from the linearized Gorkov equation, were able to construct a free energy functional which is valid for pure superconductors in strong magnetic fields and for fluctuations of small spatial extent; they found in particular that for large B non-local effects become important in a manner not apparent from a superficial examination of the theory. It turns out that these effects, rather than the detailed treatment of high energy fluctuations, lead to a cut-off field considerably less than expected from PAW-like considerations.

In a later paper⁽¹⁷⁾ these authors obtained the same results from another approach to the microscopic theory, and were able to extend their analysis to include the case of a superconductor with impurities. The

same results were independently arrived at, using a different technique, by Kurkijarvi, Ambegaokar and Eilenberger.⁽¹⁸⁾ The most stringent condition on how "dirty" a sample can be accurately represented by these theories is the requirement that the uncertainty in energy of an electron state of definite momentum should be much less than the energy width of the BCS attractive interaction. If this latter is taken to be $k_B \theta_D$, we find that one must have $\xi_0/\ell \ll 0.18 (\theta_D/T)$. Here ξ_0 is the BCS coherence length = $.18 \hbar v_F / (kT)$, ℓ is the electron mean free path, θ_D is the Debye temperature. With this restriction, the theory indicates that the cut-off field should increase with increasing dirtiness as $(1 + 0.88 \xi_0/\ell)^2$; for ξ_0/ℓ as high as 16, the deviation from this dependence is no more than ~20%. This implies that these theories do not go over to a PAW-type result once the non-local effects are suppressed, since the latter is expected to vary as $H_{c2}(0) \sim (1 + \xi_0/\ell)$.

A paper by Maki and Takayama⁽¹⁹⁾, which is supposed to cover the dirty limit ($\xi_0 \gg \ell$), leads to results in substantial disagreement with the above theories. They use a GL type of functional which, when minimized, leads to the time dependent GL equation. A functional integral using this form leads to an expression like Eq. 6, with an additional term in $E_{n,q}$ given by $[(\pi \hbar)^2 / 8m \xi(0)^2] |m|$, and a corresponding sum over m . These extra terms are described as "dynamical fluctuations", and the results obtained are advertised as following from a correct treatment including these terms. However, the microscopic theories cited above also include "dynamical" terms, and these authors claim that the results given by Maki and Takayama follow primarily from their inexplicably dropping a large contribution at some point. In any case, the reported results indicate a

falloff of $M'(T_c)/(\sqrt{H} T_c)$ in high fields with a shape not too different from the microscopic theory; the predicted cutoff field, however, varies as $H_{c2}(0)$, which is quite different from the microscopic theory.

Finally, we mention a paper by Usadel⁽²⁰⁾ in which he points out that for the extreme dirty limit, a term which is ignored in the previous microscopic theory in fact becomes quite important. When it is retained, he finds that the magnetization can be calculated for $B < H_{c2}(0)$; unfortunately, this range yields only a small part of the fall-off from the Prange limit. A reasonable extrapolation suggests that the cut-off field is $\sim 2H_{c2}(0)$. This result is limited in validity to the extreme dirty limit ($\xi_0/2 > 50$).

The term in question was previously ignored because it does not diverge around $T_{c2}(H)$. Usadel points out that this criterion is used to neglect a great many diagrams in the microscopic theory as presently formulated, and suggests that some of these may turn out to be more significant than was imagined. A similar point has been made by Patton and Wilkins,⁽²¹⁾ who point out that the microscopic results for dirty superconductors contain a large contribution from non-singular terms.

In Fig. 1 we summarize the predictions of these various theories for the field dependence of the magnetization at $T = T_c$, where each has been scaled, if possible, by the field H_g at which it is predicted that $-M'(T_c)/(\sqrt{H} T_c)$ is just 1/2 the Prange value.

Fig. 1. The magnetic field dependence of the fluctuation-induced magnetization M' at T_c , as predicted by various theories. The indicated scaling field H_s in each case is that at which M' is half the Prange value.

B. Previous Experiments

The major previous experimental work on this subject was done by a group at Harvard and is summarized in a paper by Gollub, Beasley and Tinkham⁽²²⁾ (hereafter referred to as GBT). It is described in more detail in a thesis by Gollub,⁽²³⁾ which involves results for indium, lead and an alloy of Pb-5% Tl. Preliminary results on tin by this group⁽²⁴⁾ were apparently not followed up; and other groups^{(25),(26)} observed anomalous behavior in this superconductor. In Ref. 25. results for In and Tl over a narrow temperature range were also reported, with results consistent with the early work of GBT. For this initial data, the samples were immersed in the liquid Helium bath and the accessible temperature range was fairly small; an attempt to fit this data to the theory of Prange was not entirely convincing, because of resulting baseline uncertainty. To determine the fluctuation magnetization unambiguously, GBT assumed that for sufficiently high temperatures it becomes entirely quenched, so that $M'(T)$ can be separated from other susceptibility mechanisms by its temperature dependence. (The Pauli spin paramagnetism and Landau diamagnetism are for all practical purposes temperature independent). This assumption is intuitively reasonable, but is not corroborated by the Prange theory, which indicates a minimum for $M'(T)$, with a subsequent rise for large T . The theory of PAW, as well as the microscopic theories, do predict that M' vanishes at high temperatures. Using an apparatus in which the temperature of the sample could be raised as high as 16 K, GBT verified that for In at all fields ΔM became independent of T sufficiently far above T_c . The same was true for Pb in fields

<50 Oe; at higher fields it was felt that with a greater temperature range full quenching of fluctuation effects would have been observed. The changes in magnetization were monitored with a SQUID magnetometer.

The results, as we have indicated, showed qualitative agreement with PAW; a graph of the normalized magnetization at T_c vs. applied field was observed to rapidly fall off from the Prange limit. Although the shape of the fall-off was quite different, another important prediction of PAW was verified: it was found that graphs of this kind for different materials would coincide if the field axis were scaled by an appropriate field, characteristic of the material. The scaling field H_s was defined as that field at which $-M'(T_c)/(\sqrt{H} T_c)$ falls to 1/2 the Prange limit. In Fig. 1 we include a plot of the empirically determined "universal" curve of normalized magnetization at T_c vs H/H_s . GBT also observed that for a given value of H/H_s , the temperature dependence of $M'(T)/(\sqrt{H} T)$ for different materials coincided if the temperature was scaled as $(\Delta T/H) (dH_{c2}/dT)$. They proposed that this "universal" behavior may be characteristic of all superconductors. It is natural, in view of the estimates of PAW, to compare the measured value of H_s with $H_{c2}(0) \equiv T_c (dH_{c2}/dT)_{T_c}$; * the ratios observed were $H_s/H_{c2}(0) = 0.046$ for In, 0.062 for Pb, and 0.25 for the Pb 5%Tl alloy. Because of the very large value of H_s for the alloy,

* Note that this definition has little to do with the actual value of $H_{c2}(0)$ which would be measured by supercooling, say.

most of the region where $|M'|$ is significantly suppressed could not be observed; in this case universal behavior is, at best, only a probable assumption. In spite of the resultant uncertainty in H_s , the substantially different dependence on $H_{c2}(0)$ for the alloy was considered significant, and GBT proposed the general relationship $H_s \propto H_{c2}(0) (1 + \xi_0/\ell)^2$, where ℓ is the electron mean free path.

Subsequent to the publication of these results the previously mentioned papers on the microscopic theory appeared; they predicted universal behavior as proposed by GBT for all but very dirty alloys, with a shape for the normalized magnetization vs $\log H$ reasonably close to the empirical curve (c.f. Fig. 1). For pure superconductors, H_s as defined above is predicted to be $0.018 \phi_0/\xi_0^2 = 0.062 H_{c2}(0)$, which can be regarded as being in reasonable agreement with the results on Pb and In. For the dirty case an additional dependence $(1 + 0.88\xi_0/\ell)^2$ appears in the theory, which is in accord with the Pb-Tl alloy.

Because of the sketchiness of the latter result, subsequent experiments on two In-Tl alloys and on pure Nb have been performed by the Harvard group. (27) They continue to see universal behavior in these materials, but for the alloys the dependence of H_s on mean free path is quite different: in both cases ($\xi_0/\ell = 7.3$ and 16 , respectively) the scaling field is given by $0.064(\phi_0/\xi_0^2) (1 + 0.88\xi_0/\ell)$ - i.e., the factor containing the dependence on mean free path appears only in the first power. For Nb it was found that $H_s = 0.025 H_{c2}(0)$, which also represents rather poor agreement with the microscopic theory. In the case of the alloys, however, the condition $(\xi_0/\ell)/(0.189 \phi_0/T_c) \ll 1$ for the validity of the microscopic theory is not met - this ratio has the value 1.27 and

2.8 for the two In-Tl alloys, and 2.0 for the Pb-Tl specimen.

After the work in this thesis was underway, a paper by Kaufman and de la Cruz⁽²⁸⁾ appeared, reporting results on pure aluminum. These results, which are discussed in more detail in a later section, disagreed significantly with those we had obtained as well as with the theory; on the basis of further work we are confident that the data presented here for Al is trustworthy.

C. Motivation for the Present Work

From the standpoint of an evaluation of the microscopic theory, measurements on Al represent several advantages: (1) in the pure limit, Al is an extreme nonlocal superconductor at all temperatures except very close to T_c ($|\Delta T| < 10^{-4} T_c$). Thus it provides a good test of whether the theory works in this limit. (2) Al is an extreme weak-coupling superconductor, which is the approximation used in the theory. (3) For Al $0.18\theta_D/T_c \approx 60$, which means that for quite large values of ξ_0/λ the microscopic theory should remain valid. A convincing test of the theory in the dirty limit requires, we feel, that the condition $\xi_0/\lambda \ll 0.18\theta_D/T_c$ be unambiguously met. (4) For a given value of ξ_0/λ , the theory predicts that the cut-off field should scale as ξ_0^{-2} - i.e., should be in Al less than 1/10 what it would be in a corresponding In alloy. Hence the magnitude of the fields required to observe the full suppression of the magnetization are correspondingly smaller. This is of no small practical importance, since measurements of this nature are particularly difficult in fields greater than a few hundred Oe.

CHAPTER III

APPARATUS AND EXPERIMENTAL TECHNIQUES

A. Brief Description

The basic notion in this experiment is that the fluctuation-induced magnetization M' can be separated from other sources of magnetization by its temperature dependence - i.e., at sufficiently high temperatures it must vanish. Hence it must be possible to vary the temperature of a sample over a considerable range, and with reasonable dispatch, while monitoring changes in its magnetization. In the case of Al this is somewhat complicated by its low transition temperature, which can be reached in a conventional He^4 bath only with the greatest difficulty. Since M' has a fairly rapid variation in temperature near T_c , it is important that high temperature resolution be obtained, at least in this region. A means for precise temperature control is also desirable.

The required sensitivity to sample magnetization, however, represents the strongest challenge. Even with the extraordinary resolution of recently developed superconducting magnetometers (which generally go under the acronym SQUID), great attention must be paid to the problem of optimizing the coupling to the sample. The microscopic theory predicts a broad maximum for $-M'(T_c)$ as a function of field whose amplitude is proportional to T_c/ξ_0 ; we find for pure Al this is just 1/10 what it is for In, so the difficulty is not inconsiderable on a scale of previous measurements. A corollary to the problem of achieving sufficient sensitivity is that of avoiding spurious signals of various kinds, which appear in bewildering profusion unless great care is taken in the design and construction of an experiment.

The experimental setup used to obtain most of the data reported here is shown somewhat schematically in Figs. 2 and 3. Briefly, its function is as follows: The sample is suspended in a vacuum space, firmly attached to a copper block. The block in turn makes weak thermal contact to a He³ pot, which is continuously pumped to a temperature somewhat below 1 K. Attached to the block are a germanium resistance thermometer and a small heater, which through a feedback arrangement can maintain the block at any selected temperature above that of the He³ pot.

The sample is suspended in, but does not touch, a pickup coil which comprises part of a superconducting flux transformer circuit. This reflects changes in the magnetic flux in the pickup coil to another coil which couples into a SQUID flux detector. The pickup coil is mounted on a copper insert which also supports the windings of a pair of "end coils" - narrow coils located in such a way that it is possible, if desired, to apply extra magnetic field primarily to the sample ends. The wires leading to these coils pass through Stycast feedthroughs in the bottom flange of the vacuum can. The main magnetic field is provided by a solenoid of Nb wire wrapped on a Micarta form outside of the vacuum can. Finally, a superconducting shield surrounds everything in order to shield out magnetic disturbances from the outside world.

The wires to the thermometer and heater pass through a feedthrough as shown into the He³ pumping line and on up to a hermetic seal at the top of the dewar. By having the pumping line pass through a quick-connect O-ring seal at the top, the entire structure comprising the He³ pot; copper block, and sample can slide up out of the pickup coil region without disconnecting any wires, making access to the sample quite simple.

Once a sample was attached to the copper block, it was lowered into the vacuum space and a seal at the top of the vacuum can could be reliably produced using indium wire as an O-ring. An 1/8" tube entering through the bottom flange is used to evacuate the vacuum region. The bottom flange also seals to the vacuum can by means of an indium O-ring. The scale of the shield, magnet, etc. were determined largely by the requirement that the SQUID structure should sit next to, rather than above or below, the measuring apparatus in order to maximize the running time.

Fig. 2. Construction of the apparatus

Fig. 3. Detail of the demountable upper section of the apparatus.

B. Elimination of Extraneous Signals

1. Building Materials.

It has been found, both in this laboratory and others^(23,29), that one is quite restricted in the materials that can be used near highly sensitive magnetic field-sensing devices - i.e., which do not produce magnetic disturbances comparable to the sample that is being measured. For instance, it has been observed that ordinary brass has a long time-dependent response to any change in magnetic field which appears to be similar to flux creep in superconductors. Stainless steel is quite magnetic at the level of sensitivity we are dealing with, particularly after having been heated to soldering temperatures. Obviously, superconducting materials will distort magnetic fields considerably; if there is a large demagnetizing factor or inhomogeneity in the superconductor, magnetic fields can penetrate it in an unpredictable and fluctuating manner, producing corresponding effects at the flux detector. In general, one should view soft-soldered joints near a pickup coil with a jaundiced eye.

These considerations lead one to favor copper as a building material. In the present apparatus, OFHC copper was used wherever possible, and solder joints near the pickup coil were of hard solder. Some of the flanges were made of brass for the sake of machining ease; however, the expedient of plating them with lead seemed to provide sufficient shielding. The screws used to fasten the bottom flange were specially made from Berillium-Copper. Other materials which appeared to be generally harmless were: epoxy, and plastics generally; used for coil forms, etc.;

GE7031 Varnish, used in various places; and ordinary masking tape, used to firmly hold down the wires leading to the pickup coil.

2. Flux Transformer

It is also easy to see that the use of a flux transformer can cause problems. Any loop in a section of the transformer that is not inside a well-shielded superconducting enclosure will tend to pick up variations in magnetic field from the outside world. For this reason, all connections between segments of the transformer should be made inside a shielded area. It was found that tightly twisted wires could run through an unshielded area without problems; a special leadplated brass box was provided for making connections between such twisted pairs. However, it was found necessary to solder a lid onto the box with Wood's Metal (as opposed to clamping it on with screws) to keep external fields from leaking in to an annoying degree. For instance, prior to the soldering remedy, the opening or closing of a nearby metal door produced a significant shift in SQUID output.

It is equally important that the temperature of the flux transformer remain uniform. The effective area inside a loop of superconducting wire includes the depth that magnetic fields penetrate into the wire bulk - i.e., λ , the penetration depth. This has a fairly strong temperature dependence: $\lambda \sim \lambda(0)[1-t^4]^{-\frac{1}{2}}$, so for a not very large temperature change we could have $\delta\lambda \sim \lambda(0) \sim 10^{-6}$ cm. If the circumference of the pickup coil is ~ 4 cm, as was the case here, the change in flux threading the coil would be $\sim H\delta\lambda(4 \text{ cm}) \sim 4 \times 10^{-6} \text{ G-cm}^2$ in an ambient field of 1 Oe; this amounts to 20 flux quanta, compared to a typical signal from the sample of half this much. It is therefore well worth the effort to keep

the flux transformer/SQUID contingent of the experiment at a constant bath temperature.

