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Thermal Conductivity and Thermal Effects in Superconducting Niobium.

Syed Mohammad Wasim

Louisiana State University and Agricultural & Mechanical College

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IN SUPERCONDUCTING NiOBium

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in

The Department of Physics and Astronomy

by

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ABSTRACT

Thermal conductivity measurements on a niobium plate of intermediate purity (\(\ell \approx \xi_0\)) were performed in the normal, superconducting, and mixed states. The lattice and electronic components of the conductivity in the superconducting state are separated. The critical temperature and the energy gap are found to be \(T_C = 9 \pm 0.1^0K\) and \(2\epsilon(0) = 3.96kT_C\), respectively. The temperature dependence of the minimum in the thermal conductivity in the mixed state suggests a decrease in both the phonon and the electron conductivities just above \(H_{cl}\). The comparative importance of each depends on a combination of temperature range and purity of the sample. The slope \(\delta K_m/\delta H\) and upper critical field parameter \(\chi_1(t)\) are found to change with temperature much faster than predicted by relevant theories.

The temperature dependence of the magnetocaloric effect, its distribution over the mixed state and the magnetization were measured in a niobium single crystal. From these results magnetocaloric cooling, enthalpy and free energy have been calculated and discussed. The irreversible hysteretic heating in the mixed state and its field and temperature dependence have been discussed in terms of the pinning forces in the light of Morton's theory. The reduced upper critical field \(h^*\) and the reduced Ginzburg-Landau parameter \(\chi_1(t)/\chi_1(1)\) as obtained from magnetocaloric measurements are again found to increase faster with decreasing temperature than predicted by the theory.

The 'flux flow' resistivity and the corresponding heat dissipation in both parallel and perpendicular fields have been
been measured and from the results $H_{c3}/H_{c2}$ has been determined, and proportionality between flow resistance and rate of heat dissipation is found.
CHAPTER I

INTRODUCTION

The purpose of the present study is a comprehensive investigation of all thermal phenomena that appear in the mixed state of intrinsic type II superconductors. Niobium was chosen as the subject of this work. The different phenomena investigated can be separated into the following three parts: the thermal conductivity, the magnetocaloric effects and the heat dissipation associated with flux flow resistance.

The Thermal Conductivity. The purpose of this part of the work is the study of the thermal conductivity of niobium in the normal ($K_n$), superconducting ($K_s$), and mixed states. It is presented in Chapter II. The focus of the work is on the behavior of the thermal conductivity in the mixed state and its dependence on magnetic field and temperature.

Previous extensive work on the thermal conductivity of niobium is mainly that of Mendelssohn and his co-workers. Their data does not extend into the temperature region above 4.2°K - a shortcoming that leaves the upper half of the reduced temperature range unexplored - and their study of the influence of an applied magnetic field lacks in interpretation for the reasons that the existence of a mixed state and the nature of niobium as an intrinsic type II superconductor were not recognized at that time. It is on these two points that the present work intends to bring more
complete results and interpretations. More recently, Lindenfeld et al. reported mixed state thermal conductivity measurements on pure and impure specimens of niobium at the Cleveland Conference. Lowell and Sousa have published a mixed state measurement for only one temperature, and Muto et al. and Noto have reported a more complete investigation of a scope similar to the present work.

Recent theoretical and experimental results were mainly concerned with the extreme limits of dirty \( \ell/\xi_0 \ll 1 \) and pure \( \ell/\xi_0 \gg 1 \) type II superconductors, these limits depending on the relative magnitudes of the electronic mean free path \( \ell \) and the coherence length \( \xi_0 \). Formulas have been obtained for the upper critical field \( H_{c2}(t) \) or the corresponding parameter \( \chi_1(t) \) by Gorkov for the pure limit and by Maki and de Gennes for the dirty limit while the general case was treated by Helfand and Werthamer and by Eilenberger in an effort to extend the results to all temperatures and impurity concentrations. Anisotropy of \( H_{c2} \) in cubic materials such as niobium was attributed by Hohenberg and Werthamer to nonlocal corrections to the Ginzburg-Landau-Abrikosov-Gorkov theory with the conclusion that for pure polycrystalline niobium, Eilenberger's curves represent only a lower limit for \( H_{c2}(t) \) and \( \chi_1(t) \).

Detailed theoretical treatment of the thermal conductivity \( K_m \) in the mixed state, for the gapless region where the applied field is close to the upper critical field, is due to the work of Caroli and Cyrot for the limit of dirty superconductors and of Maki for the limit of pure type II superconductors. This leaves
the intermediate range still without a theory. There are also very few experimental results on superconductors of this intermediate category.\textsuperscript{14} It is, therefore, notable that the samples studied here are in this intermediate range which makes the comparison of the results to existing theory and to measurements on purer niobium\textsuperscript{4} interesting. Limited agreement is found with the dirty limit theory\textsuperscript{12} in the sense that linear behavior of $K_m(H)$ is found in the region close to $H_{c2}$, with a finite slope at $H_{c2}$, and the slope $\partial K_m/\partial H$ does go through a maximum as the temperature is varied. But experimental slopes have a much steeper variation with temperature, leading to values up to 10 times larger than expected from theory. The earlier treatment by Dubeck et al.\textsuperscript{15} inserting in the results of Bardeen, Rickayzen, and Tewordt\textsuperscript{16} (hereafter referred to as BRT) a field-dependent gap parameter, though it is open to serious objections\textsuperscript{12} in the gapless region, is still found to be quite successful for the description of the minimum of $K_m$ but only at temperatures where phonon conduction is predominant ($K_{gs} > K_{es}$). A detailed comparison of the present work with the results of Ref. 4 reveals that a sudden decrease of the electronic conductivity $K_{em}$, upon entry in the mixed state, has to be postulated in addition to the decrease of the phonon conductivity $K_{gm}$.

In Chapter II, Sec. I, we review briefly the techniques of measurement; Sec. II covers the results on thermal conductivity in (A) the superconducting and normal states and (B) the mixed state.
The Magnetocaloric Effect and the Hysteretic Heating. The magnetocaloric effect in superconductors i.e. the change in temperature which under adiabatic conditions reflect the change in entropy when the transition from the superconducting to the normal state takes place in presence of a magnetic field was predicted and observed by Mendelssohn and Moore\textsuperscript{17} and more recently by Yaqub.\textsuperscript{18}

Unlike type I superconductors, it is predicted\textsuperscript{11} that the magnetization and entropy of type II superconductors change continuously in the mixed state, starting from the lower critical field $H_{c1}$ and terminating with a second order phase transition to the normal state at the upper critical field $H_{c2}$. This suggests that for a thermally isolated sample a monotonic increase or decrease in the applied magnetic field in the mixed state should produce a monotonic decrease or increase in the temperature. Reversible magnetocaloric effects in type II superconductors have been previously reported by Wasim \textit{et al.},\textsuperscript{19} Ohtsuka and Takano,\textsuperscript{20} Goedemoed \textit{et al.},\textsuperscript{21} Barnes and Hake,\textsuperscript{22} and by Flippen.\textsuperscript{23} In actual measurements, when the applied magnetic field is increased monotonically from $H_{c1}$ to $H_{c2}$ in the mixed state, the total caloric effect consists of two parts:

(i) The reversible magnetocaloric effect $Q_r$ which appears as a cooling in increasing fields and reverses to a heating in decreasing fields. This part is characterized by its reversibility and may be said to be due to the decoupling of the superconducting electron pairs.

(ii) The irreversible hysteretic dissipation of heat that appears in the mixed state any time the magnetic field is changing.
The rate of heat $Q_{irr}$ evolved can be said to be caused by normal electron currents generated by the motion of the flux lines.\textsuperscript{24}

Because of the higher magnitude of the irreversible heating at lower temperatures and in less perfect crystals, observation of ideal magnetocaloric effect is often hampered. This irreversible heating sometimes leads to a fluctuation in the magnetic moment $M$ and the total heat development $\dot{Q} = \dot{Q}_r + \dot{Q}_{irr}$. This effect has been recognized by Zebouni \textit{et al.}\textsuperscript{25} and Goedemoed \textit{et al.}\textsuperscript{26} as being associated to flux jumps when the sample enters the mixed state. Gorter\textsuperscript{27} has shown from thermodynamic considerations that when the magnetic moment $M$ and the heat development $Q$ of a type II superconductor are measured at the same temperature during the magnetization process, it is possible to calculate the variation in the enthalpy $E$ in the mixed state, which in turn can be used to check the criterion for flux jumping.

The purpose of this part of the present work is to make a detailed study of the temperature dependence of the magnetocaloric effect on a niobium single crystal and of its distribution throughout the mixed state. Magnetization measurements have been made to calculate the enthalpy in the mixed state and Gorter's criterion for flux jumping has been studied. At higher temperatures where the irreversible heating is smaller, the reversible magnetocaloric effect is preponderant and the associated variation of the entropy in the mixed state is calculated. The upper critical field $H_{c2}$ and the corresponding Ginzburg-Landau-Maki parameter $\lambda$ have been compared with the existing theories and previous experimental
results. This is presented in Chapter III.

**The Flux Flow Resistance and Associated Heating in the Mixed State.**

Abrikosov characterizes the mixed state as a lattice-like structure of quantized flux lines. These flux lines play an important role in nonequilibrium phenomenon as created by the presence of transport current $I$. Under this condition the flux lines are subject to a driving force exerted by the Lorentz force. In an ideal type II superconductors, when the transport current $I$ is applied at right angles to the applied field $H$, the flux lines are expected to move in a direction at right angles to both $I$ and $H$ in order to equalize the magnetic pressure. However, in practice, lattice defects of various kinds present in the material effectively pin down the flux lines and enable the specimen to sustain non uniform flux line densities. If the specimen is made thermally stable, it can be driven into a state wherein the Lorentz driving force exceeds the pinning force and the flux lines undergo a viscous flow. These moving flux lines induce an electric field $E$, which is observed as a resistive voltage drop $V$ in the direction parallel to $I$. This is the so called "flux flow" resistivity. The creation of an induced electric field $E$ is a significant departure from London's concept of $E = 0$ in type I superconductors. The voltage drop leads, as was first shown by the present work, to a power dissipation of the form $P = VI$, which appear as an increase in the temperature of the specimen. Assuming that the velocity of the flux lines is proportional to the
Induced field, theory predicts that at a fixed value of the applied field, the voltage developed should vary linearly with the applied current. Many experiments confirm the linear flux flow behavior for high transport current densities. The deviation from the "ideal" linear behavior at low current densities has been the subject of much discussion and some controversy. The popular view appears to be that the departure from linearity is due to interactions with the surface and with volume defects (e.g. dislocations, and non uniformity), which are particularly effective at low values of I where the electromagnetic forces on the fluxoids are relatively small compared to the pinning forces.

Saint-James and deGennes have solved the Ginzburg-Landau equation for the wave function in the presence of a plane boundary between the superconductor and an insulator. As a result of the calculation they have shown that for H parallel to the surface of the specimen, a superconducting surface sheath exists between \( H_{c_2} \) and \( H_{c_3} \) where \( H_{c_3} = 1.69 H_{c_2} \). For fields perpendicular to the surface, the solution reduces to that of Abrikosov and no remanent superconductivity is expected beyond \( H_{c_2} \). This has been confirmed by Hempstead and Kim, Aulter et al., and Druyvesteyn et al. from resistive measurements. A wide variation in \( H_{c_3}/H_{c_2} \) ratio has been found extending up to 4.3, depending on the nature of the surface.

This part of the present work is presented in Chapter IV and deals with the flux flow measurements and the corresponding power dissipation on a niobium and a vanadium plate. A comparison with
the theory and other experimental results has been made. The resistive and thermal transition, with particular reference to the value of the ratio $H_{c3}/H_{c2}$, has been studied to compare with the theory of Saint-James and deGennes.
CHAPTER II

THE THERMAL CONDUCTIVITY OF NIOBium

1. Experimental Method

The annealed sample was supplied by Materials Research Corporation\textsuperscript{40} in the form of a plate \(0.01 \times 3.0 \times 0.435\) inches from triple zone refines material (Marz grade). A typical analysis shows 170 parts per million (ppm) total impurities, of which 100 ppm of tantalum, 8 ppm of carbon, 6.4 ppm of tungsten, 23.4 ppm of nitrogen and 4 ppm of oxygen are the largest contributions.

The resistance ratio was found to be \(\Gamma = \frac{R_{300}}{R_N} = 29\) and the residual resistance \(\rho_0\) was measured to be \(5.2 \times 10^{-7} \Omega \text{ cm}\). This low value of the resistance ratio suggests high concentration of structural defects and incomplete annealing. From the measurement of \(\rho_0 = \sigma^{-1}\), the electronic mean free path \(l\) was estimated by using the relation \(D = \sigma/2e^2N(0) = 1/3 V_F^2\tau\) where \(D\) is the diffusion constant. We get \(l = V_F\tau = 3\sigma/2e^2N(0)V_F\) where \(\sigma\) is the residual electrical conductivity, \(N(0)\) is the density of states, and \(V_F = 3 \times 10^7\) cm/sec is the Fermi velocity. \(N(0)\) was calculated by using the relation \(N(0) = 3\gamma/m^2k^2\), where \(\gamma = 7.85\) mj/mole deg\(^2\) is the electronic specific heat constant. This yields a value of \(l = 328\) A which is of the same order of magnitude as \(\xi_0 = 390\) A reported by French\textsuperscript{41,42} and 430 A by Finnemore, Stromberg, and Swenson\textsuperscript{42} (hereafter referred to as FSS).

The main apparatus and measuring techniques were an evolved and extended form of those used in the earlier work of Grenier.
et al.\textsuperscript{43} and their description will be brief. The sample inside a vacuum calorimeter was clamped in a brass sample holder which itself was screwed into a copper post extending up into the liquid helium bath. The temperature of the sample could be raised to 10°K with the brass sample holder acting as a thermal resistor between sample and heat sink. Two heaters of Constantan wire No. 40 were wound, one at the bottom of the sample and the other on the sample holder. The heater on the sample holder was used to raise the temperature of the sample in the range 4.2°K to 10°K and also to drive the sample normal thermally after each field cycle to eliminate the trapped flux. The sample heater was used to establish a thermal gradient along the sample for the heat conductivity measurements. The thermal gradient along the sample varied from 20 m°K at the lowest temperature to about 100 m°K at the highest temperature. A "well-matched" pair of 50 Ω, 1/10 W Allen-Bradley carbon resistors was used for thermal conductivity measurements, and the thermometers were calibrated against the vapor pressure of liquid helium in the temperature range of 1.4°K to 4.2°K and against a calibrated germanium thermometer\textsuperscript{44} in the range 4.2°K to 10°K. The temperature measuring circuit was in the form of a bridge, two arms of which were carbon thermometers and a difference of temperature would result in an unbalance voltage in the measuring arm of the bridge. All measurements were done with dc methods. The circuit was designed so that the voltage and current of each thermometer could also be measured separately. Current in the thermometers was varied from 4 µA at T < 4°K to
about 10 μA at higher temperatures. At each temperature $T$ the bridge was balanced by adjusting the current in the two thermometers so that to a zero heat current in the absence of the magnetic field there corresponded a zero signal on the recorded. The temperature of the bath was then lowered to $T - \Delta T_0$ where $\Delta T_0$ ranged from around 150 m°K at higher temperature to about 30 m°K at the lower temperature. The sample heater was then switched on, and the heat current was adjusted so that the thermometer closest to the sample heater read the same voltage as at $T$. This procedure has the advantage that the temperature difference $\Delta T$ can be computed from the unbalance voltage $\Delta V$ through the use of the characteristic $R(T)$ curve of only one thermometer, in this case the one closest to the heat sink. Measurements over a period of months showed that the slopes $\Delta T_0/\Delta R$ were reproducible within 4%. For this reason, we plotted $\Delta T_0/\Delta R$ against $T$ on a semilog paper and used the values from the smoothed out curve. Point by point measurements of $K_m$ were made in the same way as those of $K_s$ at increasing values of magnetic field until it was found that $K$ was constant at $H > H_{c2}$.

It was observed that at temperatures above 3.5°K carbon resistors had considerable magnetoresistance. This was measured by balancing the thermometers at the temperature $T$ and then recording the signal $\Delta V$ as a function of the applied magnetic field without setting the thermal gradient across the sample. This signal was added or subtracted from the conductivity signal depending on whether the magnetoresistance was negative or positive. All measurements were made with the direction of the magnetic field parallel to the large
face of the sample in order to minimize demagnetization effects.

II. Experimental Results and Discussion

A. Thermal Conductivity in the Superconducting and Normal States

The temperature dependence of the thermal conductivity of niobium in the superconducting state, $K_s$, and in the normal state, $K_n$, is plotted in Fig. 1 and partly tabulated in Table 1. The temperature at which the $K_s$ and $K_n$ curves intersect one another is taken as the critical temperature $T_c$ and is found to be $9.0 \pm 0.1^\circ\text{K}$.

The straight line which very nearly fits the normal state points is obtained from the residual resistance $\rho_0$ by assuming the validity of the Wiedemann-Franz relation $K_n = L_0 T/\rho_0 (\rho_0 = 5.2 \times 10^{-7} \Omega \text{cm}, K_n = 47.01 \text{Wcm}^{-1}\text{K}^{-1})$. A slight tendency of the experimental points to fall below the Lorentz line at temperatures close to $T_c$ seems genuine and corroborates the results obtained by Muto et al. and can be attributed to the existence of a small resistive component due to scattering of electrons by phonons.

In the major remaining part of the temperature range, the nearly exact fit of the experimental points to the Lorentz relation indicates that scattering of electrons by impurities is predominant in the normal state.

In the superconducting state, the presence of a local maximum in $K_s$, already observed by Calverley, Mendelssohn, and Rowell\textsuperscript{1} and Connolly and Mendelssohn\textsuperscript{1} (hereafter referred to as CM) in niobium, tantalum and vanadium, and by Sharma\textsuperscript{45} in tantalum, is recognized as being due to the lattice contribution to the thermal
Niobium 10 mils plate

$T_c = 9 \, ^\circ K$

$\circ K_S \quad K_{en} = 47.01 \, T$

$\triangle K_n$

$-K_{en}$

Fig. 1
TABLE I. Temperature dependence of thermal conductivity parameters. \( K \) is in mW-cm\(^{-1}\)-K\(^{-1}\), \( H_{c2} \) is in G.

<table>
<thead>
<tr>
<th>( T )</th>
<th>( t )</th>
<th>( K_s )</th>
<th>( K_{gs} )</th>
<th>( K_{es} )</th>
<th>( H_{c2} )</th>
<th>( \chi_1 )</th>
<th>( [K_{\text{min}}]_{\text{exp}} )</th>
<th>( [K_{\text{min}}]_{\text{cal}} )</th>
<th>( K_{\text{min}}/K_s )</th>
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<tbody>
<tr>
<td>9.0</td>
<td>1.0</td>
<td>423</td>
<td>423</td>
<td>1.14</td>
<td>no min.</td>
<td>no min.</td>
<td>no min.</td>
<td>no min.</td>
<td></td>
</tr>
<tr>
<td>8.4</td>
<td>.933</td>
<td>374</td>
<td>380.0</td>
<td>421.0</td>
<td>1.209</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>.994</td>
</tr>
<tr>
<td>8</td>
<td>.888</td>
<td>341</td>
<td>342.5</td>
<td>765.4</td>
<td>1.348</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>.987</td>
</tr>
<tr>
<td>7.3</td>
<td>.811</td>
<td>286.5</td>
<td>286.54</td>
<td>1238.4</td>
<td>1.344</td>
<td>285.0</td>
<td>&quot;</td>
<td>.994</td>
<td></td>
</tr>
<tr>
<td>6.8</td>
<td>.755</td>
<td>247.0</td>
<td>4.0</td>
<td>242.94</td>
<td>1548.0</td>
<td>1.337</td>
<td>244.0</td>
<td>&quot;</td>
<td>.972</td>
</tr>
<tr>
<td>6</td>
<td>.666</td>
<td>180.0</td>
<td>2.87</td>
<td>177.13</td>
<td>2253.2</td>
<td>1.504</td>
<td>174.0</td>
<td>&quot;</td>
<td>.965</td>
</tr>
<tr>
<td>5.45</td>
<td>.605</td>
<td>146.0</td>
<td>13.0</td>
<td>133.0</td>
<td>2597.2</td>
<td>1.521</td>
<td>142.0</td>
<td>&quot;</td>
<td>.916</td>
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<tr>
<td>4.47</td>
<td>.497</td>
<td>95.0</td>
<td>24.0</td>
<td>71.0</td>
<td>3250.8</td>
<td>1.603</td>
<td>88.0</td>
<td>&quot;</td>
<td>.916</td>
</tr>
<tr>
<td>4.1</td>
<td>.455</td>
<td>78.0</td>
<td>27.89</td>
<td>50.11</td>
<td>3474.4</td>
<td>1.627</td>
<td>71.0</td>
<td>&quot;</td>
<td>.916</td>
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<tr>
<td>3.09</td>
<td>.343</td>
<td>70.0</td>
<td>55.72</td>
<td>14.28</td>
<td>3930.2</td>
<td>1.643</td>
<td>37.0</td>
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<td>.528</td>
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<tr>
<td>1.95</td>
<td>.216</td>
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<td>122.0</td>
<td>4420.4</td>
<td>1.722</td>
<td>14.5</td>
<td>14.0</td>
<td>.118</td>
<td></td>
</tr>
</tbody>
</table>
conductivity which becomes prominent as the electronic contribution becomes smaller with decreasing temperature and scattering of the phonons by the conduction electrons in the superconducting state decreases.

The conductivity in the superconducting state can be divided into three temperature regions. The results indicate that between $T_c$ and $3.5\,\text{K}$ electron conduction is dominant; between $3.5\,\text{K}$ and $2\,\text{K}$ it is mostly due to phonons scattered by electrons; and below $2\,\text{K}$ the heat conduction can be assumed to be due to phonons scattered by imperfections and boundaries as was demonstrated by the measurements of CM below $1\,\text{K}$.