3. Magnet and Shield

It is clear that both the main magnet and the end coils couple so strongly into the pickup coil that very good regulation of the current in these coils is necessary; in fact, the only adequate solution is to operate them in the "persistent mode" - i.e., shunted with a length of superconducting wire so that the entire circuit is superconducting. Hence if a current is established, it persists indefinitely. To establish a current, it is necessary to drive the shunting portion of wire normal as current is applied to the coil leads, then allow it to go superconducting before the current is removed. One simple way to do this is to selectively heat a section of the shunting wire to above its transition temperature - such a scheme is called a "thermal switch" (T.S.). It can be shown that with the T.S. off (wire superconducting), any change in current feeding the magnet wires is reduced in the magnet windings by approximately the ratio of the T.S. inductance to the magnet inductance. Since this represents a very large attenuation, it can be assumed that the trapped current does not significantly change if the feeding current is reduced to zero after being trapped. Also, this inhibits external noise from coupling to the magnetometer via the current leads.

Occasionally, for purposes of calibration, it is necessary to have the magnet T.S. on while monitoring the SQUID output as some parameter is changed. This seems to produce $\sim 1/4\phi_0$ of noise in the pick-up coil, which means that for good resolution rather large flux excursions must be induced; in measurements of this nature, it is useful to use the flux-

counting mode of SQUID detection, to be described later.

The superconducting shield surrounding the experiment consisted initially of lead plated on a length of copper tubing; when it was discovered that this could not remain uniformly superconducting in fields larger than ~ 100 Oe., it was replaced by .005" Nb foil spot welded to form a tube which could just slip over the copper sleeve.

4. Performance

In spite of these precautions, the apparatus showed less than ideal behavior: in applied fields greater than ~ 10 Oe, a long slow drift in the output of the magnetometer became observable, scaling roughly with the field, and depending to some extent on the temperature of the sample/copper block. In general, it was possible to cope with this by taking data pointwise; i.e., sit at a given temperature long enough to determine the rate of drift on a strip-chart recorder, then shift rapidly to a new temperature and do the same thing. The time required for a change in temperature was at most ~ 1 min (for cooling), and the apparent magnetization at the new temperature could be accurately extrapolated back to the beginning of the temperature change - thus giving the true change in sample magnetization. The system was also subject, at all fields, to occasional sudden jumps in the apparent flux at the pick-up coil, particularly during a change in temperature. By observing both positive and negative excursions for a given temperature difference, a double check was obtained that no such jump had occurred.

Finally, at very large fields ($H \geq 100$ Oe), a sort of relaxation phenomenon with period ≤ 30 sec begin to superimpose itself on the output drift; this was again roughly proportional in peak-to-peak amplitude to

the applied field, and amounted to a source of noise. Another source of noise at high fields is the physical vibration of the sample. This produced noise primarily at frequencies ~ 100 Hz, which could be fairly well filtered out, provided the SQUID output followed the excursions linearly. The most important factor in reducing vibrational noise turned out to be careful anchoring of the various pumping lines in such a way as to prevent passage of pump vibrations. When this was done, the peak-to-peak excursion was ~ 1 flux quantum ($\sim 10^{-6}$ Gauss)* in a field of 300 Oe. Low pass filtering with a 1 sec. time constant reduced this value by ~ 100 , so that the dominant contribution to the noise was always the relaxation phenomenon described above.

* Throughout this thesis the unit Gauss refers to magnetization
($= (B-H)/4\pi$) and Oe represents an applied field (H).

C. Temperature Measurement and Control.

The block whose temperature was to be controlled was machined from OFHC copper; Fig. 2 shows the means by which firm mechanical contact to the He^3 pot is achieved while maintaining good thermal isolation - without use of offensive materials (e.g., stainless steel, solder). At the lower end of the block, a teflon spacer centers the insert structure and to some extent prevents vibrations.

The heater consists of a miniature 1/8 watt metal-film resistor slipped into a close-fitting hole drilled in the block, with a layer of grease to improve the thermal contact. The value of this resistor is of course somewhat arbitrary; the decision in this case was made by the requirement that the internal structure of the resistor not include any Kovar. Among the available candidates, the only one meeting this requirement had the value 250 K Ω , which was therefore the value used.

The thermometer used was a doped Ge resistor (Solitron # SP 2301) in a 3-terminal AC resistance bridge configuration. This circuit is shown in a simplified version in Fig. 4b. It is designed to reject as much as possible the effects of stray resistances and capacitances. It can be seen that the effect of the lead resistances R_L cancel out to the extent that they are equal: one adds to R_x and the other adds to the balancing resistor R_b . As far as stray capacitances are concerned, only the one labeled C_x can have any effect: C_1 is driven by a low impedance, C_2 bridges two points at the same potential, as does C_3 when the bridge is in balance.

Capacitance C_x can, in principle, be balanced by a variable capacitor

(a)

(b)

Fig. 4. (a) The resistance bridge circuit.
(b) Simplified version of the bridge, showing possible stray resistances and capacitances.

C_b shunting the balancing resistor; however, it is easy to show that the error introduced by omitting this is negligible: suppose that $R_x = R_b = R$, and that the total voltage across the transformer output $= 2V_o$. Then we find that for the voltage δV at the balance point (using complex notation)

$$\frac{\delta V}{V_o} \approx 1/2 j\omega R(C_x - C_b) + 1/4 \omega^2 R^2(C_x^2 - C_b^2)$$

If the in-phase component of the signal is observed, using a lock-in amplifier, then only the second term appears at the output. In the event of a resistive imbalance δR (with no capacitance present), we would observe an in-phase signal $(\delta V/V_o) = 1/2(\delta R/R)$; hence the capacitance imbalance leads to an apparent resistive imbalance

$$\delta R_{\text{eff}} = \frac{R}{2} \cdot R^2 \omega^2 (C_x^2 - C_b^2)$$

It is unlikely that stray capacitance in the wiring would amount to more than a few hundred pico-farads. If we take $\omega \approx 2\pi f \sim 10^3/\text{sec}$, $C \sim 10^{-10} \text{f}$, $R \sim 10^4 \Omega$, we find $\delta R_{\text{eff}} \sim 5 \times 10^{-3} \Omega$, which is completely acceptable. Another advantage of this configuration is that a single-ended preamplifier can be used.

The absolute accuracy of the bridge readout depends on how accurately the transformer is center-tapped; the model used here is guaranteed to be within 1% of center. In the actual circuit used, shown in Fig. 4a, a means for adjusting the center tap to within at least a part in 10^5 of center is illustrated. By varying the tap on the 200 Ω potentiometer, as much as $\pm 1/2\%$ of the output voltage can be added to the center tap voltage. To make this adjustment, a known resistor was used as R_x , the same value was dialed for R_b , and the potentiometer was adjusted until the

bridge read null. The $200\ \Omega$ potentiometer shunts the output of the transformer with an impedance much less than that of R_x and R_b (during normal cryogenic use). Since the loading of the transformer is nearly constant for typical changes of R_x , one need not worry about phase shifts, etc. as a function of resistance.

The purpose of the matched $10\ \Omega$ resistors is to limit the power dissipated in R_x under "worst case" conditions to $\sim 10\ \mu\text{w}$, which will not damage it. The frequency chosen to drive the bridge was $\sim 200\ \text{Hz}$, which is low enough to avoid capacitance problems and high enough to allow a fairly fast response time.

The thermometer and heater were both mounted on the copper block as far as possible from the pickup coil. A length of the wires leading to the thermometer was glued to the copper block with GE7031 varnish in order to improve thermal contact. By using the superconducting transition of a sample as a secondary thermometer, the power coefficient of the offset temperature between the block and the resistance thermometer could be measured, and was found to be $35\ \text{mK}/\mu\text{w}$ in the vicinity of the transition temperature of Al. Usually the bridge was operated at a drive voltage level $V_o = 2.5\ \text{mV}$, which near T_c ($R_x \sim 12\ \text{K}\Omega$) produces a power dissipation of $\sim 6 \times 10^{-10}$ watts in the resistor, resulting in a negligible offset from the block temperature. The thermometer was calibrated against a second Ge resistor (Cryocal 280) which had been calibrated in the range $1.0\ \text{K} \leftrightarrow 8.0\ \text{K}$ for a four-terminal configuration. The resistance varies from $18,750\ \Omega$ at $1.0\ \text{K}$ to $1,000\ \Omega$ at $4.0\ \text{K}$.

A disadvantage of the three-wire bridge configuration is that the contact resistance to the Germanium is included in the measured resist-

ance. It was observed, again by using the superconducting transition as a standard, that after thermal cycling the calibration of the resistor could change by $\sim 10-20 \Omega$ (around T_c), probably because of changes in the contact resistance. For this reason, the superconducting transition was precisely located at the beginning of each run. No observable change in calibration was observed in the course of a run.

To provide the weak thermal connection between the He^3 pot and the copper block, a 14 cm length of #36 copper wire was fastened at either end to the block and the pot with pressure contacts. This length was arrived at, more or less by trial and error, to provide a compromise between two conflicting requirements: (1) the time required for the block to cool down from the upper to the lower temperature limits of interest must not be too long - i.e., the thermal connection must not be too weak; (2) if the link is too strong, the He^3 will boil off at an excessive rate when the block is held at a high temperature. For this experiment, temperatures higher than $\sim 3 \text{ K}$ were rarely needed. To hold the block at 3.2 K , approximately 1 mW of power was required in the heater, which boils off the He^3 at $\sim 1 \text{ cc}/20 \text{ min}$. Given that only a fraction of a run is devoted to temperatures this high, the time between fillings of the He^3 pot was typically 5-6 hours. To cool from 3.2 K to 1.0 K took $\sim 1 \text{ min}$, which is quite reasonable.

The feedback system for the heater should have an adjustable bias current level which can be set to approximately the power needed to hold the block at the desired temperature; the off null signal from the bridge should then add to or subtract from this appropriately if the temperature drifts away in either direction from the set value. The

circuit used for this is shown in Fig. 5a. It is essentially a differential amplifier with only a single output polarity allowed. The voltage level at one of the inputs determines the bias current, and the control signal (bridge output) is applied to the other input. The unipolar output is necessary since the basic controlling parameter (the heater power) depends on the square of the output current. The strength of the corrective feedback is determined by the lock-in amplifier sensitivity, the setting of switch S, and potentiometer R_2 .

If the bias level is changed while the system is controlling, the average value of the control signal must change by approximately the same amount in order to keep the heater power nearly the same; this means that the temperature at which one is controlling has been shifted slightly from the set value. Hence sweeping the bias voltage causes the temperature to sweep correspondingly; the range of temperatures covered depends on the sensitivity setting of the lock-in amplifier as well as the bias voltage range. This provides a convenient way to sweep through the very sharp superconducting transition slowly enough to maintain thermal equilibrium: a ramp voltage of the desired rate is applied to the bias input (Ext. mode). A simple variable rate ramp generator is shown in Fig. 5b. Sweep rates as low as 1 mK/min could be easily achieved with this setup.

In Appendix A a model is developed for this type of feedback arrangement which qualitatively accounts for most of the features that are observed.

Fig. 5. (a) Heater feedback circuit.

(b) Ramp generator used to sweep temperature.

D. Flux Transformer Considerations

To measure fields at locations remote from the SQUID itself, a flux transformer, shown schematically in Fig. 31a, must be used to carry the information to the SQUID. It consists simply of a pickup coil at the site of interest connected to a "secondary" coil which couples as strongly as possible into the SQUID, everything being made of superconducting wire. Briefly, the principle of operation is as follows: If the pickup coil was closed upon itself, any change in the external field would simply induce enough current in the coil to shield it from the volume inside the coil. As it is set up here, the inductance of the secondary coil acts as an impedance to current flow, so that the pickup coil is only partially able to shield out the external field change; the current induced in the circuit produces, via the secondary coil, a corresponding field change in the active volume of the SQUID. We can see that there is a trade-off situation: If the inductance of the secondary is too large, it will excessively reduce the shielding current in the circuit for a given external field; if it is too small, the field it produces in the SQUID for a given current will be correspondingly diminished. This is worked out in detail in Appendix B, where we find that the optimum setup requires that the two inductances be equal. The pickup coil used in this experiment consisted of 18 turns of 0.005" Nb wire wrapped on an epoxy form 1.3 cm. in diameter by 1.8 cm. long, resulting in a predicted inductance of 2.3 μ H. The secondary coil consisted of one layer of 0.003" Mo-50%Re wire closewound on a micarta rod 1.25 mm in diameter for a length of 1.4 cm, giving a total of 130 turns;

the predicted inductance is $1.9 \mu\text{H}$. Thus the system was close to optimum from the point of view of flux transformer design. The thickness of the brass shield and the wire used for the secondary coil limited the filling factor for this coil in the SQUID hole (2.0mm diameter) to ~ 0.4 . In Appendix B it is shown that a figure of merit for effectiveness of coupling into a SQUID is $M/\sqrt{L_s}$. From measurements of the sensitivity to magnetic field at the pickup coil, a value of $5.6 \times 10^{-6} \text{H}^{1/2}$ was deduced for this parameter in my setup. This should be compared to values as high as $\sim 12 \times 10^{-6} \text{H}^{1/2}$ observed for coils of higher filling factor in a slightly larger SQUID²⁹ (c.f. Fig. 32). Hence one route to improved sensitivity lies in getting a better filling factor.

The results in Appendix B indicate that the sensitivity to magnetic field in the pickup coil increases roughly as (diameter)^{3/2}. Clearly, this applies equally to the sensitivity to magnetization of a cylindrical sample suspended in the coil, assuming the filling factor is fixed. This fact motivated the choice of rather large samples for this experiment - the typical diameter was $\sim 3/8"$, with a length of $\sim 3"$.

For very high purity samples, there is an additional reason for using a large size, related to the existence of random currents due to Johnson noise. These result in a fluctuating magnetic field which can be shown³⁰ to have the r.m.s. value $\langle B^2 \rangle \sim 4\pi kT/V$, where V is the volume over which B is averaged. For the present experimental setup, V is not easily defined; it can be said roughly to be that volume of the sample that couples strongly into the pickup coil. Hence large samples will produce less Johnson noise.

The above discussion assumes that none of the Johnson noise is rejected by filtering. Whether or not this is the case depends on the

ratio τ/τ_{ave} , where τ_{ave} is the averaging time constant (usually 1 sec) and τ is the characteristic relaxation time for the decay of circulating currents in the sample. The frequency spectrum for the field fluctuations is given by

$$\langle B^2 \rangle_{\omega} = \frac{4\pi kT}{V} \frac{2}{\pi} \frac{\tau}{1+\omega^2\tau^2}$$

For $\tau/\tau_{ave} > 1$, essentially all of the noise is concentrated within the bandpass of the output filter, and the above analysis applies. This was true for a high-purity indium sample that was measured; the r.m.s. Johnson noise in this case was 4-5 times the intrinsic SQUID noise. For the pure aluminum samples used, the eddy current time constant was ~ 0.2 sec, and the opposite limit $\tau/\tau_{ave} < 1$ applied. In this case, filtering rejects all but a fraction $\sim \tau/\tau_{ave}$ of the total noise power. We have $\tau \propto D^2/\rho$, where D is the sample diameter and ρ is the resistivity. Since $V \propto D^2$, it is apparent that the post-filtering field noise $\langle B^2 \rangle \sim (4\pi kT/V) \times (\tau/\tau_{ave})$ is independent of D in the second limit. For the aforementioned aluminum samples, the Johnson noise was 2-3 times the SQUID noise - i.e., it represented an apparent fluctuation in magnetization of $\sim 7 \times 10^{-9}$ G peak-to-peak. When the output was recorded on strip-chart recorder for > 1 min, a visual determination of the average magnetization could be made with a factor of 3-4 better resolution.

E. The Magnetometer

1. Operation

In order to achieve the sensitivity to magnetic field that is required for this experiment, it is necessary to use a superconducting flux detector of some sort. The type used here, the "A.C. SQUID" configuration, is by now the most commonly used and can even be purchased commercially³¹. Its principle of operation is very well described in a number of papers^{29,32,33,34}, of which the most comprehensive to date is probably the one by Giffard, Webb and Wheatley²⁹. I will therefore restrict myself to a very brief description: It is well known that a superconducting ring must enclose a magnetic flux which is some multiple of the flux quantum $\phi_0 = (hc/2e) = 2.07 \times 10^{-7} \text{ G-cm}^2$. In general, there will be a net persistent current flowing in the ring of sufficient magnitude to make up the difference between the (arbitrary) "applied" flux in the ring and the actual quantized value. The principle of any superconducting flux detector is to somehow measure this "shielding current," thereby monitoring the value of the external flux modulo ϕ_0 .