The temperatures at which the local minimum and maximum in $K_s$ occur, $3.5\,\text{K}$ and $2\,\text{K}$, respectively, are in fortuitous agreement with the results found by CM. In recent measurements of $K_s$ by Muto et al. on a niobium specimen with resistance ratio of 1900, it is interesting to note the apparent absence of any significant phonon contribution at lower temperatures as shown by the smallness of the local maximum in their results. A possible explanation is that as the purity increases, the electron contribution $K_{es}$ to the conductivity, which is limited by impurity scattering, increases accordingly while the phonon contribution $K_{gs}$ which is limited by electron scattering stays unchanged to a first approximation. As a result the increase of $K_{gs}$ with decreasing temperatures becomes comparatively less important and the associated local maximum tends to flatten out.

Analysis of the normal state conductivity in terms of the
different scattering mechanisms is made by using the formula given by Makinson for a free electron model. The electronic thermal conductivity $K_{en}$ at temperatures $T < \Theta/10$ ($\Theta$ is the Debye temperature) is given by

$$\frac{1}{K_{en}} = aT^2 + \frac{b}{T}$$

(1)

where $a = 95.3 \frac{N_a^{2/3}}{K_\infty \Theta^2}$ and $b = \rho_0 / L_0$. $N_a$ is defined as the effective number of conduction electrons per atom, $K_\infty$ is the limiting value of the electronic thermal conductivity at high temperature, $\rho_0$ is the residual electrical resistivity and $L_0$ is the Lorentz number. The first term on the right in Eq. (1) represents the electronic thermal resistivity limited by phonon scattering and the second term represents the electronic thermal resistivity due to impurity scattering. Figure 2 gives a plot of $T/K_n$ against $T^3$, which within the experimental scatter has been approximated by a straight line. The slope of the straight line gives the value of the constant $a = 2.3 \times 10^{-6} \text{ cm}^{-1} \text{ mW}^{-1} \text{ K}^{-1}$. The intercept on the $T/K_n$ axis gives $b = 20.8 \times 10^{-3} \text{ cm}^{-2} \text{ mW}^{-1}$ which differs by 2% from the result obtained from the residual resistivity measurements. These values of $a$ and $b$ indicate that for temperatures very close to $T_c$, the contribution of phonon scattering to the resistivity is at most 8% of the total thermal resistivity. The experimentally determined value of $a$, using $\Theta = 275^\circ\text{K}$ and $K_\infty = 580 \text{ mW cm}^{-1} \text{ K}^{-1}$, indicates an effective number of conduction electrons per atom $N_a = 1.0891$; but if one
uses the value $\Theta = 241^\circ K$ found$^{47}$ in the temperature range $3^\circ K - 10^\circ K$, then $N_a = 0.733$ is obtained. We do not find any phonon conducti-

vity in the normal state as seen in Fig. 1. The preponderance

of impurity scattering for both $K_s$ and $K_n$ allows us to make a
direct comparison of the temperature dependence of $K_s/K_n$ to the

theory of Bardeen, Rickayzen, and Tewordt. The BRT relation for
the case of elastic impurity scattering of electrons is$^{16}$

$$\frac{K_{es}}{K_{en}} = \frac{2F_1(-y) + 2y \ln(1 + e^{-y}) + y^2(1 + e^y)^{-1}}{2F_1(0)}$$

(2)

where $y = \frac{\epsilon(t)/kT}{[\epsilon(t)/\epsilon(0)] \cdot [\epsilon(0)/kT_c] \cdot 1/t}$, $\epsilon(t)$ being

the half-width of the energy gap at temperature $T$ in the Bardeen,

Cooper, and Schrieffer$^{49}$ theory (hereafter referred to as BCS).

The temperature dependence of $\epsilon(t)/\epsilon(0)$ has been calculated by

Mühlischlegel$^{50}$ based on the BCS theory, and from this a

temperature dependence of $y$ has been calculated for different

values of $\epsilon(0)/kT_c$. The term $F_1(-y)$ is given by the expression

$$F_n(-y) = \int_0^\infty z^n dz / 1 + \exp(z + y).$$

$F_1(-y)$ has been tabulated by

Rhodes$^{51}$ for $-y$ from 0 to 4 and has been extrapolated in the

present work to higher values. In Fig. 3 we have plotted the

experimental values of $K_s/K_n$ against the reduced temperature. We

find a good fit of the upper range to the BRT expression for

$2\epsilon(0) = 3.96 kT_c$ as represented by the solid line in Fig. 3.

There is agreement from $t = 1.0$ to $t = 0.65$. This confirms that

at higher temperatures the contribution of phonon conductivit
Fig. 3

- Niobium, experimental
- BRT, for $2\varepsilon(0) = 3.96 kT_c$
in the superconducting state is negligible. Below \( t = 0.65 \) the experimental curve \( K_s/K_n \) departs from the theoretical curve \( K_{es}/K_{en} \) due to the increasing contribution of the phonon conductivity.

The electronic thermal conductivity in the superconducting state \( K_{es} \) has been calculated from Eq. (2) with the energy gap \( 2\epsilon(0) = 3.96 kT_c \) by substituting for \( K_{en} \) the value obtained from the residual resistivity using the Wiedemann-Franz law. The electronic and total conductivity in the superconducting state has been plotted in Fig. 4 on the log scale against \( T_c/T \) on the linear scale. Zavaritskii\(^52\) has shown empirically that the electronic thermal conductivity of superconductors in the impurity scattering region can be approximated by an exponential of the form \( K_{es} \propto \exp[-pT_c/T] \), where \( p \) has different values for different metals and is a measure of the energy gap. The use of an exponential temperature dependence for \( K_{es} \) follows from the use by Heisenberg\(^53\) of the electron gas formula which contains a specific heat term and the experimental low temperature behavior of \( K_s \) showing an exponential dependence. This lead Goodman\(^54\) to note that the existence of an energy gap would effectively produce such a dependence for the specific heat term and this would lead to the observed exponential temperature dependence of \( K_s \). In the limit of \( T \) tending to \( T_c \) where, as we have mentioned before, the electrons are mostly scattered by impurities and the thermal conductivity in the superconducting state is mainly electronic, we have approximated the log \( K_s \) vs \( T_c/T \) curve by a
Nb POLYCRYSTAL
10 mils plate
$T_c = 9^\circ\text{K}$

$K_s (\text{mV} \cdot \text{cm}^{-1} \cdot \text{deg}^{-1})$

$T_c / T$

Fig. 4
straight line. This gives a slope of \( p = 1.888 \) which is much higher than the values obtained from specific heat measurements

\[ \frac{C_{es}}{\gamma T_c} = a \exp[-p T_c/T] \]

by Van Der Hoeven and Keesom \(^{47}\) \((p = 1.53)\), Leupold and Boorse \(^{55}\) \((p = 1.52)\), and Da Silva et al. \(^{56}\) \((p = 1.62)\). The BCS theory gives a value of \( p = 1.44 \) from the exponential temperature dependence of the electronic specific heat in the superconducting state which leads to the energy gap at absolute zero to be \( \frac{3.52 kT_c}{4} \). Following Goodman, \(^{54}\) Van Der Hoeven and Keesom, \(^{47}\) and Mamiya et al. \(^{57}\) we have estimated the energy gap at absolute zero for our sample by using the relation

\[ 2\varepsilon(0) = \frac{p}{1.44} \left( \frac{3.52 kT_c}{4} \right) \]

Using the value of \( p = 1.888 \), we find \( 2\varepsilon(0) = 4.61 kT_c \). This differs significantly from the value of \( 2\varepsilon(0) = 3.96 kT_c \) obtained by comparing \( K_s / K_n \) with the theory of BRT and shows that Zavaritskii's \(^{52}\) approximation gives only an approximate value of the energy gap. The value of the energy gap at absolute zero obtained for our sample has been compared with previous results and these are shown in Table II.

The phonon conductivity \( K_{gs} \) in the superconducting state has been obtained by subtracting the electronic component \( K_{es} \) as obtained from BRT theory, from the total thermal conductivity \( K_s \). This has been plotted against the reduced temperature in Fig. 5 along with \( K_{es} \) and tabulated in Table I. As explained earlier, it shows that \( K_{gs} \) is maximum at \( t = 0.22(T = 2^0K) \). It decreases with increasing temperature and at \( t = 0.65 \) it represents less than 4% of \( K_s \). BRT have pointed out that in the temperature region \( t = 0.4 \) to \( t = 0.6 \), the ratio \( K_{gs} / K_{gn} \) may be proportional to \( T^{-5} \).
TABLE II. Comparison of experimental results on the energy gap in Nb.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Technique Used</th>
<th>$2\varepsilon(0)/K_{Tc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present work</td>
<td>thermal conductivity</td>
<td>3.96</td>
</tr>
<tr>
<td>Connolly and Mendelssohn$^a$</td>
<td>thermal conductivity</td>
<td>3.5</td>
</tr>
<tr>
<td>Muto et al.$^b$</td>
<td>thermal conductivity</td>
<td>3.80</td>
</tr>
<tr>
<td>Goodman$^c$</td>
<td>specific heat</td>
<td>3.7 (4.0)</td>
</tr>
<tr>
<td>Leupold and Boorse$^d$</td>
<td>specific heat</td>
<td>3.69</td>
</tr>
<tr>
<td>Da Silva et al.$^e$</td>
<td>specific heat</td>
<td>3.72</td>
</tr>
<tr>
<td>Van Der Hoeven and Keesom$^f$</td>
<td>specific heat</td>
<td>3.70</td>
</tr>
<tr>
<td>French$^g$</td>
<td>magnetization</td>
<td>3.62</td>
</tr>
<tr>
<td>Perz and Dobbs$^h$</td>
<td>ultrasonic attenuation</td>
<td>3.75</td>
</tr>
<tr>
<td>Levy et al.$^i$</td>
<td>ultrasonic attenuation</td>
<td>3.5</td>
</tr>
<tr>
<td>Townsend and Sutton$^j$</td>
<td>tunneling (Nb/Sn)</td>
<td>3.84</td>
</tr>
<tr>
<td>Gaiever$^k$</td>
<td>tunneling (Nb/Sn)</td>
<td>3.6</td>
</tr>
<tr>
<td>Sherrill and Edwards$^l$</td>
<td>tunneling (Nb/Pb)</td>
<td>3.59</td>
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<td>Bonnet et al.$^m$</td>
<td>tunneling (Nb/Sn)</td>
<td>2.8</td>
</tr>
<tr>
<td>Richards and Tinkham$^n$</td>
<td>infrared absorption</td>
<td>2.8</td>
</tr>
</tbody>
</table>

$^a$See Ref. 1.
$^b$See Ref. 4.
$^d$See Ref. 55.
$^e$See Ref. 56.
$^f$See Ref. 47.
$^g$See Ref. 41.
Fig. 5
This has been observed by Laredo.\textsuperscript{58} Experimentally it has been found by Sladek\textsuperscript{59} that $K_{gs}/K_{gn}$ is proportional to $T^{-n}$ where $3 < n < 6$. Assuming $K_{gn}$ to be proportional to $T^2$ implies that, from BRT's theory, $K_{gs}$ should be proportional to $T^{-3}$. We find that between $t = 0.3$ to $t = 0.55$, $K_{gs}$ is proportional to $T^{-(2.4 \pm 0.1)}$ which appears to be significantly different from the theory but falls within limits that corroborate Sladek's results.

B. Mixed State Conductivity

1. Minimum of $K_m$ in the Mixed State. The thermal conductivity of niobium as a function of the applied field has been measured from $T = 8.64^\circ$K to $T = 1.95^\circ$K and representative results are shown in Fig. 6. For all temperatures above and excluding $T = 1.95^\circ$K, it is found that the thermal conductivity remains constant up to the lower critical field $H_{c1}$. A decrease in the conductivity occurs at $H_{c1}$ where the magnetic field starts penetrating the sample. This decrease reaches a minimum at fields slightly above $H_{c1}$, then starts increasing slowly until it attains a constant value at the upper critical field $H_{c2}$. The depth of the minimum as well as the sharpness of the drop become more pronounced as the temperature is lowered. Similar behavior in the mixed state has also been observed on In-Tl alloys by Sladek,\textsuperscript{59} on In + 3% Bi alloys by Dubbeck \textit{et al.},\textsuperscript{15} on Nb$_{0.8}$Mo$_{0.2}$ alloy and pure niobium by Lowell and Sousa,\textsuperscript{3} on pure niobium by Muto \textit{et al.}\textsuperscript{4} and Noto,\textsuperscript{4} and on Pb-In alloys by Muto \textit{et al.}\textsuperscript{60} and Mamiya.\textsuperscript{60}

The existence of a minimum of the thermal conductivity in the
Fig. 6
mixed state is generally explained, on the basis of the mechanism proposed in the "effective gap approximation,"\textsuperscript{15} as the result of the decrease of the lattice conductivity $K_{gm}$ concomitant with the increase of the electronic conductivity $K_{em}$ as the applied magnetic field is increased from $H_{c1}$ to $H_{c2}$. Representative curves, calculated on the basis of this approximation - introducing a reduced field dependent energy gap $\epsilon(H,t)/\epsilon(0,t)$ and using the tables given by Linderfeld and Rohrer\textsuperscript{61} - are shown in Fig. 7, and predicted values of the minimum are listed in Table I together with the corresponding experimental values. One notes that the existence of a minimum, in this model, depends on the algebraic sum of the slopes of the monotonic field dependent curves $K_{gm}(H)$ and $K_{em}(H)$. Table I shows that the value of the minimum calculated in this approximation agrees fairly well with experiment for lower temperatures where phonon conductivity is preponderant. For increasing temperatures, a minimum is still found experimentally where the calculated value is zero. This persistence of the minimum is not trivial, as explained below.

The comparison of our results with those of Muto et al.\textsuperscript{5} and Noto\textsuperscript{4} leads to a fundamental remark: The data of Ref. 4, concerning the minimum of the thermal conductivity in the mixed state, cannot be explained by a decrease of the phonon contribution as has been done above. The reason is that, from the data,\textsuperscript{4} it is clear that the phonon contribution $K_{gs}$, even at its maximum value, is much smaller than the decrease in conductivity ($K_{s} - K_{min}$) observed at all temperatures above $t = T/T_c = 0.365$. It is,
therefore, imperative to postulate that the decrease \((K_s - K_{\text{min}})\) is due, at least in part, to a decrease in the electronic contribution \(K_{\text{em}}\) upon entry in the mixed state, a possibility mentioned recently by other authors.\(^{62}\) Possibly a scattering of the electrons by the Abrikosov flux lines can be conjectured, which the comparison between the average flux lines separation \((\sim 0.1 \mu)\) and electron mean free path in the sample of Ref. 4 \((\sim 1 \mu)\) does not rule out. With the postulated decrease in \(K_{\text{em}}\), one can write \(K_m = K_{\text{em}} + \frac{W_{\text{ei}}}{W_{\text{ef}}}\) where \(W_{\text{ei}}\) is a thermal resistivity term due to the scattering of uncondensed electrons by impurities and possibly phonons, and \(W_{\text{ef}}\) is a resistive term due to scattering of these electrons by the flux lines. The term \(W_{\text{ei}}\) decreases smoothly as the field is increased from \(H_{c1}\) to \(H_{c2}\) while \(W_{\text{ef}}\) would increase, go through a maximum \(\left(\frac{W_{\text{ef}}}{W_{\text{ef}}}\right)_{\text{max}}\) and decrease back to zero at \(H_{c2}\). One can distinguish 3 possible experimental situations: (1) the impurity scattering is very large, \(W_{\text{ei}} \gg \left(\frac{W_{\text{ef}}}{W_{\text{ef}}}\right)_{\text{max}}\) which would be the case of alloys,\(^{15}\) and the minimum is then fairly accounted for by the drop in \(K_{\text{gm}}\) like in the "effective gap approximation";\(^{15}\) (2) the impurity scattering is very small, \(W_{\text{ei}} \ll \left(\frac{W_{\text{ef}}}{W_{\text{ef}}}\right)_{\text{max}}\) and \(K_{\text{em}} \gg K_{\text{gm}}\) which would be the case of very pure intrinsic type II samples, like the pure niobium of Ref. 4; the minimum is then due to the field-dependence of \(W_{\text{ef}}\); (3) the impurity scattering is of intermediate strength and \(W_{\text{ei}} \sim \left(\frac{W_{\text{ef}}}{W_{\text{ef}}}\right)_{\text{max}}\). We believe this third case to correspond to the results of the present work and the origin of the minimum may then depend on the temperature range. At low
temperatures where \( K_{gs} > K_{es} \), the minimum is mostly due to the drop in the phonon conductivity and good agreement is found with the "effective gap' calculations. At higher temperatures, \( K_{gs} < K_{es} \), the influence of a drop in \( K_{gs} \) becomes negligible but a minimum might still appear due to the influence of the variation in \( W_{ef} \). Table I shows evidence of this transitional behavior since one can see that the minimum at temperature \( t > 0.5 \) is unaccounted for by the "effective gap" approximation. In Fig. 8, we have plotted \( K_{min}/K_s \) for our data and that of Ref. 4; the presence of two distinct regions above and below \( t = 0.5 \) is characteristic of our results and we conjecture that below \( t = 0.5 \) the influence of the decrease in the phonon conductivity is predominant while above this temperature it is the variation of the electronic conductivity which becomes responsible for the mixed state behavior. The insert in Fig. 8 shows the steep decrease of \( K_{gs}/K_s \) as the temperature is raised from below to above \( t = 0.5 \).

This suggested scattering of the electrons by the flux lines deserves, in our opinion, some further investigation.

2. The Temperature Dependence of \( H_{c2}(t) \) and \( \chi_1(t) \). A theoretical study of the temperature dependence of the upper critical field has been made by Gorkov\(^5\) who has calculated a lower bound to \( H_{c2} \) at \( T = 0 \) for pure specimens and has proposed a simple interpolating polynomial for \( H_{c2}(T) \) to link his \( T = 0 \) point with known results at higher temperatures. Maki\(^6\) and deGennes\(^7\) have calculated the temperature dependence of \( H_{c2}(t) \) and the
Fig. 8
corresponding ratio of the parameter \( \chi_1(t)/\chi_1(1) \) for dirty specimen where \( \chi_1(t) = H_{c2}(t)/2H_c(t) \). Helfand and Werthamer have solved exactly the eigenvalue equation for \( H_{c2}(t) \) for all temperatures and for all concentrations of the impurities. They have defined a parameter \( h^* = H_{c2}(t)/(-dH_{c2}(t)/dt)t=1 \) and have shown its temperature dependence for pure and dirty limits. This parameter has the advantage of being independent of any assumed temperature dependence for \( H_c(t) \). In Fig. 9 we have plotted \( h^* \) against the reduced temperature \( t \) along with Helfand and Werthamer's theoretical results for pure and dirty superconductors. We find that our results agree more with the dirty limit in the plot; although considering that the present sample has \( l \approx l_0 \), we should expect the experimental points to fall closer to the pure limit curve. This type of discrepancy using the \( h^* \) vs \( t \) plot has also been reported recently on Pb-In alloys by Dubeck, Aston, and Rothwarf who find that their results on a 28 at. % In alloy sample falls closer to the pure limit than their 1.5 at. % In alloy which falls closer to the dirty limit.

To find \( \chi_1(t) \) we need the thermodynamic critical field \( H_c^* \). In the absence of magnetization measurements we have calculated \( H_c(0) \) by using the BCS relation \( H_c(0) = \sqrt{2\gamma/2T_c} \), which connects \( H_c(0) \) with the electronic specific heat constant \( \gamma \) and the critical temperature \( T_c \). The published values of \( \gamma \) range from 7.50 mJ/mole deg\(^2\) to 7.85 mJ/mole deg\(^2\). Using \( \gamma = 7.85 \) mJ/mole deg\(^2\) and \( T_c = 9.0^0K \), we find \( H_c(0) = 1940 \) Oe. Assuming a parabolic temperature dependence, we have calculated
Fig. 9

\[ \frac{\delta_{c2}}{(-\frac{dH_{c2}}{dt})_{t=1}} \]

- \( \lambda = 0, \, t = \infty \)
- \( \lambda = \infty, \, t = 0 \)
$H_C(t)$ which has been used to calculate $\chi_1(t) = \left[ (H_{c2}(t)) / 2 H_C(t) \right]$ where $H_{c2}(t)$ is the experimentally determined value of the upper critical field from thermal conductivity measurements in the mixed state. Ohtsuka\textsuperscript{67} has also followed this method to calculate $H_C(t)$ and $\chi_1(t)$ from the magnetocaloric measurements. The parabolic temperature dependence assumed for $H_C(t)$ has recently been confirmed by the magnetization measurements of French\textsuperscript{41} and does not, as a consequence, introduce a source of error.

The extrapolated value of $\chi_1(t)$ at $t = 1$ is found to be $\chi_1(1) = 1.14 \pm 0.03$. This value is surprisingly large when compared to French's\textsuperscript{41} $\chi_1(1) = 0.83$ for instance, but one can show that this reflects only the short electronic mean free path in the present sample. Theory requires that $\chi_1(t) = \chi(1)$ at $t = 1$ where $\chi(t)$ is the Ginzburg-Landau parameter connected to the weak field penetration depth $\lambda_0$ and the thermodynamic critical field $H_C$ by $\chi(t) = 2/\pi e H_C(t) \lambda_0^2 \Lambda C$. Goodman\textsuperscript{68} has extended Gorkov's theory and has shown that $\chi(t)$ can be separated into two components, $\chi(t) = \chi_0 + \chi_\ell$. $\chi_0$ is a constant characteristic of the pure metal and $\chi_\ell$ is dependent on the electronic mean free path given by the relation $\chi_\ell = 7.53 \times 10^3 \rho_0 \gamma^{1/2}$ where $\gamma$ is the specific heat constant and $\rho_0$ is the normal state resistivity in $\Omega \cdot cm$. Using $\rho_0 = 5.2 \times 10^{-7} \Omega \cdot cm$ and $\gamma = 7.162 \times 10^4$ ergs/cm$^3$ deg$^2$, we find $\chi_\ell = 0.331$ and $\chi_0 = 0.81 \pm 0.03$. This value of $\chi_0$ agrees very well with the value 0.815 reported by French\textsuperscript{41} from magnetization measurement and is comparable to 0.87 by Rosenblum\textsuperscript{et al.}\textsuperscript{69} from resistivity measurements and 0.78 by FSS also from
magnetization measurements. It is, therefore, the component $x_1$, depending on the mean free path, which is responsible for the large value $x_1(1) = 1.14 \pm 0.03$ found here. Though it is large when compared to 0.78 by FSS, 0.83 by French, and 0.92 by Ikushima et al. in much purer samples ($\Gamma > 800$) it is smaller than the value 2.37 found by Da Silva et al. for an impure sample ($\Gamma = 7$).