To make an A.C. SQUID, the ring is interrupted at some point by a weak link - a section which can support only a relatively small persistent current without going normal. If the applied field of interest has superimposed on it an A.C. field of sufficient amplitude, then the shielding current in the ring will periodically reach its critical value i_c , at which point the flux in the ring will collapse to a smaller (quantized) value. If the A.C. field amplitude is slowly raised from zero, there will be a point when these transitions just begin to happen, leading to a marked nonlinearity in the inductive response of the ring. It is clear that the point at which this happens depends linearly on the D.C. persistent current

in the ring - i.e., the ambient flux. The experimental setup used to monitor this is quite simple: the ring is made to couple to the inductor of a parallel tank circuit which is driven at its resonant frequency by a current source. Fig. 6a shows a trace of the A.C. voltage across the tank as a function of the drive current for two extreme values of applied flux: zero and $\pm 1/2 \phi_0$ (modulo ϕ_0). It can be seen that the variation with flux in the onset of non-linearity results in a modulation of the A.C. voltage by the applied flux if the drive current is biased at an appropriate level. This response must have a periodicity of a flux quantum, typically as shown in Fig. 6b.

The information produced by this configuration can be ultimately traced back to the transitions induced in the ring during each A.C. cycle; it seems reasonable, then, that the more transitions induced per second, the more information will be available -- i.e., the amplitude of the voltage modulation shown in Fig. 6b. will be more or less proportional to the A.C. frequency. For this reason, the frequency used is generally in the radio frequency range, typically some tens of MHz.

The construction of the ring used for this experiment, kindly supplied by Mr. Robert Buhrman, is shown in Fig. 7. There are actually two rings, in a symmetric configuration with a common weak link. This is produced by screwing down the pointed Nb screw until it just makes contact with the flat screw underneath. Since the entire structure is made of the same material (Nb) and is relatively massive, it has the useful property of being able to gracefully survive the thermal contraction involved in cycling between cryogenic and room temperatures without changing the strength of the contact. If in addition the device is sealed in a can with a helium atmosphere and protected from gross mechanical and thermal shock, it can become

Fig. 6. Response of the SQUID circuit (a) as a function of r.f. current, for different values of the D.C. flux, and (b) as a function of the D.C. flux, for various levels of the r.f. current.

Fig. 7(a) Construction of the magnetometer with a point contact weak link.

Fig. 7(b) The magnetometer holder and protecting can.

a reliable, practical instrument. The one used here was cycled from helium temperature perhaps 50 times and required no readjustment during this time.

In general, weak-link devices are extremely susceptible to high-frequency interference from radio stations, motors, etc. For this reason, rather elaborate protective measures must be taken. In this experiment, these included:

(a). The entire experiment was done in a screened room, which effectively cuts out frequencies above 15 kHz. It was generally possible, however, to operate with the door open.

(b). The SQUID is enclosed in a Pb-plated copper can whose only opening to the outside is via a single coaxial feedthrough used for the r.f. drive/detection. As is shown in Fig. 7b, between the flux sensitive part of the SQUID and the coil carrying the signal current there is interposed a brass tube of wall thickness ~ 0.005 ", which effectively shields high-frequency signals from the SQUID while allowing low-frequency signals to pass (but with some loss of filling factor).

(c). The electronics for the SQUID are very carefully shielded, with r.f. bypassing used for all low-frequency signals entering the SQUID can.

Some practical considerations in the use of a SQUID ought to be noted:

(1) It is apparently impossible to make a functioning SQUID whose hole is greater than ~ 8 - 10 mm^2 ; in general, the signal/noise decreases as the hole size increases. Hence the advantage in maximizing the hole size is not as obvious as it first seems, and the value used for this SQUID ($\sim 3 \text{ mm}^2$) is not too far from optimum. (2) The critical current of the point contact must lie within a rather narrow range for the SQUID to operate properly; if it is greater than $\sim 10 \phi_0 / L_H$ (L_H = inductance of the hole) anomalous behavior sets in, while on the other hand it must clearly be greater than $\sim \phi_0 / L_H$.

Since practical point contacts exhibit a rather large temperature dependence of the critical current,³⁵ this means that for a given adjustment, the SQUID will work well only over a certain range of temperatures - typically ~1 K. Furthermore, the temperature should be constant in the course of a measurement. (3) For the configuration used here, it was observed that there were large low-frequency fluctuations in flux for any temperature above the λ -point, as well as very large excursions accompanying any change in temperature. Below T_λ , both types of "noise" disappeared. Presumably, this effect is due to thermal gradients, either in the SQUID body or the surrounding can.

2. Detection and Feedback Considerations

As can be seen in Fig. 6b, when the SQUID tank circuit is appropriately driven with a constant r.f. current, the r.f. voltage amplitude is modulated as a function of applied flux by something between a sine and a triangle waveform. In the following (c.f. ref. 36), I assume that it is exactly sinusoidal; i.e., $V_{rf} = \cos(2\pi\phi/\phi_0) + \text{const.}$ It is convenient for the purposes of detection to apply an "audio" frequency (i.e., quasi-static in comparison to the r.f. response) field to the SQUID: thus, $\phi = \phi_{DC} + \delta\phi\sin\Omega t$. If this is inserted in the above expression for V_{rf} , and carried to second order in $\delta\phi$ in a Taylor expansion about ϕ_{DC} , we find:

$$V_{rf} = \text{const.} + \cos \frac{2\pi\phi_{DC}}{\phi_0} \left[1 - \frac{1}{2} \left(\frac{2\pi\delta\phi}{\phi_0} \right)^2 \right] - \left[\frac{2\pi\delta\phi}{\phi_0} \sin \frac{2\pi\phi_{DC}}{\phi_0} \right] \sin\Omega t \\ + \left[\frac{1}{2} \left(\frac{2\pi\delta\phi}{\phi_0} \right)^2 \cos \frac{2\pi\phi_{DC}}{\phi_0} \right] \cos 2\Omega t$$

The detected r.f. voltage will in general include an "audio" signal with frequency components at Ω and 2Ω , proportional respectively to $\sin(2\pi\phi_{DC}/\phi_0)$ and $\cos(2\pi\phi_{DC}/\phi_0)$. These signals can be separately extracted by using two lock-in amplifiers set to detect at Ω and 2Ω , and will be of comparable size

if $\delta\phi \sim \phi_0/2\pi$. If their outputs are connected to the x and y inputs of an oscilloscope, the result will be a dot which traces out a circle on the scope face as ϕ_{DC} is advanced. This obviously provides a much clearer visual representation than a simple sinusoidal response and frequently is useful for diagnostic purposes. For instance, if the dot fluctuates in such a way as to remain always on the circular path, it can be interpreted as actual changes in the input flux; if it fluctuates in random directions, it is due to electronic noise of some sort; and if it fluctuates always towards the center of the circle, it is probably due to varying r.f. interference, which might modulate the critical current of the SQUID. In addition, this setup provides the basis for a digital output by simply counting revolutions of the dot. Anadex, for instance, sells an up/down counter which will add/subtract a count every time either the x or y signal makes a zero crossing, the counting direction being determined by the polarity of the other signal. This allows one to follow large flux changes without limit, with a resolution of 4 counts/flux quantum.

Much greater resolution than this is, of course, possible; the apparent flux noise at the SQUID using a 1 sec. averaging time is less than $10^{-3}\phi_0$. To obtain this resolution in combination with large dynamic range, some sort of negative feedback scheme is necessary. There are two schemes that are suitable for use with a flux transformer. In the first, shown in Fig. 31b, the output of the SQUID electronics is converted via the feedback resistor R_f into a current that couples flux into the SQUID hole. Since any small excursion in the SQUID flux ϕ from null results in a strong counter-acting response due to the feedback, the tendency is for ϕ to remain always nulled (modulo ϕ_0). Hence the appearance of an applied flux ϕ_a is accompanied by a equal and opposite flux ($-M_2 i_2$), and $i_2 \approx -\phi_a/M_2$ is a measure

of the applied flux. Actually the SQUID output voltage $= i_2 R_f$ is monitored; for strong feedback, this will be significantly reduced from the open-loop value. In Appendix B it is shown nevertheless that the signal/noise ratio at the SQUID output is the same with or without feedback.

The second type of feedback (Fig. 31c) also keeps the SQUID flux null - in this case, by maintaining the total flux turns in the flux transformer constant with the aid of a coil that couples directly into the transformer.

The main difference between the two types of feedback lies in the effective impedance that the secondary coil presents to the primary. In the first scheme, the flux in the secondary is kept nearly constant - i.e., the inductance is effectively zero.

Since the primary is shunted by almost no inductance, it responds to a change in external field with a large shielding current leading to a corresponding distortion of the magnetic field distribution around the coil. For magnetization measurements, this means that the applied field H is changed when the magnetization of the sample changes, by an amount $\leq (-\delta M/4\pi)$. Hence if there is a susceptibility change $\delta\chi$, we find $\delta M \approx \delta\chi/(1+\delta\chi/4\pi)$. For the present measurements, where $\delta\chi \leq 10^{-7}$, this leads to negligible error. If the entire superconducting transition was to be observed, however, feedback of this type would not be appropriate.

For the second type of feedback, the effect is to keep the current in the transformer nearly constant, which means that the pickup coil is presented with a very large apparent inductance in the secondary. Hence there is very little distortion of fields near the pickup coil, and the measurement is more nearly "passive". An advantage of the first type of feedback is that the feedback coil is necessarily already in place, in the form of the r.f. tank coil. The second type requires addition of a second coil,

with attendant care being taken with respect to r.f. shielding, etc. For this experiment, both types were available, and it was demonstrated that they gave identical results; in practice, the simpler Type I was most often used.

An important parameter in this, as in most other negative feedback arrangements, is the loop gain G . This is a dimensionless parameter that describes, in this case, the vigor with which the flux at the SQUID is maintained null. It can be roughly determined, for either of the two schemes mentioned above, by measuring with the feedback loop open: (1) $(d\phi/dV_B)$, the number of flux quanta coupled into the SQUID per volt applied at point B (see Fig. 31), and (2) $(dV_A/d\phi)$, the magnetometer output voltage per flux quantum in the vicinity of $\phi = 0$. The product of these is the loop gain. We notice that for a pure sinusoidal SQUID response, the above quantity (2) is just $(2\pi|V_{\max}|/\phi_0)$ where $V_{\max}$ is the maximum output voltage swing. The largest possible excursion of the SQUID flux ϕ_s with the feedback on obviously corresponds to $V_{\max}$ at the output - i.e., to a fed back applied flux of $V_{\max} d\phi/dV_B = (\phi_0/2\pi) G$. Thus for large loop gains the dynamic range can be tens or hundreds of flux quanta, while the resolution is limited only by SQUID noise ($\sim 10^{-3}\phi_0$).

To calibrate the system with feedback, we note that, as is observed in Appendix B, there is a master equation relating ϕ, ϕ_x , and i_2 for both types of feedback. The desired calibration parameter is $(di_2/d\phi_x)$ in the presence of feedback; if the feedback is strong enough, this parameter is very close to $(\partial i_2/\partial \phi_x)_\phi = -(\partial \phi/\partial \phi_x)_{i_2} / (\partial \phi/\partial i_2)_\phi$ where the r.h.s. comes from the existence of the quoted master equation. Both the numerator and denominator can be determined empirically, in the absence of feedback, by simply counting flux quanta while varying ϕ_x or i_2 respectively. The result-

ing quantity differs from the actual calibration by a factor of order $(1 + 1/G)$.

Clearly from the point of view of dynamic range, linearity, and calibration accuracy, as large a value of G as possible is desirable. The limitation on the size of G is imposed by the requirements for stability: to avoid the possibility of oscillations, the high-frequency roll-off of G should not occur any faster than $1/f$ (6 db/octave). The frequency response of the system extends to frequencies where $G \sim 1$. For the audio modulated SQUID, the high frequency cutoff should be at less than some fraction of the modulation frequency - this sets an upper limit on G at all lower frequencies.*

To help understand the operation of feedback, the representation of Fig. 8 is useful. We have plotted simultaneously as a function of SQUID flux ϕ the output voltage V_A , and the voltage V_B required to produce a flux ϕ via the feedback coil. The intersections of these two curves represent the possible states of the system when the feedback loop is activated - i.e., when the constraint $V_A = V_B$ is applied. Only half of the solutions, as indicated, represent stable equilibrium. A large loop gain is implied by a large amplitude for the oscillations of V_A and/or a small slope for V_B vs ϕ . For large G , there are clearly a large number of possible solutions - as many, in fact, as the dynamic range in flux quanta of the system. A change in the applied flux ϕ_a is most easily represented by sliding the curve V_A vs ϕ along the ϕ axis; it can be seen that for any of the solutions, this results in a voltage change $\delta V \approx (dV_B/d\phi)\delta\phi_a$. There is little to choose between the many solutions for a given ϕ_a , except that most of them

* It was found for this system that for a unity loop gain frequency as high as $1/2 \Omega$ it remained stable.

Fig. 8. Schematic graph for determining possible states of the SQUID feedback system.

Fig. 9. Circuit for activating the feedback loop and filtering the output voltage.

Fig. 10. The SQUID electronics package.

A: AMF MODEL VI-40-10M-50 VIDEO PREAMPLIFIER

T: NORTH HILLS BA 0900 WIDE BAND TRANSFORMER

C₁: 1-30 pf PISTON TRIMMER

C₂: 4-75 pf BUTTERFLY TRIMMER

represent a large offset relative to small changes in ϕ_a . In general, if the feedback is activated as indicated in Fig. 31 - i.e., by simply connecting the output of the SQUID electronics to the feedback circuit, the system can end up in any one of the many possible states. If it is desired that the system should initially be in the state nearest zero output voltage, it is necessary to make the feedback connection ahead of the 6 db/octave filtering that is required for stability. A simple way to do this is shown in Fig. 9. The SQUID electronics are set for maximum bandwidth, so that the initial R-C combination provides the only filtering in the feedback loop. The system bandwidth with feedback is much larger than that indicated by the 0.5 sec time constant in the loop; the second R-C filter and follower were added since for this experiment only D.C. signals are of interest.

Since the SQUID is very sensitive to extraneous r.f. fields, it seemed desirable to include all the r.f. components of the electronics in a single shielded, compact enclosure, which is shown schematically in Fig. 10. The coaxial line leading from the SQUID tank circuit enters an especially well-shielded region, where it is connected to a low noise, high input impedance wideband amplifier. In this region it is possible to apply various low-frequency flux signals to the SQUID by injecting r.f. by-passed currents into the tank circuit coil. Normally, these would include (1) an audio frequency modulation field for the purpose of SQUID detection; (2) a potentiometer-adjustable D.C. field offset; and (3) an external connection, which could be used in the "flux-nulling" type of negative feedback. Note that in the latter case the 1 M Ω resistor of the rf bypass network serves as part of R_f in the feedback loop.

The only high-frequency signal which makes it into this region is the

the r.f. drive frequency. The small 0.1 pf. coupling capacitor presents a high enough impedance to amount to a current source driving the tank circuit. It was found that at the frequency of operation (~ 3 MHz) an ordinary ten-turn potentiometer was adequate as an attenuator for varying the r.f. drive current. Although the amplitude stability of the r.f. drive is not very crucial, the frequency stability is, due to the high Q (>200) of the tank circuit. The only simple oscillator that is good enough in this respect is the crystal controlled type. The procedure was to determine the resonant frequency of the tank for the experimental configuration that was to be used, and then order a crystal of the correct frequency. Capacitor C_1 is used for fine-tuning the resonance.

Detection of the r.f. voltage across the SQUID tank circuit is performed by transistor Q_1 in conjunction with capacitor C_3 . The transistor is biased with just a trickle (5 μ A) of standing current - i.e., in the most nonlinear part of its transconductance characteristic. One finds that an r.f. voltage as small as ~ 2 mV rms applied to the base produces sufficient rectifying action to be detected. The $\times 100$ gain of the preamplifier in combination with the 5:1 step-up of the transformer are sufficient to amplify the r.f. voltage across the SQUID tank coil (typically ~ 10 μ V) to a level that can be easily detected. Capacitor C_3 is charged up during each positive cycle, and can only be discharged through the 70 K Ω emitter resistor. Hence this R-C combination determines the fastest change in r.f. voltage amplitude that can be observed. Transistor Q_2 is connected as a diode and serves to remove the D.C. voltage offset resulting from the base-emitter voltage of Q_1 . The 1 M Ω potentiometer can be used to trim the offset exactly to zero.

The high input impedance of this detector allows the use of a high- Q

tuned filter at the input to reject noise outside the bandwidth of interest; this is tuned by capacitor C_2 . Most of the tuning adjustments indicated above only had to be made once, provided no significant change in the experimental configuration was made - indeed, from one run to the next only the r.f. level had to be readjusted.