The ratio $x_1(t)/x_1(1)$ has been plotted in Fig. 10 along with the theoretical results of Eilenberger for the pure case ($\xi_0/\xi_{tr} = 0, \xi_{tr} = \xi$) and for the intermediate case ($\xi_0/\xi_{tr} = 1, \xi_{tr} = \xi$). Theoretical results of Maki for dirty alloys ($\xi_0/\xi = \alpha$) and the experimental results of French are also shown in the same figure. We find that as observed earlier, $x_1(t)/x_1(1)$ increases with decreasing temperature at a much faster rate than the theory predicts. The extrapolated value of $x_1(t)/x_1(1)$ at $t = 0$ is found to be 1.53 which is 20% higher than the theory for the pure sample and 10% smaller than the experimental result on one of the purest samples investigated so far. However, it is higher by 6% when compared to Da Silva et al. results on less pure samples ($\Gamma = 7$). It appears, therefore, that the experimental values of $x_1(0)/x_1(1)$ found for niobium cover a range which reflects the comparative purity of the samples, but all values are larger than expected from theory.

This systematic discrepancy may be related to the results obtained by Hohenberg and Werthamer. They have shown that for
Fig. 10
cubic crystals like niobium the anisotropy in $H_{c2}$ arises from the nonlocal corrections to the GLAG theory which would give a nonespherical Fermi surface condition and not from the anisotropy of the normal metal Fermi surface itself. From the calculation, they have shown that the anisotropy depends on the impurity and temperature; the anisotropy being higher for low $t$ and high $\xi$, and that Eilenberger's theory represents a lower limit for $H_{c2}(t)$ and $\chi_1(t)$. Although the expression cannot be evaluated directly, it is expected that $\chi_1(0)/\chi_1(1)$ will be higher than 1.26 for pure specimens, but for our sample of intermediate purity the value of 1.53 might be too high to be explained on these grounds.

3. The Slope of $K_m$ for $H$ Close to $H_{c2}$. Caroli and Cyrot\textsuperscript{12} have predicted that for a dirty type II superconductor ($\xi << \xi_0$) the electronic thermal conductivity in the mixed state is proportional to $(H_{c2} - H)$ near the upper critical field $H_{c2}$, which is the gapless region, and that the ratio of the slope of the thermal conductivity to the slope of the magnetization near $H_{c2}$ is a universal function of temperature. For our sample which has $\xi \approx \xi_0$, we find that $K_m \propto (H_{c2} - H)$ not only near $H_{c2}$ but also over a wide range of the mixed state. This has also been observed by Lowell and Sousa\textsuperscript{3} on Nb$_{0.08}$Mo$_{0.2}$ alloys, by Lowell and Mendelssohn\textsuperscript{72} on Nb-Ta alloys, and by Lindenfeld \textit{et al.}\textsuperscript{73} on In-Bi alloys. Maki\textsuperscript{13} has shown that for a pure type II superconductor ($\xi >> \xi_0$) the thermal conductivity in the mixed state near the upper critical field $H_{c2}$ is proportional to
We do not find any such field dependence of the conductivity, but it has been observed for pure niobium samples by Lowell and Sousa \(^3\) and by Muto et al. \(^4\). In the case of a sample of intermediate purity \((l \approx \xi_0)\) like the one investigated here, it is interesting to note that we have unambiguous agreement with the constant slope behavior predicted by the dirty limit theory of Ref. 12 (see Fig. 6), but large discrepancies appear when a quantitative comparison is made of the temperature dependence of the slope \(\partial K_m / \partial H\). Caroli and Cyrot's results\(^{12}\) give

\[
\frac{dK_m}{dH} \bigg|_{H=H_{c2}} = \frac{2 \pi c k_B}{e} \frac{x[\psi(1)\left(\frac{1}{2} + x\right) + x\psi(2)\left(\frac{1}{2} + x\right)]}{\psi(1)\left(\frac{1}{2} + x\right)}
\]

where the slope of the magnetization \(dM/dH\) near \(H_{c2}\) is given by Abrikosov's theory\(^{74}\) as

\[
-4\pi \frac{dM}{dH} = \frac{1}{1.16 (2x^2 - 1)}
\]

The parameter \(x\) is related to the electron pair lifetime \(\tau_K\) by the relation \(x = \left[\frac{4\pi k_B T \tau_K}{\gamma}ight]^{-1}\) and is defined by

\[
\ln \frac{T}{T_c} = \psi\left(\frac{1}{2}\right) - \psi\left(x + \frac{1}{2}\right)
\]

where \(\psi(x)\) is the digamma function, and \(\psi(1)(x)\) and \(\psi(2)(x)\) are defined by

\[
\psi(1)(x) = \sum_{n=0}^{\infty} \frac{1}{(n + x)^2}
\]
\[
\psi^{(2)}(x) = -2 \sum_{n=0}^{\alpha} \frac{1}{(n+x)^3} \quad .
\]

From Eq. (5) \( x \) has been calculated\(^{75} \) and the right hand side of Eq. (3) has been evaluated. To make a quantitative comparison of our experimental slopes with the theory, we have substituted our experimentally determined \( x_1(t) \) in place of \( x_2(t) \) in Eq. (4). This leads to a calculated value of \( dM/dH \) which is an upper limit of the actual value since it has been shown by Maki and Suzuki\(^{76} \), Eilenberger\(^{9} \), and Caroli, Cyrot, and deGennes\(^{7} \) that for any temperature \( t \), \( x_2(t) \geq x_1(t) \). This inequality has been confirmed\(^{41} \) by FSS and French\(^{41} \) in pure niobium and the equality has been confirmed on alloys by McConville and Serin\(^{71} \) and by Bon Mardion \textit{et al.}\(^{77} \). The upper limit for the theoretical value of \( dK/dH \) obtained in this manner and our experimental results are both plotted in Fig. 11 against the reduced temperature \( t \). The theoretical results show a maximum at \( t = 0.3 \), whereas the experimental results show a maximum at \( t = 0.75 \). Also the magnitude of the observed maximum of \( dK/dH \) is about ten times higher than the theoretical prediction. This disagreement has been noted by Lowell and Mendelssohn\(^{72} \) on Ta-Nb alloys. The Rutgers group\(^{2} \) has also reported at the Cleveland Conference on superconductivity that for their impure niobium sample the disagreement between the theory and experiment was about 30\%, while for pure niobium the experimental result was higher by a factor of 40 as compared to the theoretical value. One can,
therefore, conclude that the experimental evidence on intrinsic type II superconductors, for samples which show a constant slope in the mixed state, points to larger values of $dK/dH$ than expected from theory and to a steeper variation with temperature.
CHAPTER III

MAGNETOCALORIC EFFECTS

A. Magnetocaloric Effect and Hysteretic Heating

When a sample is enclosed in a vacuum calorimeter and the magnetic field is swept, two alternative manifestations of its magnetocaloric effect can be observed depending on the thermal contact between the sample and the bath: (i) when the sample is thermally isolated from the bath and the magnetic field is swept, an overall integrated magnetocaloric effect is observed which gives the total amount of heat $Q$ produced as a function of the applied field. The observations of Ohtsuka and Takano,\textsuperscript{20} Barnes and Hake,\textsuperscript{22} and Flippin,\textsuperscript{23} are of this type. In increasing fields, the temperature of the sample starts decreasing at $H_{c1}$; this variation continues monotonically as the field is increased and stops at the upper critical field $H_{c2}$. There is no magnetocaloric cooling above $H_{c2}$ and the temperature of the sample starts drifting under the influence of heat leaks till it attains the bath temperature. Similar observations have also been made by the author on a vanadium single crystal under the above described experimental conditions. (ii) When the sample is in a limited thermal contact with the bath and the magnetic field is varied, the temperature of the sample reflects at each instant the rate at which heat is evolved. This is the case in the present work and in the work of Goedemoed \textit{et al.}\textsuperscript{21} We measure the rate of heat evolved $Q$ as a function of the applied field, all through the mixed state.
The detailed description of the procedure to calculate $Q$ from the experimental data is given in Appendix I.

Figure 12 shows a plot of the rate of heat evolved $\dot{Q}$ against the applied magnetic field for different temperatures above $4.2^\circ K$ and figure 13 shows the same plot for $4.2^\circ K$ and lower temperatures. In these two figures, cooling of the sample is denoted by positive sign and heating by negative. Starting from zero the magnetic field was swept at the constant rate of $5.73 \text{ Oe/sec}$. We note that because of the uniform rate at which the external magnetic field is changing, the above curves also represent the rate of heat evolved $\dot{Q}$ as a function of time. Above $3.2^\circ K$ the temperature of the sample decreases sharply at the lower critical field $H_{c1}$, reaches a minimum, then starts increasing slowly as the field is kept increasing, and finally comes back to the temperature of the bath after the upper critical field $H_{c2}$ has been reached.

Ohtsuka and Takano$^{20}$ have shown, by comparing their magnetocaloric data to their specific heat measurements, that the field at which the magnetocaloric effect disappears is the upper critical field $H_{c2}$. Below $3.2^\circ K$ (see fig. 13) mixed caloric behavior is observed: irreversible heating appears, localized in the region immediately above $H_{c1}$, while reversible cooling is still observed in the region preceding $H_{c2}$. This region over which the cooling still appears decreases as we go lower in temperature and finally disappears at about $1.4^\circ K$ as shown by the curve for $1.4^\circ K$ in figure 13 and measurements by Zebouni et al.$^{25}$ on the same sample.

Figure 12 also shows the magnetocaloric effect in the reverse
field for representative temperatures. Heating appears at \( H_{c2} \) which increases with decreasing field and reaches a maximum near \( H_{c1} \). The heating does not disappear at \( H_{c1} \) as one would expect. This may be due either to a time lag in the response of the thermometer, or more probably to incomplete exclusion of the flux at \( H_{c1} \) (trapped flux). To take into account the thermal relaxation time of the system the upper critical field has been taken at the point where the temperature of the sample starts increasing sharply toward the bath temperature rather than the point where the sample actually reaches the bath temperature.

The heat evolved in the mixed state consists of two parts. The first part is due to the magnetocaloric effect. As the sample is magnetized from the superconducting state to the normal state under adiabatic conditions, its entropy increases from \( S_s \) in the superconducting state to \( S_n \) in the normal state. If no heat is supplied to the sample during the magnetization process its temperature decreases. From thermodynamic considerations, maximum cooling should appear at \( T_c/\sqrt{3} \) and it should be zero at \( T = 0^\circ K \) and at \( T = T_c \). The second contribution to the heat evolved in the mixed state is due to the irreversible heating. The mechanism responsible for the heating is explained in the next paragraph.

Visualizing the mixed state in terms of quantized flux lines whose density \( n \) gives the induction \( B = n\phi_0 \), where \( \phi_0 = 2.07 \times 10^{-7} \) G/cm\(^2\) is the flux quantum, the current density \( J \) in the shielding region is created due to the changing flux density inside the superconductor through Maxwell's equation \( \text{curl} \, B = 4\pi J \).
presence of this current density a Lorentz force $F_L$ acts on the flux structure. The reaction to this force is provided by inhomogeneities in the material creating local variations of the mean free energy of the flux structure. If a force equal to the local energy gradient is applied, a fluxoid will leave its minimum energy site and move into the neighboring minimum after the energy maximum in between has been passed. The energy between the maximum and the minimum is completely dissipated. This concept is called flux pinning and the imperfections are referred to as pinning sites. A second contribution to the reaction to the Lorentz force, independent of flux pinning, comes from the resistance to flux flow which is characterized by a viscosity $\eta$. If the actual speed of the flux line is $v$, and the pinning force is $F_p$, then

$$F_L - F_p = \eta v$$

(8)

For a semi-finite slab, where flux density $B$ varies with the $x$ coordinate ($F_L = -\frac{1}{4\pi} \frac{\partial B}{\partial x}$) and flux moves with velocity $v$ in the $y$ direction, Morton has shown that, writing $F_L = F_p + \eta v$ or per unit volume:

$$J(B + B_0) = \alpha_c + \eta v \frac{B}{\phi_0}$$

(9)

where $J$ is the shielding current density, $\alpha_c$ is the pinning force per unit volume of the material, $B_0$ is a constant for the material, $\eta$ is the viscosity coefficient per unit length of fluxoid, $\phi_0$ is the flux quantum and $B/\phi_0$ is the number of flux lines per unit area.
The power dissipation which is the product of the shielding current and the electric field induced by the motion of the flux lines
\[ E = B \mathbf{v} = \int \mathbf{B} \, dx \] has been shown by Morton \(^{80}\) in the limit of small \( \eta \) to be

\[ Q = \frac{H^3}{8\pi k_\alpha C} \left[ 1 - \frac{16 \eta H H_0^2}{3\rho_0 \pi^3 \alpha C} \right]^{1/2} \text{erg/cm}^2 \text{s} \quad (10) \]

Although the above expression has been derived for a slab, it is qualitatively confirmed by the features of the irreversible heating observed in the present work. Taking into account the experimentally observed fact \(^{81}\) that the pinning force \( \alpha_c \) increases with decreasing temperature, equation (10) shows that the irreversible heating should increase with decreasing temperature which agrees with the present observations (see figure 13). The appearance of pure cooling and its quasi-reversible behavior at all temperatures above 3.2°K as shown in figures 12 and 13, shows that the effect of irreversible heating is smaller than the magnetocaloric cooling at higher temperatures. As the temperature is lowered the magnetocaloric cooling decreases (see figure 12 and figure 16 for \( T < T_c / \sqrt{3} \) whereas the irreversible heating increases and below a certain temperature, about 1.4°K, heating is found extending over the whole mixed state.

The distribution of heating in the mixed state and its sharp maximum near \( H_{c1} \) could be related to the behavior of the pinning force per unit volume \( \alpha_c \). Wipf \(^{82}\) has shown by measuring the torque under static condition that the pinning force per unit volume is
maximum just above $H_{c1}$ and then decreases linearly to 0 at $H = H_{c2}$ (see insert, fig. 13). The pinning forces oppose the motion of the flux lines and create a friction-like phenomenon. The dissipation of heat associated with this friction can in the words of Wipf be described as follows: "Movement of the flux lines (or bundles) leads to energy losses. These are due to vibrations of the lattice, stimulated by the release of the pinning centres, and vibrations of the flux lines themselves with emission of high frequency noise (not observed to date)". It is interesting to note with Wipf that there could be a proportionality relation between the pinning force and the magnetization, though there is no clear ground for such an assumption. It seems more likely that the relation is between the pinning force strength and the amount of hysteresis, from which it follows that the heating should be maximum in the region near $H_{c1}$, where maximum hysteresis is always observed. It is for this reason that this phenomenon is described here as hysteretic heating.

The production of heat at $H_{c1}$ below $3.2^0K$ in the present case is just opposite to that observed by Goedemoed et al. Their magnetocaloric measurements on a bundle of a hundred niobium wires (diameter = 0.01 cms and length = 3.3 cm) show that pure cooling is produced above $6.0^0K$ and pure heating below $4.2^0K$. At $5.3^0K$ they find mixed behavior, but contrary to the present case, they observe cooling localized in the region immediately above $H_{c1}$. This could be due to the result of the overall behavior of different wires which may have different characteristics depending
on their impurity content and structural defects content and is not a genuine physical phenomenon.

As the pinning centres density increases with increasing impurities and increasing density of structural defects, the pinning force per unit volume $\alpha_c$ will increase accordingly and the irreversible heating according to Morton's calculation, in such samples, will be higher than in a more ideal sample. This has been demonstrated by Zebouni et al. on pure and impure niobium samples. The appearance of heating at higher temperature in reference 21 on a relatively impure sample also supports Morton's result.

B. Magnetization Measurements

To calculate the reversible heat, magnetization measurements have been made at $4.2^\circ K$ and $2.1^\circ K$ by the standard heat pulse technique in fields transverse to the axis of the cylindrical sample and the results are shown in fig. 14. A detailed description of the experimental procedure is given in Appendix II. The results show that the magnetic moment increases linearly with the applied field in the pure superconducting state, reaches a maximum at $H_{c1}$ then starts decreasing in a continuous manner in the mixed state and goes to zero at the upper critical field $H_{c2}$. A completed Meissner effect, exclusion of flux from the body of the specimen, was in evidence below $H_{c1}$, although the slight non-linearity of the curves could be due to end effects as the measurement was made in a transverse field. Near $H_{c1}$, the rounding
of the curves has also been observed by FSS and French on pure samples and by Gorter et al. and Meyerhoff and Beall on impure samples and is probably caused by enhanced local flux gradients at surface imperfections. Immediately following \( H_{c1} \) the magnetization curve does not undergo a sharp fall of the type observed in very pure samples. It is possible that in the less pure and un-annealed sample, the flux lines which penetrate at \( H_{c1} \) are pinned down at the impurity and dislocation sites, thus creating a shielding current and slowing down the further penetration of magnetic field.

Figure 14 also shows the magnetic moment measured in the decreasing field. There is very little hysteresis near \( H_{c2} \) but considerable hysteresis is found at lower fields and it is maximum at \( H_{c1} \). As we have seen this is related to the localization of heat in the mixed state. Unlike French's and FSS's results, a remanent moment is observed when the field is decreased to zero. This irreversibility seems to increase with decreasing temperature as is evidenced by the amount of remanent moment at zero field which shows that \( M = 15 \text{G} \) and \( 22 \text{G} \) at \( T = 4.2^0\text{K} \) and \( 2.1^0\text{K} \), respectively. This could be due to the interaction between flux filaments and the surface which precludes complete reversibility as proposed by Livingston and Beans. On the other hand this could be the effect of cold work as observed by Gorter and by Meyerhoff and Beal. The irreversibility due to cold work has also been suggested by Lowell. As shown in reference cold working increases the number of dislocations in a metal and as a
consequence there is an increase of the irreversibility due to the increase in the number of flux pinning sites provided by the dislocations.

Love et al. have found for their indium and thalium alloys that by jarring the samples before each measurement, the magnetization above $H_{c1}$ for increasing and decreasing fields could be made to nearly coincide. Similar results have been found by Radebaugh and Keesom on vanadium and by Gorter on niobium. For $H > H_{c1}$, the magnetization in increasing fields is lowered after jarring whereas in decreasing field it is increased. This is because the energy produced by jarring the sample unpins the flux lines so that an equilibrium situation may be brought about, and also lowers the surface current which can produce intrinsic hysteresis effects.

The lower critical field $H_{c1}$ at 4.2°K and 2.1°K is found to be 498 ± 15 Oe and 722 ± 20 Oe respectively. This is comparable to $H_{c1}$ of 516 ± 20 and 645 ± 20 Oe obtained from the magnetocaloric measurements for the same temperatures. In the same manner, the upper critical field $H_{c2}$ of 3646 ± 25 Oe and 4850 ± 25 Oe at 4.2°K and 2.1°K agree within 2% with the results obtained from the magnetocaloric measurements. This proves that the critical fields of type II superconductors can be measured reliably by magnetocaloric measurements.
1. The Thermodynamic Functions. It has been shown by Goedemoed et al.\textsuperscript{90} that for the first quadrant of the loop, the first law of thermodynamics gives

$$-\int \text{MdH} = T \Delta S - \Delta Q + \Delta F$$  \hspace{1cm} (11)

where all the quantities are taken per unit volume. The first term on the right hand side of the equation represents the reversible heat required in the magnetization process (the magnetocaloric effect), $\Delta Q$ is the total heat evolved, the term $\Delta F$ is the difference in thermal free energy between the normal and the superconducting states and is related to the thermodynamic critical field $H_c$ by $\Delta F = H_c^2/8\pi$. If the electronic specific heat of the normal and superconducting phases are assumed to be respectively proportional to $T$ and $T^3$ we have

$$T \Delta S = 4 \Delta F \frac{t^2}{1 - t^2}$$  \hspace{1cm} (12)

with $t = T/T_c$.

Graphical evaluations of $-\int \text{MdH}$ and $\int \Delta Q dt$ have been made which are used to calculate the reversible heat $T \Delta S$, the free energy $\Delta F$ and the thermodynamic critical field $H_c$. The results are shown in Table III for $4.2^\circ K$ and $2.1^\circ K$ along with that of Goedemoed et al.\textsuperscript{90} for $4.2^\circ K$ for comparison. The value of $\Delta F$, $H_c$ and $T \Delta S$ agree with the results of reference 90 within 1.5%. But, for $4.2^\circ K$ for instance, $H_c = 1343G$, is found which is 10% lower than that of French's purer niobium. An explanation for this discrepancy may
<table>
<thead>
<tr>
<th>Temperature</th>
<th>$T \Delta S$ ($10^5$ erg/cm³)</th>
<th>$\Delta F$ ($10^5$ erg/cm³)</th>
<th>$H_c$ (Oersted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2°K</td>
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<td>0.71</td>
<td>1343</td>
</tr>
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<td>0.18</td>
<td>0.80</td>
<td>1419</td>
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<tr>
<td>4.2°K</td>
<td>0.80</td>
<td>0.70</td>
<td>1325</td>
</tr>
</tbody>
</table>

of reference 90
be due to the limited heat contact of the sample with the bath: if the sample were thermally isolated a larger temperature decrease in the mixed state would have been observed and a larger value of $H_c$ would be calculated. Assuming the magnetization curve to be correct and assuming for $H_c$ a value in line with the values reported from isothermal magnetization measurements ($H_c = 1510$ at $4.2^0K$) the expected heat development $\Delta Q$ is found to be $1.27 \times 10^5$ ergs/cm$^3$, which is about 27% higher than the measured value. This gives a rough estimate of the systematic error made in measured $\dot{Q}$ when the sample is in limited thermal contact with the bath.

The variation in the magnetic enthalpy $dE = dQ - MdH$, where $dQ$ is the heat supplied to the sample, has been calculated. The experimentally determined values of $\intMdH$, $\int dQ$ and $\Delta E$ are shown in figure 15 vs. the applied magnetic field strength. It is found that, both for $4.2^0K$ and $2.1^0K$, $\Delta E$ in the mixed state is always smaller than $\Delta E_n$ (normal state) for all values of the field. Under this condition, according to Gorter$^{27}$ no flux jump should occur and the absence of flux jump in the present work confirms Gorter's criterion. Gorter's argument also implies that no flux jump should occur whenever there is a decrease in temperature in the mixed state, which also agrees with the present observations. It also agrees with Goedemoed et al.$^{21}$ work where flux jumps are found only when $\Delta E > \Delta E_n$, and no flux jumps occur whenever there is a cooling in the mixed state.