Fig. 11. Schematic diagram of the sample-magnet-shield configuration.

F. Calibration

It was shown previously that using a large sample helps improve the signal/noise of a magnetization measurement. The other side of the coin involves the difficulty in obtaining the magnetization calibration factor (flux quanta/Gauss) when the size of the sample is comparable with that of the persistent current magnet and the superconducting shield. When this is the case, one finds that the coupling of the sample to the magnet and shield lead to a complicated additional coupling to the pick-up coil. Of course, the calibration can be determined empirically - by replacing the sample with a solenoid of known dimensions and measuring flux quanta/Ampere. However, such a calibration would apply only to a sample of exactly the same size as the solenoid, while the sizes of actual samples tested varied over a 50% range. Hence it is necessary to attempt a calculation of the calibration factor as a function of sample size.

During actual measurements, the magnet is in the persistent mode; i.e., since no voltage is developed across the magnet leads, the total flux-turns remain constant. It is easy to convince oneself that provided the windings are evenly spaced, this is equivalent to saying that the volume average of the axial component of magnetic field within the magnet remains constant. The existence of the superconducting shield generates the additional constraint that for any plane cutting through the shield, the enclosed flux must average to zero. Referring to Fig. 11, the latter condition becomes for a perpendicular plane that cuts through the sample and one which does not, respectively,

$$(1) \quad B_s d^2 + B_1(D_1^2 - d^2) + B_2(D_2^2 - D_1^2) = 0$$

$$(2) \quad B_3 D_1^2 + B_4(D_2^2 - D_1^2) = 0$$

where B_s is the magnetic field in the sample and the remaining subscripts pertain to the regions indicated. Here I have assumed that the magnetic fields are everywhere parallel to the solenoid axis. It is convenient to define $H_o = \frac{4\pi}{c} nI$, where I = magnet current, n = magnet winding density. Since I is the same everywhere, we have $H_o = B_1 - B_2 = B_3 - B_4$, from Maxwell's equations. In addition, I call $M = B_s - B_1$; this differs by a factor of 4π from the sample magnetization as normally defined in c.g.s. units. With these substitutions, the above equations become:

$$(1') Md^2 + B_1 D_2^2 = H_o (D_2^2 - D_1^2)$$

$$(2') B_3 D_2^2 = H_o (D_2^2 - D_1^2)$$

we now calculate the volume averaged magnetic field within the magnet volume - i.e., the flux-turns: In the region containing the sample, we have the contribution

$$\phi_I \propto [B_s d^2 + B_1 (D_1^2 - d^2)] \ell = [Md^2 + H_o D_1^2] (1 - D_1^2/D_2^2) \ell$$

where the r.h.s. comes from eliminating B_1 with eq. (1') above. Likewise, we find that the region not containing any of the sample gives the contribution

$$\phi_{II} \propto B_3 D_1^2 L = H_o D_1^2 (1 - D_1^2/D_2^2) L.$$

Combining these, we find $\phi_{tot} \propto [H_o V_M + M V_s] (1 - D_1^2/D_2^2)$ where V_s and V_M are the volume of the sample and magnet, respectively. Hence, if $\phi_{tot} = \text{constant}$ (magnet in persistent mode), a change in sample magnetization δM leads to a change in magnet current given by $\delta H_o = - (V_s/V_M) \delta M$. Finally, we must compute what is actually observed, the flux in the pick-up coil: $\phi_p = \frac{\pi}{4} [B_s d^2 + B_1 (D_p^2 - d^2)] = \frac{\pi}{4} (1 - D_1^2/D_2^2) [Md^2 + H_o D_p^2]$, where D_p is the diameter of the pick-up coil. For a given M , if the magnet is in the persistent mode we have

$$\delta \phi_p \propto [\delta M d^2 - \frac{V_s}{V_M} D_p^2 \delta M] = \delta M d^2 [1 - \frac{\pi D_p^2}{4 V_M} \ell].$$

If the magnet current is held constant, we have $\delta \phi_p \propto d^2 \delta M$. Finally, we can write

$$(\partial \phi_p / \partial M)_{H_o} = C_1 d^2$$

$$(\partial \phi_p / \partial M)_{\phi} = C_1 d^2 (1 - C_2 \ell)$$

where C_1 and C_2 are geometry-dependent factors. For a dummy sample consisting of a solenoid of accurately known dimensions and winding density, both calibration factors could be measured by counting flux quanta while the solenoid current was ramped a known amount, with the magnet thermal switch either on or off (constant H_o or ϕ). Then the constants C_1 and C_2 could be calculated, so that the calibration for a sample of any size can be subsequently predicted.

Some comments on the validity of this approach can be made:

(1) The most serious problem is that the assumption of axial fields everywhere is obviously wrong, and this leads to significant errors. In particular, it is found that the measured value of C_1 differs from the predicted one by ~30%, while C_2 is off by a factor of 2. However, it seems not too much to hope for that these equations contain at least the correct dependence on sample dimensions, provided the latter are not too different from the ones used to determine C_1 and C_2 . It is felt that the accuracy of the calibration for all of the samples used was correct within a few percent, which in view of other uncertainties is quite adequate.

(2) The effect of shielding currents in the pick-up coil was ignored. This assumption was vindicated by the observation that identical results are obtained in magnetization measurements whether flux-nulling or current-nulling feedback is used, indicating that the presence or absence of these currents has little effect.

(3) Likewise, the effect of the end coils was neglected in this calculation. For the dummy sample it was observed that the sensitivity to

magnetization is the same whether the thermal switch for these coils was on or off, which amounts to an empirical justification for this simplification.

(4) With the magnet in the persistent mode, certain basic notions about the coupling of the sample to the pick-up coil are wrong. In particular, if a change in magnetization is localized at the ends of the specimen, the primary coupling to the coil is via the magnet - i.e., a change in magnet current is induced which produces a change in the applied field in the pick-up coil. It turns out that the polarity of this indirect coupling is reversed from the expected signal due to the direct coupling.

The calibration of the magnet can be obtained simply by setting $M = 0$ in eq. (1'): $B_1/I = \frac{4\pi}{c}(1 - D_1^2/D_2^2)$. The quantity in parenthesis, which for the present configuration has the value .46, is a measure of how much this calibration factor is reduced due to the presence of the superconducting shield. Since the effect of the shield is significant, neither the calibration factor nor the field configuration can be empirically measured at room temperature. The calculated value, 74.6 Oe/Ampere, was used for analysis of data.

Since the magnetization due to fluctuations is expected to depend only weakly on field, no effort was made to improve field homogeneity with extra windings at the magnet ends; however, it is expected that the presence of the shield will improve this over the free-standing value, for which the homogeneity is calculated to be within 3% over the sample length.

When the sample is superconducting, the applied field ($= B_1$) is different for a given magnet current than the value calculated above. It can be estimated, with somewhat less confidence, by setting $M = -B_1$ in eq. (1'); we find that it is increased over the above calculated value by

a factor $(1 - d^2/D_2^2)^{-1} = 1.12$ for a sample diameter of $3/8"$. This means that if the superconducting transition is observed by sweeping temperature at constant magnet current, the beginning of the S-N transition will be apparently smeared out over a temperature range $\Delta T \approx .12 H/(dH_c/dT)$; this effect dominates the intrinsic transition width for fields greater than a few tenths of an Oe.

It is, of course, impossible to observe the full transition in fields greater than a few milli-Oe using the full sensitivity of the SQUID. The sensitivity can be reduced, however, by inserting a large series inductor in the flux transformer. Using a shielded inductor with an estimated inductance of 5 mH, an attenuation of ~ 1000 was obtained; this allowed us to monitor the full transition in fields as high as 30 Oe, using the flux counting scheme outlined in Sec. III E (2) in conjunction with a D-A converter. From the above discussion, it is clear that the "normal" end of the apparently broadened transition is the appropriate point to pick off $T_c(H)$. A plot of H vs $T_c^2(H)$ was made for a pure polycrystalline Al sample, and yielded the expected straight line; using the above calculated magnet calibration gave the slope 68.7 Oe/K^2 , vs. a value 70.2 Oe/K^2 observed in Ref. 37 in the vicinity of T_c . This agreement was considered a fairly good self-consistency check on the magnet and thermometer calibrations.

It is also of interest to estimate the maximum local field/current produced by the end coils; a simple calculation indicates that for a free-standing coil of the same dimensions the field at the center is given by 30 Oe/A . We might expect that in the presence of a superconducting shield this is reduced by a factor similar to that derived for the main solenoid: $(1 - D^2/D_2^2) = .69$, giving $\sim 20 \text{ Oe/A}$. The free-standing coil formula predicts that the axial field falls off as $(D/2x)^3$ where x is the distance

along the axis from the coil. At the pick-up coil, this factor is $\sim 1/85$, so the expected coupling into the pick-up coil is $\sim 5 \text{ Oe/A}$. This coupling can be measured, by injecting current into the end coils while keeping both the main magnet and end coil thermal switches on, and is found to be $.07 \text{ Oe/A}$ - i.e., almost an order of magnitude less than predicted. Apparently, the effect of the shield is to cause fields from the end coils to fall off much more rapidly than in the free-standing case.

A final calibration procedure was to determine the background temperature-dependent magnetization signal due to the copper block, etc.; this was done by taking data with no sample but with a copper sample holder attached. The results were found to be linear in field - in particular, there is no temperature dependent signal in zero field, implying that the coupling of the heater current to the pick-up coil is negligible. In Fig. 12 the results are plotted vs $1/T$ as an equivalent susceptibility for a sample $3/8"$ diameter x $3"$ long. I believe that the main contribution to this background is the paramagnetic Curie susceptibility of the copper nuclei in the controlled block; this leads to an apparent diamagnetic $1/T$ law since the coupling to the pick-up coil is primarily via the magnet, which reverses the polarity as was discussed above.

Fig. 12 The background temperature-dependent signal of the apparatus, in the absense of a sample. For the sake of easy comparison, it is plotted as an equivalent magnetization for a sample 3" long x 3/8" diameter.

G. Resistivity Measurements

For the alloys, it was necessary to determine the electron mean free path; this is related to the resistivity by the relation³⁸ $\ell(\text{cm}) = 1.6 \times 10^{-6} R$, where R is the resistance ratio: $R = [\rho_p(273)/\rho(4.2)]$. Here $\rho(T)$ is the resistivity of the alloy, and $\rho_p(T)$ is the resistivity of pure Al. Using Matthiessen's rule this can be related to measurements on the alloy at room temperature $\equiv (273+t)$ K and 4.2 K: $R = [\rho(273+t)/\rho(4.2) - 1] (1 - \alpha t)$. Here α is the temperature coefficient of resistance for pure Al at $0^\circ\text{C} = 0.0043/\text{deg}$.

For samples of the size considered here, the most convenient method for measuring the resistivity is the eddy-current decay technique of Bean et.al.³⁹. This method is based on the fact that if there is a step change in the applied longitudinal field on the sample, it will at first be shielded from the interior by surface shielding currents; these will die away with an ultimate time constant determined by the sample dimensions and resistivity. In general, the time constant $\tau \propto 1/\rho$, with a proportionality constant determined by sample dimensions. Since only a ratio of resistivities appears in the expression for R , it is not necessary to know this constant. Taking 22°C as room temperature, we have finally $R = 0.91 [\tau(4.2)/\tau(273+t) - 1]$.

A simple apparatus was constructed for making these measurements; it consisted, essentially, of a magnet (primary) coil for providing the excitation field, and several secondary coils arranged at various positions along the sample's length. The primary coil consisted of 8 close-wound layers of #30 copper wire, and provided a more or less uniform field along the sample length. The secondary coils were rather narrow and wound as close to the sample diameter as possible, in order to probe a relatively small section of the sample; these each consisted of ~500 turns of #40

copper wire. All these coils were arranged concentrically around a phenolic tube into which a sample could be slipped. This structure was mounted at the end of a length of thin-wall stainless steel tubing, so that it could be immersed in Helium.

In Fig. 13 a schematic diagram of the electronic configuration used, with typical waveforms, is shown. A square wave applied to the "drive" input periodically turns the current in the primary coil on and off, via the power transistor shown. The supply for this current, indicated as + V, was typically several dry cell ignition batteries connected to give 4-6 V. We are interested in recording the decay after the "off" transition, since this is closer to a true step change and has a better defined asymptote. The diode at the "sync" output is designed to suppress any positive voltage pulse accompanying the "on" transition. The 10 K Ω resistor shunting the primary coil helps damp out excessive ringing immediately after the energizing current is switched off. Finally, the diodes shunting the secondary coil output prevent excessive voltage spikes induced by the magnetic field steps from overloading the input of the preamplifier, while they allow the lower voltage exponential decay to pass undistorted.

To monitor this decay after it had been preamplified, a Fabritek digital signal averager was used, both to average out noise at the low voltage end of the decay and to serve as a high resolution "storage scope"; after recording 64 or 128 sweeps, the data could be digitally read out and plotted on semilog paper. Typically, perfect exponential behavior was observed over 2 decades of signal amplitude, and a ratio of time constants accurate to within a few percent could be obtained for a given sample. Also, a determination of the resistance ratio at various positions along the sample length could be made, giving some indication of its homogeneity.

Fig. 13. The electronic configuration used to observe eddy-current decays in the samples, with various waveforms indicated.

H. Sample Preparation

Both single and polycrystals of pure Al were used. The polycrystal samples were prepared from the highest grade Al available from Materials Research Corp. in the form of 3/8" rod, with a nominal 5-9's purity. A single crystal in a size close to that desired was also obtained from this company, made with the same grade of Al. The resistance ratio for these samples was ~ 1000 , which is by no means the state of the art in Al, but was deemed satisfactory. As to specific impurity content, we have only the "typical analysis" of this material, which includes .5 ppm Fe, .2 ppm Cr; and $<.1$ ppm Mn, Co, and Ni. Several single crystals were grown by the Cornell MSC facility in graphite crucibles of $\sim 3/8$ " diameter. These had a resistance ratio of ~ 300 , and little is known of their impurity content.

The alloy specimens were all in the form of polycrystals. Of those finally used, two (Al-.15 at.%Ag and Al-.3 at.%Si) were prepared by MRC using highest grade starting materials. Several others were made in the local MSC facility by dilution of standard concentration alloy material with pure Al. These materials were melted together in a graphite crucible for at least 1 hour, then chill cast in a copper mold of 1/2" diameter, and finally swaged to a diameter of 3/8". Samples were made with impurity concentrations of 0.1, 0.5, and 0.8 at.% Si as well as .05 at.% Ag. The specific contents of other impurities are again not known for the alloys.

The single crystals were cut to the right length with an acid saw. With a frequently changed etching solution of 45% HCl, 15% HNO₃, and 15% HF, a single cut required ~ 24 hrs. In order to reduce the diameter of a specimen and remove possible strained regions near the surface, an electro-polishing method was used. This left a somewhat uneven surface, so that only an average diameter (obtained by weighing the specimen) could be

specified.

The poly-crystalline samples were cut and shaped by ordinary machining techniques. After preliminary smoothing with #600 grit sandpaper, they were polished either chemically or electrolytically, and then annealed at a few tens of degrees below the melting point (660°C for pure Aluminum) for several days in a vacuum furnace. In the course of being removed from this furnace, the specimens received a "slow cool" - i.e. they were cooled to room temperature in a period of at least 10 minutes. If it was desired that a sample be quenched, it was reheated to the annealing temperature in air for ~ 1 hour and then plunged in a bucket of cold water.

A final layer was removed from the sample surface either by polishing or with an etching solution (10% HF, 10% HNO_3), and it was ready to be glued into a holder. The polycrystalline specimens, both pure and alloy, had a grain size $\geq 1\text{mm}$ typically.