In a first approximation, for all temperatures ($T > 4.2^0K$) where an approximately reversible magnetocaloric effect is observed
Figure 15

$\Delta E_n$

$\Delta E$

$H(KOe)$

$\int MdH$

$\int -dQ$

2.1°K

4.2°K
(i.e., irreversible heating is negligible) it is assumed that $dS = dQ/T$. Under this assumption the difference in entropy $dS = S_s - S_n$ between the superconducting and normal states has been calculated and is shown in figure 16. From thermodynamic treatment it can be shown that $dS = 0$ at $T = 0$ and $T = T_c$, and will be maximum at $T = T_c/\sqrt{3}$. For the present case where $T_c = 9.2^\circ K$, this maximum should occur at $5.31^\circ K$ which is in excellent agreement with the experimental results. No measurement of this nature has been reported before. The behavior of $dS/T$ in the mixed state has also been calculated and is shown in figure 17 for different temperatures. The values of $S_n/T$ ($H = H_{c2}$) have been normalized to the value obtained at $4.2^\circ K$. The results confirm Abrikosov's prediction that the entropy changes continuously in the mixed state, starting from the lower critical field $H_{c1}$ and terminating at $H_{c2}$. No cooling is observed at $H_{c2}$ which confirms that the transition from mixed state to the normal state is of second order, which is different from type I superconductors, where the transition to the normal state in the presence of magnetic field is of first order. From the entropy calculation, the electron specific heat constant (Sommerfeld's constant) $\gamma$ is calculated and is found to be $0.50 \text{ mJ deg}^{-2}\text{cm}^{-3}$. This is about 27% smaller than the value obtained from specific heat studies by Leupold and Boorse. This discrepancy is again thought to be due to the thermal heat leak between the sample and the bath which has been discussed earlier.
$S_g - S_n \ (\text{erg}^{-\circ} \text{K}^{-1} \cdot \text{cm}^{-3} \times 10^4)$
\[ \frac{\Delta S}{T} \text{(erg}^{-\circ \text{K}}\text{K}^{-2}\text{cm}^{-3} \times 10^4) \]

\[ H(\text{KOe}) \]

Fig. 17
2. The Upper Critical Fields. A detailed study of the upper critical field $H_{c2}$, the corresponding parameter $h^* = [H_{c2}/-dH_{c2}(t)/dt]_{t=1}$, and the Ginzburg-Landau-Maki parameter $\chi_1(t)$ has already been made in Chapter II B2 from thermal conductivity measurements. In this section, these parameters have been calculated from the magnetocaloric measurements and have been compared with different theories and experimental results, particularly with the results of reference 20.

To find $h^*$, the slope $[dH_{c2}(t)/dt]_{t=1}$ has been calculated and is found to be 6420 Oe. This is considerably higher than the value 4905 Oe found by Ohtsuka and Takano. This is not surprising as it is known that the rate of change of $H_{c2}$ with temperature depends on the resistivity ratio $\Gamma$. $dH_{c2}/dt$ increases with decreasing $\Gamma$ and as Ohtsuka and Takano have a purer sample ($\Gamma = 800$), they find $dH_{c2}(t)/dt_{t=1} = 4905$ Oe, which is small as compared to the present result on a sample of $\Gamma = 51$. The variation of $h^*$ with $t$ has been tabulated in table IV and also shown in fig. 18 along with Helfand and Werthamer's theoretical results for pure and dirty superconductors and the results of reference 20. It is found that between $t=1.0$ and $t=0.5$ the present results agree quite well with Helfand and Werthamer's theory and also with Ohtsuka and Takano's experimental results. Below $t = 0.5$ it is found that $h^*$ increases with decreasing temperature faster than the theory predicts but slower than the results of Ohtsuka and Takano. The behavior of $h^*$ at $t = 0$ is discussed in some detail in the next paragraph.

The expression for $h^*$ at $t = 0$ can be obtained from Helfand and Werthamer's theory as follows:
<table>
<thead>
<tr>
<th>$T^\circ K$</th>
<th>$t$</th>
<th>$H_{cl}/0e$</th>
<th>$H_{c2}/0e$</th>
<th>$h^*$</th>
<th>$H_{c1}/H_{c}$</th>
<th>$\chi_1$</th>
<th>$\chi_1(t)/\chi_1(1)$</th>
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<td>8.25</td>
<td>0.896</td>
<td>118.8 ±15</td>
<td>670 ±20</td>
<td>0.104</td>
<td>382.5</td>
<td>0.2922</td>
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<td>7.5</td>
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<td>204.7 ±15</td>
<td>1204.0 ±20</td>
<td>0.187</td>
<td>648.1</td>
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<td>6.5</td>
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<td>1892 ±20</td>
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<td>-</td>
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<td>$H_{c2}$ Oe</td>
<td>$h^*$</td>
<td>$H$ Oe</td>
<td>$H_{c1}/H$</td>
<td>$\chi_1$</td>
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<tr>
<td>---------</td>
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<td>0.3573</td>
<td>1.791</td>
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</table>
\[ h = \frac{\ln C_2(t)}{\ln (C_2(t)/C(t))} \]

Fig. 18
Taking $\delta = \sqrt{2} \lambda_L(0)$ as in BCS approximation, we have

$$h^*(0) = \frac{\gamma e^*}{6\pi} \left( \frac{\epsilon(0)}{K T_c} \right)^2 \frac{\sqrt{2}}{\delta} \lambda_L(0)^2.$$  \hspace{1cm} (13)

where $\gamma$ is the Euler's constant, $e^*$ the exponential (the asterisk has been attached to distinguish it from electron charge) is the zero field energy gap at $0^\circ\text{K}$. $D$ is a constant given in the BCS approximation as $D_{\text{BCS}} = \frac{8\pi^2}{6\zeta(3)} = 9.384$, $\zeta(3)$ being Riemann's zeta function. Using $D_{\text{BCS}} = 9.384$ for $D$ and $\epsilon(0)/K T_c = 1.76$ as predicted by BCS theory, Helfand and Werthamer have calculated $h^*(0) = 0.724$ for the pure limit. This is small compared to the present result of 0.8. This discrepancy between observed and theoretical values of $h^*(0)$ could even be larger because experimentally $D$ and $\epsilon(0)/K T_c$ have always been reported\textsuperscript{20} to be greater than 9.384 and 1.76 respectively. For an example, arbitrarily choosing $\epsilon(0)/K T_c = 1.85$ and $D = 12.3$ Ohtsuka and Takano\textsuperscript{20} have calculated $h^*(0) = 0.61$ from Helfand and Werthamer's theory. From thermal conductivity measurements it is found in Chapter II B2 that $h^*(0) = 0.69$. This small value of $h^*(0)$ as compared to 0.72 from the theory could be due to the high value of $D$ and $\epsilon(0)/K T_c$ as explained above.

The discrepancy between experiment and theory has been conjectured to be due to strong electron-phonon coupling\textsuperscript{8} or anisotropy effects.

The strong coupling effect can be ruled out, as vanadium which follows weak coupling prediction of BCS has also been found\textsuperscript{89} to
exhibit this discrepancy in $h^*(0)$. Hohenberg and Werthamer have shown that the anisotropy of $H_{c2}$ leads to a correction which should enhance $h^*(0)$. The anisotropy in $H_{c2}$ for Nb has been observed but the enhancement factor involves unknown quantities related to the Fermi surface and it is not known to what extent it may account for this discrepancy. Ohtsuka and Takano have suggested that a major part of the discrepancy may be accounted for if one takes $\sqrt{2} \lambda_L(0)/6 = \sqrt{D/D_{BCS}}$ in equation (13) instead of 1 as in BCS approximation.

Assuming a parabolic temperature dependence of the thermodynamic critical field, $H_c(t)$ has been calculated by taking $H_c(0) = 1940$ Oe. This has been used to calculate the parameter $\chi_1(t)$. The extrapolated value of $\chi_1(t)$ at $t = 1$ is found $\chi_1(1) = 1.145 \pm 0.015$. This gives the value of $\chi_0 = 0.991$ and $\chi_2 = 0.153$, as calculated from Goodman's relation $\chi(1) = \chi_0 + 7.53 \times 10^3 \rho_0 \gamma^2$, where the individual terms are explained in Chapter 11. This value of $\chi_0$ is high as compared to 0.87 by Rosenblum et al. 0.81 by French, 0.78 by FSS and 0.92 by Ikushima and may be due to the error in the resistivity measurement.

The ratio $\chi_1(t)/\chi_1(1)$ has been plotted in fig. 19 along with the theoretical results of French and also tabulated in table IV. Again as observed earlier $\chi_1(t)/\chi_1(1)$ increases at a faster rate than the theory predicts. The extrapolated value of $\chi_1(0)/\chi_1(1)$ is found to be 1.58, which is 24% higher than predicted from the theory. This confirms the earlier remarks that $\chi_1(0)/\chi_1(1)$ found for niobium cover a range which reflects the comparative purity of the samples, but all values
Fig. 19

- Present Data
- Eilenberger

\[
\frac{\kappa_1(t)}{\kappa_1(1)}
\]

\[\frac{\xi_0}{1_{tr}} = 0\]
\[\frac{\xi_0}{1_{tr}} = \alpha\]
are larger than expected from the theory. This behavior is not related to the strong coupling effect and may be related to the anisotropy effect in $H_{c2}$ as calculated by Hohenberg and Werthamer.

3. The Lower Critical Field. A calculation by Neumann and Tewordt\textsuperscript{94} shows that to first order in $t$, for a niobium sample of $\chi = 1.145$ and $\alpha = 0.067$, where $\alpha$ depends on the electronic mean free path of the sample

$$H_{c1}/H_c = 0.69 [1 + 0.55(1 - t)] .$$  \hspace{1cm} (15)

This shows that $H_{c1}/H_c$ should increase linearly with decreasing temperature. As shown in fig. 20 $H_{c1}/H_c$ does seem to increase linearly with decreasing temperature but disagrees in magnitude with the theory being smaller by a factor of 2. A linear fit, shows that $H_{c1}/H_c = 0.3045 [1 + 0.18(1 - t)]$. Although French and FSS find $H_{c1}/H_c$ to increase with increasing temperature, the magnitude of their result is within 10\% to the theory. These conflicting experimental results from magnetization on one hand and from the magnetocaloric effect on the other hand do not allow a clear conclusion to be reached. One notes that surface conditions can distort appreciably the observed value of $H_{c1}$. 
CHAPTER IV

FLUX FLOW RESISTANCE AND HEAT DISSIPATION

A - Flux Flow Resistance and Associated Heating

As explained earlier in Chapter I, the concept of flux flow has grown out mainly through the work of Kim et al.\textsuperscript{29} A brief account of the empirical theory of Kim et al.\textsuperscript{29} is given here to understand the flux flow mechanism and its implications on the present experiment. Choosing a frame of reference, where the applied field is in the $z$-direction, and the array of flux vortices in the $x$-$y$ plane, the presence of transport current $J$ in the $x$-direction generates a gradient in the flux line density $n$, so that from Maxwell's equation, one gets

$$\frac{\partial B}{\partial y} = \frac{\phi_0}{c} \frac{\partial n}{\partial y} = \frac{\mu_0}{c} J$$  \hspace{1cm} (16)$$

and the Lorentz force is given by

$$\frac{\partial}{\partial y} \left( \frac{B^2}{2\mu_0} \right) = \frac{BJ}{c} = \frac{n \rho J}{c}.$$  \hspace{1cm} (17)$$