Particularly for the single crystals, it was considered quite important that a smooth, strain-free surface without pits, scratches, etc. be achieved, in order to enhance supercooling. Probably the most useful electropolish that was found for this purpose uses an electrolyte of 40% (ortho-) phosphoric acid, 35% ethyl alcohol, 25% water at $\sim 70^{\circ}\text{C}$, with a stainless steel cathode. The voltage across the cell for optimum polishing is $\sim 25\text{ V}$, which leads to a current density $\sim 100\text{ mA/cm}^2$. At the temperature used, the alcohol evaporates away fairly rapidly, and must be occasionally replaced. The power dissipated in the cell ($\sim 70\text{ W}$) was found to be enough to maintain the solution at the proper temperature. This large dissipation can in fact lead to a sort of thermal run-away unless a current-limiting resistor is placed in series with the voltage source. The "standard" electropolishing solution, consisting of 35% perchloric acid, 65% acetic anhydride, was

found to produce a finish as good as the above formula, but with a current density ~20 times smaller; also, there is considerable danger with a solution of this sort unless great care is taken⁴⁰. The samples were held above the electrolyte with a strain-free holder made of teflon, which served to provide a pressure-contact between the specimen and a strip of Al foil. Since the entire sample could not be immersed, the procedure was to polish first one half and then the other. Unfortunately, for both the solutions mentioned above, the region of the sample just at the surface of the solution tended to be somewhat pitted. The only way around this is to use a chemical polish; of the many formulas tried, only one came even close to producing a surface comparable to the electropolished ones: this consisted of 78% phosphoric acid, 15% sulfuric acid, 7% nitric acid, 1g cupric nitrate, and as much Boric acid as will dissolve (~.5 g). Used at ~110°C, this was marginally successful for the pure samples and fairly good for the alloys. It leaves a reddish residue on the surface which is easily removed by dipping the sample in nitric acid. For any of the preceding polishes, the sample should be plunged into cold water immediately after it is removed from the solution, and washed for several minutes in cold running water. One or another of these polishes was generally used to etch away .1 - .2 mm of the surface from the single crystal samples that were received as cast.

Most of the magnetization measurements reported here for pure single crystals were made on the sample from MRC, which had a higher resistance ratio than the locally grown versions. Two pure polycrystal samples were shown to give identical results and collectively comprise the "polycrystal" data.

I. Typical Running Procedure

After a sample was glued into a holder, it was attached to the copper

block and the vacuum can was sealed with an indium O-ring; it was then evacuated through the pumping tube and sealed off with a valve at the top of the dewar. The hang-down was precooled to liquid nitrogen temperature by being suspended overnight in the dewar. Care was taken to transfer liquid He into the dewar very slowly, since it was observed that for too rapid transfers a rather large field could be trapped in the superconducting shield. Immediately after the transfer, the He bath was pumped down to a temperature somewhat below the λ -point (where the SQUID works best) and subsequently held at this temperature with the rubber manostat.

In the meantime, the sample/copper block remained near LN_2 temperature because of the lack of any efficient heat exchange mechanism; to speed up the cooling rate, He^3 gas at a pressure considerably higher than its equilibrium vapor pressure at the bath temperature was admitted to the pumping line/ He^3 pot region. The tendency of the gas to condense on the cold walls of the pumping line and drip down into the pot rapidly brought the pot to the bath temperature, so that the main limitation in the cooling rate of the sample was the weak thermal link between the pot and the copper block. As soon as the block had reached the bath temperature (which took 30-40 min) and all the He^3 was condensed in the pot, the latter was pumped down to a temperature well below 1°K . No effort to regulate the temperature of the pot was made. Measurements could now proceed by varying the temperature of the copper block.

At the beginning of every run the transition of the sample was observed; usually this was done by slowly sweeping the temperature, as was described above, with a field ~ 2 mOe in the main magnet. The temperature shift of the transition from the zero-field value is negligible at this field level. The magnetometer output was monitored with the flux-counting scheme, and

converted to an analog signal with a D-A converter. This signal went to the vertical input of an X-Y recorder, while the lock-in amplifier output from the thermometer bridge drove the horizontal axis. The thermometer resistance corresponding to any position along the X-axis could most easily be determined by replacing the thermometer with a resistance box, leaving all other settings unchanged; this resistance was adjusted until the recorder pen was positioned at the point of interest.

The alloy specimens (but not the pure ones) had a tendency to trap a great deal of flux as they were cooled through their transition, at least at these low field levels. To properly observe such transitions, the procedure was as follows: the sample was initially cooled to well below T_c with no ambient field. A field of ~ 2 mOe was then applied, and the sample was warmed slowly through its transition, while the flux was monitored.

Having by this means determined the location of T_c to the necessary accuracy, it was now possible to take the magnetization data. This was done pointwise, by switching the temperature of the sample between two values. For most of the samples the quantity of primary interest is $M'(T_c)$, so that the temperatures used were T_c and a value sufficiently high to suppress the fluctuations - usually 3.2 K. Between temperature excursions the output of the magnetometer (in a feedback mode) was monitored on a strip-chart recorder long enough to observe the trend in apparent magnetization at the temperature of interest; the true change in M could be subsequently determined from the graph paper by measuring the (extrapolated) displacement in SQUID output. In general, the resolution provided by the recorder was less than the noise, and so was adequate. During these operations the main magnet and end coils were in the persistent mode with the desired field trapped. While the field was being changed a thermal switch in the flux

transformer circuit was activated, in order to prevent the establishment of large shielding currents.

CHAPTER IV: PRELIMINARY OBSERVATIONS.

A. Pure Al.

1. The Bulk Transition

In Fig. 14 typical superconducting transitions plotted as susceptibility vs. temperature at constant (small) applied field are shown, for both a polycrystal and single crystal of pure Al. The relative position of the two curves along the temperature scale is not significant, due to the possibility of small shifts in thermometer calibration following thermal cycling. The polycrystal has quite a narrow transition - $\sim 3 \times 10^{-4}$ K, which is not unusual for high-purity material free from strains. In view of the large grains in the polycrystal, however, the significantly different shape of the single crystal sample is most extraordinary. Both curves give every indication of representing an equilibrium situation - i.e. both show virtually no hysteresis for temperature sweeps in the reverse direction (except for supercooling). Likewise, the shape of both transitions remains the same for applied fields ranging from very small (~ 1 mOe.) to at least 1 Oe. Considerable effort was expended to convince myself that these curves are really representative of single and polycrystals, respectively: in particular, several other single crystals, presumably with different crystal orientations from the one shown, were tested. All showed the same basic structure: a long tail extending to low temperatures, leading to a steep slope at the high temperature end.

The low temperature tail reaches the fully superconducting state at a definite point (~ 5 mK below the high temperature end of the transition), as opposed to an asymptotic approach. The effect was apparently independent of annealing history, surface condition, etc. In some early measurements on Al⁴¹ where the transition was monitored by sweeping the field at constant temperature, it was observed that near T_c the transition width is

Fig. 14. Typical shape of the S-N transition for single- and poly-crystalline samples of pure Al. The relative positions (along the temperature axis) of the two curves are not significant.

constant (~ 0.3 Oe) for single crystals, but approaches zero for polycrystals. This is equivalent to a constant temperature width ~ 2 mK, as observed in this work. Specific heat measurements⁴², however, do not correlate with our results; broad transitions (~ 2 mK) were observed for polycrystals in low fields, which became narrower for fields ≥ 3 Oe.

Finally, Fassnact and Dillinger, using an A.C. inductance bridge configuration, have observed broadened transitions as much as 60 mK wide in separated isotopes of Zn⁴³ and Ga⁴⁴ for fields less than ~ 0.5 Oe. Since isotopically mixed specimens of these elements showed no such effect, and since naturally occurring Al is isotopically pure, they have suggested⁴⁵ that their observations and those on Al represent some sort of enhanced fluctuation effect that can occur only for materials with extremely long phonon mean free paths. It is supposed that this condition requires isotopic purity. Some comments might be made on this conjecture: (1) Whatever it is that they are seeing in Zn and Ga bears little qualitative resemblance to the phenomenon in Al: i.e., the width of the transition is much greater, the shape is different (with a long tail extending to high temperatures), and there is a strong dependence on field. (2) Their measuring technique samples only a thin layer of the specimen near the surface; indeed, it was reported in ref. 43 that altering the surface preparation had a significant effect on the broadening. In contrast, our measurements, as well as those of ref. 41, are essentially at zero frequency and monitor the state of the entire sample volume. (3) Their explanation fails to account for the most striking feature of this observation, the difference between a single and polycrystal. (4) If our broadened transitions are to be ascribed to fluctuations, they must in any case be distinguished from the "conventional" fluctuations that are being studied here - i.e., fluctuations from the normal

towards the superconducting state. It can be seen in Fig. 14 that the supercooled state, in which the "conventional" fluctuation mode is operative, does not coexist with a state of the sample midway through the transition, where macroscopic superconductivity is clearly present. On the scale of this plot the contribution of the conventional fluctuations is invisible. I conclude that the observations of Fassnacht and Dillinger are probably not related to the present phenomenon, which remains unexplained.

Apart from general mysteriousness, the single crystals pose a problem for these measurements in that the fluctuation magnetization varies significantly in low fields over the temperature width of the transition, so that $M'(T_c)$ is uncertain to this degree.

2. Supercooling

There are several reasons that it is advantageous to obtain large supercooling for this experiment:

1. A supercooled sample is definitely normal - i.e., if any superconducting regions develop in the sample, no matter how small, they will grow until the sample reaches its equilibrium state, implying an abrupt diamagnetic change. In a sample with no supercooling, one is not quite sure that a diamagnetic change in magnetization as the temperature is lowered is not in fact due to a long high-temperature tail in the equilibrium S-N transition. If the sample shows supercooling behavior - i.e., makes an abrupt transition at some temperature below $T_c(H)$, one can feel quite confident that the magnetization observed prior to the transition is entirely due to fluctuations.

2. It is expected that the fluctuation magnetization will continue to grow as the temperature is lowered below $T_c(H)$; this region has not been compared with the theory heretofore.

3. Whatever the reason for the broadened transition in single crystals, it seems reasonable that there is a thermodynamic critical temperature that can be located more precisely than this transition implies, which is the relevant origin for the fluctuation magnetization $M'(T-T_c)$. If this point exists, it could be localized by measurements of "ideal" supercooling. Such supercooling, where superconductivity is nucleated homogeneously in the sample surface, was distinguished by Faber⁴⁶ from a situation wherein a flaw of some sort in the sample nucleates superconductivity. The experimental manifestation as observed by Faber of these two types of supercooling is indicated in the phase diagram of Fig. 15. The shaded region represents those values of temperature and field for which supercooling is possible. The line segment marked H_S^F maps out the lower limit of supercooling for which a flaw represents the limiting factor; as different portions of the specimen are sampled, this segment in general varies in slope and placement, depending upon the nature of the flaw. Faber's argument was that at temperatures sufficiently close to T_c , any flaw will eventually become ineffective as a nucleation site - presumably when the coherence length is comparable to the size of the flaw; when this point is reached, the supercooling observed is "ideal" - i.e., characteristic of the entire sample. This is represented by the segment labeled H_S^I . It is predicted by G-L theory¹, and was observed by Faber that $H_S^I(T) = 2.4 \kappa H_c(T)$, where $\kappa = \lambda(T)/\xi(T)$ is approximately constant near T_c . Thus the ideal supercooling curve must extrapolate to T_c as $H \rightarrow 0$; this T_c could perhaps be identified as the genuine thermodynamic one. It should be noted that if a non-ideal segment of the supercooling curve is extrapolated to zero field the result will not be T_c .

The problem in obtaining substantial supercooling in a large sample

Fig. 15. Phase diagram of a type I superconductor, showing the effect of flaws on the region of possible metastability of the normal phase (shaded region).

is that unless a means is found to probe relatively small areas of the specimen, a bad flaw anywhere along the sample can prematurely nucleate superconductivity. With the configuration of this experiment, it was possible to screen out flaws at the ends of the sample by applying a large field with the end coils in that region; this nevertheless left a substantial region near the center susceptible to nucleation sites. The procedure was generally to slowly lower the temperature with a given current trapped in the main magnet and end coils until the sample abruptly went superconducting; this point was typically reproducible to within ~ 0.1 mK. In Fig. 16 the minimum supercooling temperature of the single crystal sample is plotted as a function of field in the main magnet for varying end coil currents: For the curve marked (a), the current in the end coils was 100 times the magnet current for each point - i.e., the maximum field near the sample ends is ~ 30 times the field at the middle. This curve appears qualitatively similar to those of Faber; at its steepest slope near T_c we find $(dH_s/dT)/(dH_c/dT) = 0.046$, which is an underestimate since the end coils add at least 10% to the field at the nucleation point. Compared with the value 0.036 measured by Faber, it would appear that even with such extreme shielding of the sample ends, ideal supercooling was not achieved. However, the critical temperature for this nucleation site can be fairly precisely located: it cannot be greater than the extrapolation to zero from the lowest field point at the "ideal" slope, nor can it be lower than an extrapolation at the measured slope. As can be seen from the transition curve (c) plotted on this temperature scale, the resulting T_c is in the vicinity of the 50% complete portion of the transition.

For curve (b) the current in the end coils was 10 times that in the main magnet; since the sample ends are less effectively shielded, it is not

Fig. 16. The maximum supercooling obtained in the single crystal sample, as a function of the field in the main magnet (a) with $\sim 30 \times$ higher field near the sample ends, and (b) with $\sim 3 \times$ larger field at the ends. The inset graph (c) shows the full N-S transition curve plotted against the same temperature scale.

Fig. 17 The maximum supercooling for the single crystal sample [$H_s(T)$] in the presence of an homogeneous magnetic field. For comparison, the equilibrium transition line $H_c(T)$ is also shown.

surprising that a more effective nucleation site has been exposed, leading to less supercooling. What is difficult to account for is the behavior close to T_c , where the nucleation site suddenly becomes more effective - just the opposite from the tendency observed by Faber. This becomes more evident for supercooling measurements in a homogeneous field (no current in the end coils), shown in Fig. 17: for fields less than ~ 60 mOe supercooling disappears altogether.

Similar behavior was observed for the pure polycrystalline samples, except that the amount of supercooling achievable was much less than for the single crystal, even for extremely inhomogeneous fields.

The difficulty in achieving large supercooling for reasonably homogeneous fields made us abandon any effort to measure M' carefully at temperatures below T_c ; indeed, due to the effect mentioned above it was difficult enough to measure M' at $T = T_c$ in fields less than ~ 60 mOe.

In general, it was found that when the sample just began to go superconducting, the effect was initially localized in the ends, either because of field inhomogeneity or demagnetizing effects. As was mentioned in Sec. III F., the coupling of this section of the sample to the pick-up coil is primarily via the magnet, which reverses the sign of the coupling from what one would normally expect. Hence, as the temperature is lowered through the transition (in the absence of supercooling) there is initially a diamagnetic change due to fluctuations, then a dip in the paramagnetic direction ($>> |M'|$) and finally a large diamagnetic change as the sample bulk goes superconducting. This apparent paramagnetic dip provided a valuable warning that bulk nucleation of superconductivity was occurring. To prevent this, it was necessary to apply extra field to the sample ends.

with the end coils. For a polycrystalline sample it was found that for fields as low as 10 mOe, a current of 4 mA (≈ 100 mOe maximum) in the end coils allowed one to lower the temperature to $T_c(0)$ with no sign that the bulk transition region had been entered. When the temperature was lowered further, the sample entered the superconducting state in the abrupt manner characteristic of a supercooled transition. All this convinces us that the data for fields ≥ 10 mOe is due exclusively to fluctuations, provided sufficient extra field near the ends is provided. The inhomogeneity of the applied field that is implied is not so serious as it might seem, since it turns out that $M'(T_c)$ varies quite slowly with field in this range.

3. Nuclear Paramagnetism

In high fields, a second source of temperature-dependent magnetization becomes evident: the paramagnetism due to the nuclear moments. This is expected to be linear in field and follow a $1/T$ Curie type dependence. At sufficiently high fields the fluctuation magnetization will be completely quenched and this will be the only temperature dependence left. Fig. 18 shows the measured change in magnetization of the pure single crystal sample plotted vs $1/T$ for several high fields, where the zero level is arbitrary. It can be seen that a Curie type paramagnetic behavior is quite well followed, with a Curie constant $\chi T \approx 7.1 \times 10^{-8}$ K. From NMR measurements we would predict a value $\chi T = 6.35 \times 10^{-8}$ K, using the Langevin equation⁴⁷. Similar measurements on several other pure samples and dilute alloys yielded values ranging from the above low of 7.1×10^{-8} K to as high as 8.0×10^{-8} K, with an average $\sim 7.5 \times 10^{-8}$ K. To some extent this variation can be accounted for by the uncertainty in calibration for the various samples. However, the fact that impurities with an electronic paramagnetic moment would in concentrations

~1 ppm add a contribution comparable to the nuclear moment makes it seem somewhat surprising that the departure from the predicted nuclear value is not even greater.

In view of the fact that the susceptibility observed in Fig. 18 is independent of field to within experimental error, it seems safe to assume that fluctuation effects at these high fields have been completely quenched. The appearance of fluctuations at lower fields is evidenced by a diamagnetic deviation of the magnetization from the Curie law slope at low temperatures, as is shown in Fig. 19. At still lower fields, the temperature dependence of the magnetization is dominated by fluctuations. In general, it can be seen that at high fields an accurate measurement of M' requires a large (percentage) accuracy both in the magnetization measurements and in one's knowledge of the Curie constant for the nuclear "background".

Fig. 18 The temperature dependence of the magnetization in fields sufficiently high to completely quench fluctuation effects, demonstrating the effect of the nuclear paramagnetism. The computed Curie constant is indicated for each field.

Fig. 19 The temperature dependence of the magnetization in "intermediate" fields, where the effects of fluctuations become evident. The dashed lines represent the contribution due to the nuclear paramagnetism, as predicted by the high-field data. The diamagnetic deviation at low temperatures is due to fluctuations.

B. Aluminum Alloys

The measurement of the fluctuation magnetization for reasonably dirty alloys presented problems of rather a different order of magnitude than for the pure case. Here the degree of "dirtyness" is represented by the ratio ξ_0/ℓ , where ℓ is the mean free path. Some of these considerations are as follows:

1. Range of Fields and Temperatures

It is expected that the cutoff field H_s will increase with increasing dirtyness - the current microscopic theory predicts a dependence fairly close to $(1 + 0.88\xi_0/\ell)^2$. This means that for a given H/H_s , the component of the actual measured temperature-dependent magnetization arising from the nuclear paramagnetism becomes larger; and an accurate measurement of M' requires a more precise subtraction of two large numbers. Furthermore, the nuclear component, which was observed to vary by $\sim \pm 5\%$ between samples, cannot be empirically obtained as was indicated in Fig. 18 if there is any significant fluctuation magnetism within a factor of two, say, of the highest useable field of the apparatus. This latter was usually ~ 150 Oe; on a good day fields a factor of 2 higher were accessible, but there weren't that many good days. For the alloys with relatively high H_s , then, a value for the Curie constant had to be assumed; it was taken to be 7.5×10^{-8} K for all samples for which it could not be empirically determined.

There is in addition a question of how far above T_c the temperature must be raised to quench all fluctuation effects - i.e., to accurately determine M' . This was of practical interest since making measurements above 3 K required a good deal of extra time and the results were generally less reproducible. If we accept the GBT proposal that $M'/(H T)$ has a universal dependence on H/H_s and $(\Delta T/H) (dH_{c2}/dT)$, then for a given value

of H/H_s the temperature interval ΔT^* required to reduce M' to zero is proportional to $H_s/(dH_{c2}/dT) \sim H_s/H_{c2}(0)$. We will see that the ratio $H_s/H_{c2}(0)$ increases from ~ 0.1 for the pure case to ~ 0.3 for reasonably dirty samples, so that in fact a larger temperature range is required. For the Al-0.15at.% Ag sample, it was found that for $H/H_s \sim 5$, the contribution to M' obtained in the temperature interval 3.2K - 4.0K was $\sim 10\%$ of $M'(T_c)$, and decreased for lower values of H/H_s . Considering other sources of inaccuracy, this error was considered acceptable, and all the data reported here were obtained in the temperature interval $T_c - 3.2$ K.

2. Homogeneity Considerations

It would seem important to obtain alloys in which very little of the solute has segregated - i.e., in which the degree of homogenization is very good. To reduce λ until it is equal to ξ_0 in Al with Si as an impurity, the concentration required (~ 0.1 at.%) is $10^3 - 10^4$ greater than the estimated maximum equilibrium concentration at room temperature - i.e., it is energetically more favorable for the solute to precipitate out, in this case, as pure silicon. The same order of magnitude of supersaturation is implied for all other potential impurities. This is not, of course, as bad as it seems for at least two reasons:

(i) The diffusion coefficient of typical impurities in Al at room temperature can be extrapolated from high temperature data and is found to be ~ 0.1 (lattice spacing)²/year - i.e., they are for all practical purposes frozen in place.

(ii) The energetically more favorable precipitated phase in general has a different lattice spacing than the host lattice, implying considerable distortion of the latter when a precipitated region forms. This amounts to a positive surface energy contribution to the free energy, so

that there is an energy barrier against nucleation of the precipitated phase.

In the actual situation, neither of these assurances is completely valid: as to the first, the apparent diffusion constant of impurities immediately following a rapid quench to room temperature from a homogenization temperature near the melting point is $\sim 10^{10}$ times greater than predicted - i.e., $\sim 10^3$ (lattice spacings)²/ sec. This high rate decays to the equilibrium value in a short time (≤ 1 min), but in the meantime solute atoms can have roamed a considerable distance. There seems to be no way around this phenomenon, which has to do with the persistence of quenched in vacancies, which provide the main mechanism for diffusion.⁴⁸ We note on the other hand that if a sample is slowly cooled from a high temperature, for the solute concentrations of interest here the

temperature at which the solubility limit is reached will in general be high enough that the (equilibrium) diffusion constant is again many orders of magnitude greater than the room temperature value.

A more serious challenge to an optimistic view of things is produced by the observation of "preprecipitation" phenomena for most of the potential solutes in Al. In the case of Ag, for instance, a variety of evidence⁴⁸ indicates that small clusters consisting of nearly pure Ag can form coherently with the host lattice; since the size of Ag atoms is very close to that of Al atoms, there is very little "surface energy" arising from lattice distortion for a spherically shaped cluster, which can grow as large as ~ 100 Å. For other solutes, aggregates in the form of platelets or needles can likewise form with no nucleation barrier.

It must be emphasized that this "preprecipitation" of a super-

saturated solution does not lower the free energy of the system as much as precipitation into a different phase would; but unlike the latter, there is no free energy barrier to the formation of clusters. On the other hand, it is not necessarily true that any supersaturated solution is subject to cluster formation. This is illustrated in Fig. 20, where we plot schematically a possible dependence of the free energy density of a solid solution f_s as a function of solute concentration c at a given temperature. In addition, we show the free energy density f' of a precipitated phase which comprises a concentration c' of the solute. The solubility limit c_0 at this temperature is the concentration at which $f_s = f'$; any concentration greater than c_0 is supersaturated, since a state of lower free energy can be obtained by plating some of the solute out into the c' phase. Although this is largely precluded at low temperatures by the nucleation barrier, another mechanism for lowering the energy of supersaturated solutions is available: suppose that in adjacent equal volumes of the sample there is a fluctuation in solute concentration such that $c \rightarrow c + \delta c$ in one section and $c \rightarrow c - \delta c$ in the other - i.e., the total amount of solute remains constant. Then we can compute the change in average free energy density:

$$2\delta f \approx \left[\frac{df_s}{dc} \delta c + \frac{1}{2} \frac{d^2 f_s}{dc^2} (\delta c)^2 \right] + \left[\frac{df_s}{dc} (-\delta c) + \frac{1}{2} \frac{d^2 f_s}{dc^2} (-\delta c)^2 \right]$$

or

$$\delta f = \frac{1}{2} \frac{d^2 f_s}{dc^2} (\delta c)^2$$

If the second derivative is negative, a saving in energy can be achieved by some sort of segregation even on a vanishingly small volume scale; this is frequently called "homogeneous nucleation", of which the clustering phenomenon is an example. The inflection point of f_s , indicated as c_1 in

Fig. 20. Schematic diagram of a possible variation of the free energy density with solute concentration in a metallic solid solution, showing the possibility of "preprecipitation".

Fig. 20, represents the highest concentration which is immune to homogeneous nucleation. As this figure indicates, it is at least possible to have a range of concentrations ($c_0 < c < c_1$) wherein the solute is supersaturated but not subject to clustering.

3. The Bulk Transition

As was pointed out earlier, the equilibrium diffusion constant at room temperature for impurities is so small that even homogeneous nucleation cannot proceed noticeably during experimental lifetimes. Therefore, the degree and nature of clustering once equilibrium is reached is determined by the precise thermal history of the sample. This was evident for an Al - 0.15 at.% Ag sample which was the first dirty sample tested. Our choice of Ag as an impurity was based initially on its relatively high solubility in Al, its effectiveness at reducing electron mean free path, and its low vapor pressure. As it turns out, Ag in Al constitutes a textbook case of clustering⁴⁹, and the present measurements showed many features that correlate with the presumed degree of aggregation.

For instance, we show in Fig. 21 the shape of the S-N transitions for an Al - 0.15 at.% Ag sample that had been annealed and then (a) quenched in water, or (b) cooled slowly. Both transitions are much broader than in pure Al, and apparently some degree of segregation has occurred in either case; one would expect, however, that clustering would have proceeded to a much more advanced stage for the slowly cooled specimen than the quenched one. Apparently this amounts primarily to a difference in the average size of the clusters, while the Ag concentration in the clusters and in the matrix remains constant⁵⁰. It has been observed elsewhere⁵¹ that the transition temperature of Al-Ag alloys remains constant as clustering proceeds; this has been interpreted within the context of a

Fig. 21. The bulk S-N transitions for some Al-Ag alloys: (a) Al-.15 at.% Ag, after a rapid quench. (b) Al-.15 at.% Ag, after a slow cool-down. (c) Al-.05 at.% Ag, after a rapid quench. This curve has been shifted in temperature relative to (a) and (b).

Fig. 22. The bulk S-N transition for an Al-.3 at.% Si alloy, for two different thermal histories. The relative position of the two curves along the temperature axis has been adjusted for the sake of comparison.

proximity effect. Our results are consistent with this observation, although we do see changing structure in the transition shape with increased clustering, implying a change of some sort in the spatially averaged properties of the system.

In Fig. 21, curve (c) we show the transition of a quenched Al - 0.05 at.% Ag alloy, displaced in temperature but with the same temperature scale. While being considerably narrower than the more concentrated alloy, the transition has a similar shape; we conclude that some degree of clustering occurred for even this very dilute case.

For most of the elements with appreciable solid solubility in Al, preprecipitation phenomena have been observed⁴⁸; the main exception to this is silicon (and probably germanium), for which no clear-cut evidence of clustering has been observed⁵². Therefore, we directed most of our attention toward Si alloys after becoming aware of this.

In Fig. 22 is shown the transition shape of an Al - 0.3 at.% Si sample, after being quenched from a homogenizing temperature and after a slow cool. The transitions for all the quenched Si alloys had the same smooth shape shown here. Those which had been slowly cooled, on the other hand, exhibited a very jumpy, yet reproducible, transition - as if the flux could enter the sample only in sudden surges, after some critical driving force had been reached. The "slow cool" curve in Fig. 22, which has been slightly repositioned in temperature for the sake of comparison, looks as if it might be aiming for the "equilibrium" value represented by the quenched curve, but rarely reaches it because of some sort of resistance to flux entry. This effect became more pronounced for the more concentrated alloys.

With the above exception, transitions of the Si alloys showed much less

sensitivity to the thermal history of the specimens, and were rather narrower for a given reduction in electron mean free path than the Ag alloys: eg., the 0.1 at.% Si and quenched 0.05 at.% Ag samples, whose resistance ratios were similar, had transition widths of ~ 1 mK and ~ 4 mK, respectively. Likewise, the 0.5 at.% Si Alloy, which was comparable in resistivity to the quenched 0.15 at.% Ag sample, had a transition width ~ 5 mK wide compared to a width of ~ 13 mK for the latter. On the basis of these observations, then, it seems doubtful that any significant precipitation of Si occurred.

CHAPTER V: FLUCTUATION MAGNETIZATION RESULTS

A. Pure Samples

In spite of the small signal levels ($|M'|_{\max} \sim 1.5 \times 10^{-7}$ G), the most reliable results from this experiment were obtained for the pure samples. This was due to the narrow transitions (for the polycrystals), the possibility of sufficient supercooling to reach T_c at very low fields, and the fact that complete quenching of $|M'|$ could be accomplished in fields that were not excessively large.

In Fig. 23 we have plotted $-M'(T_c)/(\sqrt{H} T_c)$ vs. $\log H$ for the pure polycrystal; the universal function of GBT provides a fairly good fit if the scaling field H_g is chosen to be 0.215 Oe. In addition, the curve marked "theory" is taken from the paper by Lee and Payne¹⁶ where I have used for the coherence length the value $\xi_0 = 1.25 \times 10^{-4}$ cm, based on supercooling measurements⁵³. This curve, which is essentially identical to the one in the paper by Kurkijärvi, Ambegaokar and Eilenberger¹⁸ is seen to fit the data better if anything than the empirical GBT function. Whether this improved fit is significant is not clear at this point. It should be noted that this curve involves no arbitrary parameters.

A problem encountered in making a similar plot for the pure single crystal is, as was mentioned, the uncertainty in T_c . When this data was taken, it seemed most natural to identify the rapidly changing, high-temperature end of the transition with T_c ; the dark circles in Fig. 24 derive from the resulting values for $M'(T_c)$. To obtain M' for lower values of T , an extrapolation could be made based on the observation that for polycrystals the quantity $(M'(T)/(\sqrt{H} T_c))$ crosses T_c at nearly the same slope for all H when plotted vs $(\Delta T/H) dH_{c2}/dT$. The single crystal low field data agreed best with that of the polycrystal if a point 0.55 mK below

the high-temperature end of the transition was chosen as T_c . These points are indicated by open circles in Fig. 24, and it is apparent that with this choice of T_c the single and polycrystals give virtually identical results. It should be noted that this choice for T_c (in the vicinity of the 50% complete portion of the transition) agrees with the choice suggested by the supercooling data.

In Fig. 24 I have also plotted, for comparison, the data of Kaufman and de la Cruz, taken from Ref. 28. Clearly the differences with the present measurements are substantial. Possible reasons for the discrepancy will be discussed later on.

Finally, the temperature dependence of M' for the pure polycrystal is shown in Fig. 25 to agree fairly well with the universal behavior proposed by Collub et. al.: a plot of $M'(T)/(\sqrt{H} T)$ vs. $(\Delta T/H)(dH_{c2}/dT)$ is quite close to the empirical results of GBT for at least two widely separated fields. Here I have used $dH_{c2}/dT = 3.3 \text{ Oe/K}$, obtained from the relation¹ $dH_{c2}/dT = \phi_0/[2\pi(.74\xi_0)^2/T_c]$. Again we have included for comparison in this figure a curve taken from Ref. 28 for a comparable field and find a significant qualitative as well as quantitative discrepancy.

To provide a check on our experimental technique, it was decided to use this apparatus to make measurements on indium, which was previously tested by GBT. The apparatus was most conveniently adapted for the higher temperature range required by condensing He^3 into the " He^3 pot" and then simply sealing off this area at the top of the pumping line. The pot temperature remained near the outer bath temperature ($\sim 2 \text{ K}$) by virtue of the tendency of the evaporated gas to condense at any cold point on the walls and drip back down into the pot. Under these conditions, temperature excursions in the range T_c (measured to be 3.41 K) to 5 K

Fig. 23. The field dependence of the fluctuation-induced diamagnetism at $T = T_c$ for a pure Al polycrystal (circles). An empirical fit of the data to the GBT "universal" dependence, as well as the prediction of the microscopic theory for $\xi_0 = 1.25 \mu\text{m}$, are also shown.

Fig. 24. The field dependence of the fluctuation magnetization for a pure single crystal of Al at $T = T_c$: (dark circles) - this work, with T_c taken to be at the high temperature end of the transition; (open-circles) - this work, with T_c selected to give maximum agreement with the polycrystal data; (crosses) - the data of Kaufman and de la Cruz.

Fig. 25. The temperature dependence of the fluctuation magnetization of a pure Al polycrystal, for two values of field. For comparison, the "universal" curves obtained by GBT near these scaled field values are shown, as well as the results of Kaufman and de la Cruz for a comparable field.

could be made fairly rapidly. Measurements above 5 K in general were not reproducible enough to be useful - according to Gollub's results, the error in $M'(T_c)$ resulting from going no higher than 5 K is less than 5% for fields less than 20 Oe, which comprises most of the interesting range. (This method was occasionally used to obtain data from Al at temperatures higher than ~ 3 K; for instance in Fig. 18).

The indium sample was prepared from 3/8" diameter high purity rod. After being annealed in air for a few hours at a temperature of 125°C, it was etched and mounted in a holder. The crystallites were rather small, $\sim$ a few tenths of a millimeter. Unlike aluminum, indium does not have cubic symmetry, and it is possible that strains introduced in a polycrystal on cooling might produce results different from a single crystal. These fears were substantially alleviated by the observation of a fairly narrow transition, ~ 0.5 mK wide, for this sample. This is 2-3 times greater than that observed by Gollub²³ for a single crystal of indium.

Because of this broader transition, measurements of $M'(T_c)$ could not be made at fields quite as low as were reported by Gollub; however, over the accessible range of fields the present results are virtually identical with his, as is shown in Fig. 26. The slightly more gradual tailing off at the high field end for our data can be ascribed partially to a correction for the nuclear paramagnetic signal, which to our knowledge was not made by Gollub. The computed value $\chi T = 9 \times 10^{-8}$ K was used for the Curie constant. A somewhat higher value due to the presence of paramagnetic impurities, as well as a correction resulting from the insufficient temperature range, could very well make the indium data identical in shape to that of the pure Al samples.

The excellent agreement between the present data and that of other

Fig. 26. Fluctuation magnetization results obtained in the present apparatus for an indium polycrystal, compared with those of GBT.

workers for In, as well as the coincidence of our results for pure Al with theory, makes us confident that these results are more to be trusted than those of Ref. 28. Without seeming presumptuous, we might venture some speculations as to why said data might be suspect:

1. Referring to the curves at similar fields observed by Kaufman and de la Cruz vs. ours in Fig. 25, we notice that close to T_c they show a somewhat similar temperature dependence, while for temperatures greater than ~ 60 mK above T_c the former curve rather abruptly ceases all temperature dependence. A second curve, shown in Ref. 28 for $H = 0.25$ Oe, indicates that at this higher field all temperature dependence has ceased for $\Delta T > 40$ mK, which is quite opposite to the trend observed for increasing fields in this and previous work. All this suggests that something in the experimental configuration used in Ref. 28 limits the temperature range within which useful data can be taken to $\lesssim 60$ mK. According to our data, this would lead to values of $M'(T_c) \sim 75\%$ and 30% , respectively, of ours at fields of 0.075 Oe and 1.1 Oe. This would go a long way in explaining the increasing discrepancy at high fields.

2. Apparently the data of Kaufman and de la Cruz was taken while slowly lowering the temperature of the He^3 bath in which the sample was immersed - i.e. it was a continuous rather than pointwise measurement. During our measurements on indium, we were particularly struck by the large momentary excursions in magnetization that accompanied any change in temperature, presumably due to eddy currents associated with temperature gradients. While these effects were not as large in Al, it seems probable that at this sensitivity the "equilibrium" magnetization can be obtained only for very slow or pointwise temperature changes.

B. Alloys

As might be expected from the discussion of alloy preparation, the results for the alloy specimens were not as well-behaved as for the pure ones, nor could they be accorded the same degree of confidence. In regard to the shape of the scaled magnetization at T_c vs $\log H$, subtle distinctions between, say, the GBT empirical curve and the prediction of the microscopic theory could hardly be made. The main quantity of substantive importance that could be obtained was the characteristic cut-off field - in deference to tradition, we use the GBT parameter H_s to describe this, and draw in the corresponding empirical curve for the purposes of comparison with data points. Also no serious effort to obtain the temperature dependence for the alloys was made, primarily because it has not been calculated in current theories.

1. Silver Alloys: In Fig. 27 we show a plot of $M'(T_c)/(\sqrt{H} T_c)$ vs. $\log H$ for the 0.15 at.% Ag sample, both for the quenched and slow cool case, with a possible fit to the GBT "universal" curve. In both cases, the location of T_c was chosen to be around the 50% complete part of their respective zero field transitions. For the quenched case in particular, the width of the transition introduces a fair amount of uncertainty for the low field points, but not enough to account for the discrepancy with the slow-cool data, which is seen to deviate considerably at low fields from the "universal" curve. To the degree that the quenched data fits the universal curve, we might take as confirmation that this sample was, as expected, more uniformly homogenized than the slowly cooled sample.

In any case, the fact that the two curves are identical in high fields implies that this is the region least sensitive to inhomogeneities in the specimen, and should be more heavily weighted for the purposes of

Fig. 27 The fluctuation magnetization at T_c for two Al-Ag alloys, with possible fits to the GBT "universal" dependence.

fitting to the "universal" curve than the low field data.

It is of interest whether the anomalously high values of $M'(T_c)$ at low fields for the slowly cooled case are due to enhanced fluctuations or to a long tail in the high-temperature end of the bulk transition extending considerably above the nominal T_c . I would tend to favor the former view for the following reasons:

(1) In general, increasing concentrations of Ag in Al tend to monotonically lower the transition temperature³⁸, in this case to ~ 55 mK below the pure T_c . Therefore, it seems impossible that a high temperature tail in the transition could extend to greater than 55 mK above the nominal T_c , which would correspond to sections of the sample having no solute at all. A temperature shift by this amount is produced by an applied field of ~ 10 Oe; we see from Fig. 27 that at this field the deviation of the slow-cooled data from that of the quenched case is already becoming apparent.

(2) One would expect that upon entering the transition region, the divergence from the expected value of $M'(T_c)$ would become quite pronounced at some more or less identifiable field. The deviation indicated in Fig. 27 of the slow cool data from the expected dependence would imply a tail in the S-N transition with an extremely slow approach to the fully normal state - i.e., more or less $\propto (\log \Delta T)^{-1}$.

(3) As evidence that effects similar in form to the fluctuation diamagnetism but considerably larger than the order of magnitude predicted can occur in dirty samples, we might mention some measurements on this sample in its as-received state - i.e., swaged down by a factor of 2 in cross sectional area. The S-N transition under these conditions was reasonably narrow - ~ 12 mK. Above T_c there was a very large diamagnetic temperature dependent signal, which for fields ≤ 20 Oe appeared to arise

from a field-independent susceptibility which had a divergence around $T_c(H)$. This susceptibility had an observable temperature dependence extending to at least 4 K, and at least in the high temperature region was observed to deviate from linear behavior for sufficiently large fields and eventually to become completely quenched. The effect was unchanged after the surface was polished. In magnitude, the susceptibility was $\sim 6 \times 10^{-6}$ 0.1 K above T_c , 3.2×10^{-6} at $(T - T_c) = 0.2$ K, and 1.8×10^{-6} at $(T - T_c) = 0.5$ K; these numbers represent an effect enormously larger than observed in "ordinary" fluctuation measurements, yet it is difficult to interpret them any other way: in particular, the divergence near $T_c(H)$ implies that superconductivity is somehow involved, while the very large temperature range and susceptibility to quenching in high fields are reminiscent of fluctuation phenomena. In any case, when it became clear that annealing this sample eliminated the effect, no further attempts to study it were made.

Returning to the case of the quenched Al - Ag alloy, we conclude that a reasonably meaningful value for H_g can be obtained by fitting GBT to the high-field end of a plot like that of Fig. 27. The fact that there is some deviation of the experimental points at low fields from universal behavior does not imply that in a (experimentally unrealizable) perfectly homogeneous alloy such behavior would not be observed. On the other hand, as we shall see, there is no particular theoretical reason to believe that it should be observed.

Results from the other, more dilute silver alloy are also shown in Fig. 27. Here the adherence to the universal behavior is much better, although there still is some "anomalous" behavior in low fields, probably for reasons similar to those discussed above.

2. Silicon Alloys

In Fig. 28 the field dependence of the fluctuation magnetization for the two most dilute Si alloys is shown, in the standard format. The points for both concentrations correspond to the "slow cool" case. Measurements of the 0.3 at. % sample were also made after it had been quenched; in high fields, the results were identical (within experimental error) to those for the slowly cooled sample. As is shown, however, $M'(T_c)$ abruptly became very large for fields ≤ 10 Oe. Its behavior in this regime (e.g., showing hysteresis with changes in temperature) suggested that the bulk transition region had been entered, even though $T_c(H)$ was ~ 60 mK lower in temperature.

In the case of silicon alloys, such a long tail in the bulk transition is not so unlikely as for silver alloys, since increasing concentrations here tend to raise the transition temperature.⁵⁴ Therefore, with a small degree of segregation of the solute it is possible that parts of the sample could be superconducting at temperatures well above the average T_c . The fraction of the sample involved to produce these effects could be very small, so that this level of segregation might not be at all apparent in the gross S-N transition.

Of course, with this hypothesis we must also explain why for the slow-cooled case such a dramatic increase in $M'(T_c)$ for low fields did not occur. We can think of two possible explanations: (i) In Ref. 52 it was concluded that dislocation loops of a type which are produced following a rapid quench can serve as nucleating sites for the precipitation of Si from a supersaturated solution. This precipitation was observed to occur at a sensible rate only at temperatures well above room temperature; it is conceivable, nevertheless, that at lower temperatures such dislocations could serve as nucleating sites for some sort of pre-precipitation - e.g., clustering. In the event of a slow

Fig. 28. The fluctuation magnetization at T_c for two dilute Al-Si alloys, with respective fits to the GBT "universal" curve.

Fig. 29. The fluctuation magnetization at T_c for two more concentrated Al-Si alloys. The GBT "universal" curve is shown for comparison. The dashed curve indicates the amount the points would be displaced if the Curie constant for the nuclear paramagnetism were increased by 10%.

cool, there would be considerably less, though still some, such nucleating sites. These could account for the small excess diamagnetism above the predicted universal curve, which seems to begin at about the same field that the much larger effect in the quenched sample does.

(ii) In the gross S-N transitions for these samples (Fig. 22) it appeared that the quenched one could effortlessly follow some imagined equilibrium transition shape, while the slowly cooled one met with some sort of resistance in its approach to equilibrium. We can suppose, then, that both specimens had the same degree of segregation, leading to a long high temperature tail in the "equilibrium" transition, but that only the quenched one was able to actually follow this tail accurately.

In any case, it must be concluded for this alloy that only the data for $H \geq 10$ Oe should be used in fitting to the universal curve, which means that the uncertainty in the H_g determination is fairly large.

The data for the 0.1 at.% Si alloy, which was also slowly cooled, is seen in Fig. 28 to closely follow the universal curve, with an abrupt break-away at ~ 1 Oe, corresponding to a tail in the transition ~ 10 mK above $T_c(H)$.

The data for the field dependence in the two most concentrated silicon alloys, at concentrations of ~ 0.5 and 0.8 at.%, are shown in Fig. 29. In the case of the 0.5% alloy, measurements were made in both the slow-cooled and quenched conditions; we again find that the data coincided for sufficiently high fields, while for fields ≤ 10 Oe the quenched sample appeared to have entered the bulk transition at $T = T_c$. For the slowly cooled specimens at both concentrations the results appear to be qualitatively different from the more dilute alloys, in that no tendency is observed for an anomalously large diamagnetic signal to appear, even in very

low fields. In relation to the hypotheses advanced for the behavior of the more dilute alloys, this would seem to correlate best, if

at all, with the second, in that it was observed that the "stickyness" of the S-N transition, or the resistance to flux motion, tended to increase with increasing Si concentration.

Also in contrast to the lower Si concentrations, these higher values show little inclination to follow the GBT curve even in high fields. For fields of this magnitude, the results depend quite sensitively on one's choice for the value of the Curie constant of the nuclear paramagnetism, as was discussed earlier. We show in Fig. 29 the change in $M'(T_c)/(\sqrt{HT_c})$ that would be implied by a value 10% larger than what was used ($\chi T = 7.7 \times 10^{-8}$ K). There is no question that by appropriately manipulating this parameter, a better fit to the "universal" expression could be obtained; however, such a procedure would not shed too much light on the subject, since there are no compelling reasons to believe that such behavior should be followed. Probably the interpretation of the results for these samples is best limited to an order-of-magnitude determination of a cut-off field, as measured by the criterion that 1/2 the Prange value is reached at this field. For both samples, the uncertainty in the Curie parameter would have little effect in this field range.

CHAPTER VI: DISCUSSION OF RESULTS

We have shown that at $T = T_c$ the shape of the field dependence of the scaled magnetization of pure aluminum is a very good fit to the prediction of the microscopic theory, while for reasonably dilute, perfectly homogenized alloys it is probably not very different.

It remains to compare the experimentally observed scaling fields H_s with the calculated values for various metals and alloys. Since theory predicts a dependence for H_s not very different from $0.018(\phi_0/\xi_0^2)^{1/2}(1+0.88\xi_0/l)^2$, we compare the measured scaling fields with this quantity in Fig. 30, as a function of ξ_0/l . In addition to the specimens from this work, we have included data obtained by GBT²² and Beasley²⁷ on Pb-Tl and In-Tl alloys (and pure samples). For comparison, the exact theoretical dependence of H_s on ξ_0/l is also shown.

The differences between the Lee and Payne and Kurkijarvi et. al. curves is due to differing approximations that were used. It is our impression that for the points calculated by Lee and Payne, a less restrictive approximation is claimed. In any case, such distinctions are irrelevant in view of the significant deviation of the dirty samples from either of the theoretical predictions.

The dependence of H_s predicted by Maki and Takayma¹⁹ is also shown: their result applies only for the limit $\xi_0/l \gg 1$. It does look as if the data conforms better to this prediction, but until the controversy regarding the correctness of their work is resolved no conclusions can be drawn.

To make this plot it was necessary to know the value of the coherence length ξ_0 for the various samples. It turns out that the microscopic expression $\xi_0 = 0.18\hbar v_F/kT_c$ is not very useful, because it does not contain a prescription on how to handle the anisotropy in the Fermi surface and

Fig. 30. A summary of experimental values of H_s , determined in this work and others, for a variety of pure and alloyed metals, as a function of the "degree of dirtiness" ξ_0 / l (ξ_0 = coherence length, l = electron mean free path). The values of H_s are scaled for easy comparison with various theories: KAE = Kurkijärvi, Ambegoakar, and Eilenberger, LP = Lee and Payne, MT = Maki and Takayama.

energy gap that occurs in real metals. We feel that the best determination of this parameter is from empirical measurements of the supercooling field, using the GL relation $T_c (dH_{c2}/dT)_{T_c} = 0.29 \phi_0 / \xi_0^2$. For Al, such measurements⁵³ lead to a value $\xi_0 = 1.25 \mu\text{m}$. The numbers used for Pb and In, (0.102 μm and 0.364 μm , respectively) have also been obtained from supercooling determinations⁵⁵. Such data is not very precise, and for the present case the uncertainty in ξ_0 is much greater than that for the electron mean free path, which is accurate to within a few percent.

The uncertainty associated with the determination of H_s for the Al alloys is difficult even to estimate, due to the various pathologies that have been mentioned. As a seat-of-the-pants judgment we would say that it varies from $\pm 5\%$ in the pure case to $\pm 20\%$ for the sample with $\xi_0/l \sim 8$. It is probably not relevant to include the two dirtiest alloys of Si ($\xi_0/l \sim 10$ and 17) in this plot, since they did not come very close to the predicted field dependence; however, the identification of a scaling field for these alloys does reinforce the conclusion that the present microscopic theory works only very close to the clean limit.

It would, of course, be interesting to determine at just what degree of dirtiness the theory begins to break down. Unfortunately, we are unable to do this because of the considerable difference between the results on the most dilute alloys of Ag and Si, which cannot be accounted for by experimental uncertainty. In view of the consistency observed among the more concentrated alloys, it seems doubtful that this difference can be explained in terms of a strong sensitivity of the results to the nature of the solute. The most likely point of view is that one or another of these samples is somehow pathological - (e.g., contains excessive amounts of iron impurity). Since the raw data shows that the reproducibility for the 0.1%

Si specimen was unusually poor, this can be considered the most suspect.

Some discussion of the materials measured by the Harvard group is probably in order: None of the alloys meet the requirement $\xi_0/\ell \ll 0.18\theta_D/T_c$ imposed by the theory, but the coincidence of the In-Tl samples with our results suggests that in a correct theory this condition may not be so stringent. The Pb-Tl alloy can, we think, be discounted from serious consideration not only because of its flagrant violation of this condition, and the considerable uncertainty in H_s , but also because the strong-coupling correction that is required in the case of Pb has not been performed for the current theory. The latter consideration suggests that the coincidence of H_s for the pure Pb sample with theory is probably accidental. We feel that the best test of the theory in the pure limit ($\xi_0/\ell = 0$) is provided by the Al and In samples, and we conclude that in this limit it is in reasonable agreement with experiment. Again it might be mentioned that the results of GBT for In have been corroborated in this work.

The temperature dependence for pure Al and In has also been shown to be in reasonable agreement with the theory. Because of the problem in obtaining representative alloys, and since there is no calculation with which to compare, the temperature dependence of the fluctuation diamagnetism in the alloys was not carefully measured.

APPENDIX A: Analysis of Temperature Feedback

Let ΔT be the difference between the actual block temperature and the desired temperature, and ΔP be the deviation of the heater power from that required for $\overline{\Delta T} = 0$. There will be noise in the output of the thermometer bridge due to electronic and Johnson noise; we incorporate this as an imaginary temperature noise T_N^* appearing at the thermometer. The "equation of motion" of the block is

$$\frac{d}{dT}(\Delta T) = \left(\frac{1}{c}\right)\Delta P, \quad (1)$$

where c is its specific heat. When the feedback loop is activated, we have in addition

$$\Delta P = -(\partial P / \partial T)(\Delta T + T_N). \quad (2)$$

Here $(\partial P / \partial T)$ is a parameter describing the strength of the feedback. If the lock-in amplifier for the thermometer bridge has a 6 db/octave roll-off with a time constant τ_F , then this parameter has a frequency dependence $(\partial P / \partial T)_\omega = (\partial P / \partial T)_0 / (1 + j\omega\tau_F)$. Combining equations (1) and (2) and writing them in terms of frequencies gives

$$j\omega(\Delta T)_\omega = -\frac{1}{\tau} \frac{1}{1+j\omega\tau_F} [(\Delta T)_\omega + (T_N)_\omega], \text{ where } \frac{1}{\tau} = \left(\frac{\partial P}{\partial T}\right)_0 / c.$$

Note that the strength of the feedback is described by a parameter with the dimensions of time, rather than the usual dimensionless "loop gain" of other feedback systems. We now solve for $(\Delta T)_\omega$:

$$(\Delta T)_\omega = \frac{-(T_N)_\omega}{G(\omega)}$$

where $G(\omega) = 1 - \omega^2\tau\tau_F + j\omega\tau$. The spontaneous response of the system is

* This should not be confused with the "noise temperature" sometimes used to describe the noise performance of an amplifier.

found by solving for the zeroes of $G(\omega)$:

$$\omega_r = \frac{1}{2\tau_F} \left[j \pm \left(-\frac{4\tau_F}{\tau} - 1 \right)^{1/2} \right]$$

In the absence of noise, ΔT evolves as $\exp(j\omega_r t)$. This prediction significantly disagrees with experimental results in that it predicts an exponentially decaying response for all values of τ and τ_F . In practice, I found that for sufficiently strong feedback (small τ) the system would break into sustained oscillations. The equation also suggests that the qualitative behavior of the system (completely damped vs oscillatory) is determined by the ratio of τ and τ_F . This was observed in the sense that stability for strong feedback would only occur if τ_F was small enough, contrary to one's intuitive feeling. Also the oscillation frequency was found to vary as the square root of τ_F for sufficiently large (τ_F/τ) , as predicted.

In an earlier version of the apparatus, the "block" being controlled was in fact a reservoir of He^4 used for cooling. Because the specific heat of He^4 is much larger than that of copper at these temperatures, the value of C was at least an order of magnitude greater, all other parameters being not much different. It was found, as suggested by the above analysis, that a much larger value of $(\partial P/\partial T)_0$ could be used before instability set in - i.e., before the same value of τ was reached.

It is not difficult to qualitatively fix up the above model in order to account for the possibility of instability: for instance, it takes some time for the heat produced in the heater to diffuse throughout the block. We might roughly account for this by rewriting the "equation of motion":

$$\frac{d}{dt}(\Delta T) = \frac{1}{C} \Delta P(t - t_D) \approx \frac{1}{C} [\Delta P(t) - \dot{\Delta P}(t) t_D + (1/2) \ddot{\Delta P}(t) t_D^2 + \dots]$$

i.e., there is a fixed time lag t_D between application of power to the heater and the ultimate warming of the thermometer. In terms of frequencies, we then have

$$j\omega(\Delta T)_\omega \cong \frac{1}{C} (\Delta P)_\omega [1 - j\omega t_D + 1/2(j\omega t_D)^2 + \dots]$$

If this is carried through keeping only the lowest order in t_D , we find that the zeroes of $G(\omega)$ occur for

$$\omega_r = \frac{1}{2\tau_F} [j(1-t_D/\tau) \pm (\frac{4\tau}{\tau} - (1 - \frac{t_D}{\tau})^2)^{1/2}]$$

and it is apparent that for $\tau < t_D$ the system is unstable.

Assuming we have a stable system, the rms fluctuation of the temperature from its mean value can be written:

$$\langle (\Delta T)^2 \rangle = (T_N^2)_\omega \int_0^\infty \frac{d\omega}{|G(\omega)|^2}$$

The effective temperature noise T_N has been converted via the feedback into actual temperature noise in the block. From dimensional considerations (using the simple model), we find that the integral for $\langle (\Delta T)^2 \rangle$ scales as $1/\tau$ times a function of (τ_F/τ) only; therefore the smallest rms temperature fluctuations will occur for weak feedback (large τ).

It is apparent from the standpoint of stability and temperature fluctuations that weak feedback is to be preferred; however, it may well be that the overriding consideration is long-term freedom from drifts. Suppose, for instance, that the average heater power P_0 required to hold the block at the desired temperature should change (i.e., there is a change in the heat leak from the block). The resulting change in the average temperature of the block will be $\Delta T = \Delta P_0 / (\frac{\partial P}{\partial T})_0 = \Delta P_0 (\tau/c)$. Hence for the greatest freedom from the effects of low-frequency system drifts, a large specific heat and tight feedback (small τ) are to be preferred.

APPENDIX B: Flux Transformer Calculations

In this section we will deal with the problem of optimizing sensitivity without using the usual "long solenoid" approximation - an approximation which turns out to be of little utility for practical situations. In addition, we demonstrate that the presence of feedback does not alter the optimization conditions, a result that is far from obvious.

As a starting point, we take the simple configuration of Fig. 31a. In the following, the subscripts p and s refer to the primary (pick-up) and secondary (SQUID) coils. It is supposed that the wires connecting the coils have negligible inductance. We first obtain the standard sensitivity formula by observing that for a closed superconducting circuit the total flux-turns must remain constant - i.e., no net voltage can be developed around the circuit. This means $\delta[N_p \phi_x + (L_p + L_s)i] = 0$, where ϕ_x is the "applied" flux, which is assumed to couple equally into every turn of the pickup coil. If M is the mutual inductance between the SQUID hole and the secondary coil, then the shielding current δi produces the measured flux

$$\delta\phi_{\text{SQUID}} = [-MN_p / (L_p + L_s)] \delta\phi_x \quad (1)$$

We first notice that if the dimensions of the two coils remain fixed, but the number of turns N_p and N_s are assumed variable, then the quantity in brackets (the "flux transfer coefficient") is a function only of N_p/N_s . If we accordingly optimize [] with respect to either of these variables, the resulting expression must depend only on the geometry (still assumed arbitrary) of the coils. It is easiest to optimize with respect to N_p : we put $L_p = \lambda_p N_p^2$, where λ_p is a geometry-dependent factor, and find that the flux transfer coefficient is maximized for $N_p^2 = L_s / \lambda_p$; i.e. $L_p = L_s$.

(a)

(b)

(c)

Fig. 31. Schematic diagrams of various flux transformer configurations: (a) a simple flux transformer. The entire circuit path must be superconducting. (b) with "flux nulling" feedback. A symmetric SQUID is implied, where $|\phi|$ is the actual flux in either hole. (c) with "current nulling" feedback. For (b) and (c) the feedback is activated by closing switch S.

This is analogous to the requirement that an amplifier's input impedance be matched to the source impedance for maximum power gain. With the above value for N_p inserted, we find:

$$\frac{\delta\phi_{\text{SQUID}}}{\delta\phi_x} = \frac{-1}{2\sqrt{\lambda_p}} \frac{M}{\sqrt{L_s}} \quad (2)$$

We note that indeed this expression does depend only on the geometry of the two coils, and as an extra bonus the geometry dependence is separated - this means that we can independently consider the optimization conditions for the primary and secondary coils.

First we consider the secondary coil, for which $M/\sqrt{L_s}$ must be maximum. This conflicts with a statement in Ref. 29 that M/L_s should be optimized, which comes from writing Eq. 2 as $\delta\phi_{\text{SQUID}}/\delta\phi_x = N_p M/(2L_s)$, where N_p is taken to be the optimizing value. The mistake arises from the notion that M/L_s should be independently maximized, since N_p depends implicitly on L_s and appears in the overall formula for the flux gain. This mistake invalidates most of the conclusions reached in Ref. 29 about optimizing the secondary coil.

It is correct, however, to independently maximize $M/\sqrt{L_s}$. If the long solenoid approximation for the secondary coil is used, we have $M \approx L_s/N_s$, and it turns out that $M/\sqrt{L_s} \approx (\text{coil diameter}) \times (\text{coil length})^{1/2}$; this suggests that the secondary coil should be made very short. However, the proximity of the superconducting SQUID body to the coil clearly causes significant distortions of the magnetic field configuration, and attempts to calculate these quantities are probably not useful. Fortunately, in Ref. 29 empirical measurements of M and L_s are reported for a number of coil configurations. They find that the mutual inductance behaves as if the windings of the coil, no matter how short it is, were spread out over

the full length of the SQUID body. The self-inductance, however, shows no such simple behavior. In Fig. 32 I show the dependence of M/L_s on the fraction of the volume of the SQUID hole occupied by the secondary coil for the examples investigated in Ref. 29; the data has been extracted from their Figs. 12 and 13. Obviously, $M/\sqrt{L_s}$ does not depend on this parameter alone, but in general it is clear that the secondary coil should have as large a diameter as is practical and have a length comparable to (but not longer than) the length of the SQUID hole - a conclusion quite different from the simple one based on the long solenoid approximation as given above.

We now turn to a consideration of the primary coil, for which $(2\sqrt{\lambda_p})^{-1}$ must be as large as possible. An expression for this can be obtained with reference to tabulated inductance tables for a cylindrical coil of arbitrary length/diameter ratio:

$$\frac{1}{2\sqrt{\lambda_p}} = 5 \times 10^3 \left(\frac{1 \text{ cm}}{D}\right)^{1/2} f(\ell/D) \quad (3)$$

where the function f has been plotted in Fig. 33. Here ℓ is the length, D the diameter of the coil. Since it turns out that f has a dependence for practical values of ℓ/D not very different from $(\ell/D)^{1/3}$, we have $(2\sqrt{\lambda_p})^{-1} \sim \ell^{1/3} D^{-5/6}$. The dependence on ℓ is so weak that there is little point in making the coil very long. The factor $D^{-5/6}$ simply indicates that for a measurement of a given flux (e.g. the magnetization of a sample of fixed diameter) the coil should closely surround the experimental volume - i.e., have the largest possible filling factor. If instead it is desired to maximize the sensitivity to magnetic field, the conclusion is quite different: in this case, we find

$$\frac{d\phi_{\text{SQUID}}}{dB_x} \left[\frac{\text{flux quanta}}{\text{Gauss}} \right] = 1.9 \times 10^{10} \frac{M}{\sqrt{L_s}} [H^{1/2}] \left(\frac{D}{1 \text{ cm}} \right)^{3/2} f(\ell/D).$$

Fig. 32. The effectiveness of the coupling to a SQUID of various coils investigated by Giffard, Webb, and Wheatley. The figure of merit $M/\sqrt{L_s}$ has been calculated from their data, and is plotted against the fraction of the volume of the SQUID hole occupied by the coils.

Fig. 33. Dependence of the function f (defined in the text) on ℓ/D , where ℓ is the length and D the diameter of a cylindrical coil.

The $D^{3/2}$ dependence dominates the dependence on length and dictates that the pickup coil be as large as possible - particularly in diameter. The conclusion that there is in principle no limit to the magnetic field sensitivity achievable may seem intuitively suspicious - however, if one thinks of the operation of a flux transformer as that of transferring magnetic energy ($B^2/8\pi \times \text{Vol}$) from one location to another, it may not seem so unlikely.

To summarize these results, the procedure for maximizing a field/flux measurement will be outlined: the shape of the pickup coil is decided on primarily by practical considerations - i.e., largest possible filling factor, largest possible diameter consistent with experimental limitations. Likewise, the secondary coil should fill the SQUID volume as much as possible. For one or another of these coils, the number of turns can be chosen as a matter of convenience - we could decide, for instance, that the secondary coil will have one close-wound layer. It is then necessary to calculate L_s , which is unfortunately complicated by the close proximity of the superconducting SQUID body to the secondary coil. The data presented in Ref. 29 indicated that for coils that fill a large fraction of the SQUID volume, L_s is of the order of half the calculated (free standing) value. This is what we would expect for a symmetric SQUID, since any applied flux must be shared between the two holes. Having calculated the inductance of the secondary coil, the number of turns required for the primary coil is $N_p = (L_s/\lambda_p)^{1/2}$, where $(\lambda_p)^{-1/2}$ can be obtained from Eq. 3. These turns should be evenly distributed along the primary coil length, so that in general they will not be close wound.

The optimization condition places a constraint only on the ratio of the inductances. The overall scale is primarily a practical consideration,

as long as the inductances are significantly greater than stray inductances of connecting wires. In Ref. 29 it is reported that tightly wound pairs of superconducting wire have $\sim 0.3 \mu\text{H/m}$ inductance.

If negative feedback is used, it will certainly have a large effect on the apparent inductance of the secondary coil; for the type shown in Fig. 3lb, wherein the flux in the secondary coil is maintained null, it is clear that the apparent inductance of L_s is reduced almost to zero. Likewise the circuit of Fig. 3lc, which nulls the flux transformer current, makes the secondary coil appear to have a very large inductance. This raises the question of whether the optimization condition for L_p is not significantly altered in the presence of feedback. To properly investigate this, we must work out the equations for feedback in detail: I begin with the flux-nulling type, shown in Fig. 3lc. $|\phi|$ is the actual flux in either hole of the symmetric SQUID, which determines the output of the SQUID electronics, L_H is the inductance of either hole, i' is the shielding current flowing in the body of the SQUID. M_1 and M_2 are mutual inductances to the two holes, and L_s is the inductance of the secondary coil for $M_1 \rightarrow 0$. We have to begin with:

$$\phi = M_1 i_1 + L_H i'$$

$$-\phi = M_2 i_2 + L_H i'$$

which is more conveniently written:

$$M_1 i_1 = 2\phi + M_2 i_2$$

$$L_H i' = -(\phi + M_2 i_2)$$

The equation for conservation of flux-turns in the transformer circuit is:

$$N_p \phi_x + (L_p + L_s) i_1 + M_1 i' = 0. \text{ With the aid of the two equations above, } i_1$$

and i_1 can be eliminated in favor of ϕ and i_2 :

$$N M_1 \phi_x + 2\phi [L_p + L_s (1-K^2/2)] + M_2 i_2 \{L_p + L_s (1-K^2)\} = 0$$

where K is the coupling coefficient between L_s and the SQUID:

$$K^2 = (M_1^2 / L_s L_H).$$

We now have a master equation relating ϕ , ϕ_x , and i_2 ; to activate the feedback loop, we close the switch as shown in Fig. 31. This establishes a condition relating i_2 and ϕ :

$$i_2 = \frac{G}{M_2} \phi$$

Here G is the "loop gain" - a dimensionless parameter which expresses the vigor with which the system is nulled.

At this point, the effects of noise must be discussed. In general, the SQUID output will include electronic and fluctuation-induced noise, which can be expressed as an apparent flux noise ϕ_N at the SQUID input; when the feedback loop is activated, this is fed back along with the actual flux ϕ , so we should write $i_2 = (G/M_2) (\phi + \phi_N)$. If this is inserted in the "master equation", one can then solve for ϕ as a function of ϕ_x and ϕ_N . However, the quantity that is monitored during feedback operation is proportional to i_2 - i.e., to $(\phi + \phi_N)$. It is found finally that

$$i_2 = \frac{G}{M_2} \times \frac{-N M_1 \phi_x + 2[L_p + L_s (1-K^2/2)] \phi_N}{[\text{Denominator}]}$$

where the denominator is independent of ϕ_x and ϕ_N .

Ultimately it is the signal/noise ratio at the output that is of concern;

this can be read off directly from the above equation:

$$\frac{(i_2)_s}{(i_2)_N} = \frac{\phi_x}{\phi_N} \times \frac{N_p M_1}{2[L_p + L_s(1-K^2/2)]}$$

The factor containing flux transformer parameters is exactly the same as was calculated for the "flux transfer coefficient" previously, and is independent of loop gain, so the optimization conditions are unchanged by feedback. Note that L_s is reduced from the calculated value, by a factor 1/2 in the limit of perfect coupling, as was anticipated for the symmetric SQUID.

A similar calculation can be performed for the current-nulling configuration (Fig. 31c). The results are exactly the same, except that the flux-coupling inductor L' is included with L_p and L_s . Since this can be made quite small, there is essentially no difference, in terms of signal/noise between the two configurations.

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