Distributing the macroscopic magnetic pressure equally to each flux line, the Lorentz force on each flux line is given by

$$F_L = \frac{J \rho_0}{c}$$  \hspace{1cm} (18)$$

When the Lorentz force $F_L$ exceeds the pinning force $F_p$, a viscous motion of the flux lines sets in which is characterized by the relation

71
where $v_L$ is the line velocity and $\eta(H,T)$ the viscosity coefficient of the medium. Due to this motion of the flux lines an electric field is created in the direction of $J$, given by the relation

$$E_o = n(v_L/c) \Phi_o = \frac{v_L B}{c}$$  \hspace{1cm} (20)

Here $E_o$ is required to be proportional to $v_L$. The effect of pinning can be eliminated from the problem by taking the derivatives of (19) and (20), i.e.

$$\frac{dv_L}{dF_L} = \frac{c}{\Phi_o} \frac{dv_L}{dJ} = \frac{1}{\eta}$$  \hspace{1cm} (21)

and

$$\frac{dE_o}{dv_L} = \frac{B}{c}$$  \hspace{1cm} (22)

Combining these two expressions, one gets

$$\frac{dE_o}{dJ} = \frac{\Phi_o B}{\eta c^2} = \rho_f$$ \hspace{1cm} (23)

where $\rho_f$ is defined as the "flux flow" resistivity. Equation (23) shows that at a fixed value of the field $B$, the flux flow resistivity is independent of the pinning force or critical current for $F_L > F_P$. This implies that for $F_L > F_P$, the $V-I$ characteristics should be linear for any fixed value of the internal field $B$.

The flow resistance and the associated heat dissipation have
been measured in the mixed state of superconducting niobium and vanadium plates, for different currents and temperatures, by conventional d.c. methods. The sensitivities of the voltage and temperatures measurements were $1 \times 10^{-7}$ v and $1 \times 10^{-4}$°K respectively. The temperature range covered lies between $t = 0.5$ and $t = 1$ and the transport current densities were relatively small, 0.35 to 21 A/cm$^2$ for niobium and 1.5 to 18.4 A/cm$^2$ for vanadium.

Figure 21 shows the flux flow voltage $V$ observed versus the transport current $I$, with magnetic field direction parallel to the large face of the plate in fig. 21a and perpendicular to it in 21b. One should note that the current densities used in these measurements are very much smaller than in most measurements of this kind. This is because for high current densities, a linear $V$-$I$ characteristic of the type of equation (23) has already been observed by Kim et al.$^{29}$ and so the purpose of the present work was to investigate the non-linear region of the $V$ versus $I$ characteristic which is observed only at small current densities. The non-linearity is very noticeable in figure 21, at applied fields small compared to $H_{c2}$. As the applied field gets closer to $H_{c2}$, the characteristic becomes closer to a linear behavior, but one can expect that pure linearity appears only at fields for which the sample is in the normal state. As a matter of fact, for those cases where the value of $H_{c2}$ is ambiguous, this criterion is of good use: all fields for which $V$ vs. $I$ shows non-linear behavior are certainly smaller than $H_{c2}$ or $H_{c3}$ depending on the geometry of the field and the sample. Thus figure
\( \theta = 0^\circ \)

- ▲ \( H = 6.63 \text{ K0e} \)
- ○ \( H = 7.22 \text{ K0e} \)
- ■ \( H = 7.57 \text{ K0e} \)
- □ \( H = 7.91 \text{ K0e} \)
- ◇ \( H = 9.24 \text{ K0e} \)

\( \theta = 90^\circ \)

- ○ \( H = 4.81 \text{ K0e} \)
- ▲ \( H = 5.16 \text{ K0e} \)
- ■ \( H = 5.51 \text{ K0e} \)
- □ \( H = 6.20 \text{ K0e} \)
- ◇ \( H = 6.83 \text{ K0e} \)
- ○ \( H = 8.25 \text{ K0e} \)

Fig. 21
21b shows $H_{c2} \geq 5850 \text{ Oe}$ and figure 21a shows $H_{c3} \geq 7250 \text{ Oe}$. This will be confirmed later by the heating curves shown in figure 27.

In figure 22 a log-log plot of the voltage versus current characteristics for both niobium and vanadium samples is shown, for different values of the reduced field $h(=H/H_{c2})$, at $T = 4.4 \text{ K}$ for niobium and $4.3 \text{ K}$ for vanadium. It is found that for both samples $V \propto (1 - I_c)^n = I^n$ where $I_c$ is the critical current when $F_L = F_P$. The power $n$ is a function of the applied field. As the reduced field $h$ is increased, the power $n$ decreases and at $h = 1$, as expected, it attains the value of 1, i.e. Ohm's law. The lower part of figure 22 shows the log-log plot of the corresponding $\Delta T$ vs. $I$ characteristic, where $\Delta T$ is the increase in temperature of the sample. Although log-log plots are sometimes misleading, they have been used here only to investigate the type of relationship that exists between the power dissipation and the flux flow resistance. The heating $\Delta T$ which is proportional to the power dissipated is shown to be also proportional to a power of $I$: $\Delta T \propto VI = I^{n'}$. It is found that the power $n'$ in the $\Delta T - I$ characteristic exceeds always by one the power $n$ found in the $V - I$ characteristics, the comparison being made for the same value of the reduced critical field $h$. This observation of $n' = n + 1$ in the $\Delta T - I$ behavior gives an independent confirmation of the non-linear nature of the phenomenon at low transport current densities as observed by many other workers$^{29,30,32}$ and for the first time confirms the existence of a relation of the type $P = VI$ in the flux flow state. This has also been confirmed independently by a plot of $\Delta T$ vs $VI$ in figure 23, which shows a direct proportionality. A careful check
VANADIUM PLATE

f = 0.32

NIOBium PLATE

(θ = 90°) t = 0.5

h = 0.95

h = 0.76

h = 0.74

h = 0.72

h = 0.70

Δ h = 0.65

Fig. 22
\( H = 7.224 \text{ KOe} \)

\( H = 7.563 \text{ KOe} \)

\( H = 7.912 \text{ KOe} \)

**Fig. 23**

![Graph](Image)
eliminated the possibility that the heating observed might be due to a Peltier effect as the carbon thermometer sensed the temperature at the level of one of the current junctions and $\Delta T$ observed did not change sign upon reversal of the transport current direction. Fig. 24 shows the $V-I$ characteristics for niobium at higher temperatures for different reduced fields and here again the power law dependence for the voltage is found over quite a large range of current values viz. $10^{-5} - 500$ mA.

The functional dependence of the power $n$ is shown in Fig. 25 against the reduced field $h$ for two different niobium temperatures and also for vanadium. It is found that $n(h)$ is a monotonic, well behaved function which decreases towards the value of 1 corresponding to the normal state Ohm's law as $H$ approaches $H_{c2}$. The observed behavior is not the consequence of sample heating because power law behavior in the resistance measurements is observed both in isothermal and in quasi-adiabatic conditions: if non-linear dependence of $V$ vs $I$ was due to heating, it should disappear when the measurements are made in isothermal conditions.

Cladis$^{33}$ has argued that the relation $\ln I \propto V^{1/2}$ accurately described flux flow behavior in type II superconductors in both the "linear" and "non-linear" portions of the $I-V$ curves, although there is no physical ground for such a relation. Any departure from this $\ln I \propto V^{1/2}$ behavior has been attributed by Cladis to sample inhomogeneity. The validity of this relationship has been disputed by Joiner$^{34}$ who has examined his own data on lead-Bismuth and lead-thalium alloys and also on other data$^{31}$ which have appeared in the
Fig. 25
literature but which were not mentioned by Cladis. Joiner concludes that Cladis relation does not adequately describe the current-voltage characteristics, but rather sometimes provides a fortuitous fit when data are obtained over a limited range of currents. The non-linearity at smaller values of the current has been explained by Kim et al. in terms of flux creep mechanism and also by Farrell et al. by postulating a non-linear effect of the Lorentz force. The present results agree neither with Cladis' relation nor with the flux creep formula \( V = K_1 + K_2 J (H + B_0) \), (where \( K_1, K_2 \) and \( B_0 \) are constants). The non-linear behavior in the moderate current range was conjectured to be due to a mechanism intermediate between flux creep and flux flow. Since the measurements are made at high \( T \), it was suggested that the viscosity coefficient \( \eta \) might be current dependent at high \( T \). Since this coefficient can be expressed in terms of the core radius of the flux lines, this would suggest a dependence of the core radius on the transport current.

Recently Jones et al. have shown on a Nb-Ta sample that the non-linearity in the \( V - I \) characteristics just above the critical current may arise from the non uniformity of the sample: when the impurities and other structural defects are distributed in the sample non uniformly, different sections of the sample will have different critical currents and the \( V - I \) characteristics for different sections of the sample will be different, but each of them will be nearly linear. When the \( V - I \) characteristic is observed over the whole sample, it actually gives by addition the overall behavior
which appears as non linear just above the critical current. This has been confirmed later by Chang and Rose-Innes by the absence of non-linearity in the V-I characteristics of a highly homogeneous Nb$_{77}$-Mo$_{23}$ sample.

Cape and Silvera and Fiory and Serin have shown that by depinning the fluxoids by superimposing a small longitudinal oscillatory field, a linear V-I behavior can be observed in the flux flow measurements at all values of the transport current. All these results confirm that the non-linear behavior in the V-I characteristics at small values of the transport current is due to the non uniform density of the fluxoids pinned along the sample and as a consequence, it now appears that the mechanism proposed by Wasim and Zebouni is not required to explain non-linearity.

B. Surface Superconductivity

A field orientation study of the surface superconductivity above $H_{c2}$ has been made by Tomasch and Joseph on well annealed Pb-Tl thick films by torque measurements, by Autler et al. on Nb wires and by Hempstead and Kim on Pb-In and Nb-Ta sheets, by resistive measurements. It is found, confirming the theory of Saint-James and deGennes, that when the applied magnetic field is parallel to the large faces of flat samples or to the length of the wires, a superconducting surface sheath exists between $H_{c2} < H < H_{c3} = 1.69 H_{c2}$; and when the field is perpendicular to the face of the sample, the superconductivity disappears at the upper critical field $H_{c2}$.

There are two properties that make the determination of the
ratio $H_{c3}/H_{c2}$ is difficult. Firstly, Tomasz and Joseph\textsuperscript{100} have shown that the ratio $H_{\theta}/H_t$, (where $H_{\theta}$ is the critical field at which the sample becomes normal for an angle $\theta$ between the sample face and the direction of the applied field, and $H_t$ is the critical field for $\theta = 90^\circ$) is very sensitive between $\theta = 0^\circ$ to $\theta = 30^\circ$. For example, for $\theta = 10^\circ$, $20^\circ$ and $30^\circ$, $H_{\theta}/H_t$ is found\textsuperscript{100} to be 1.5, 1.31 and 1.2 respectively. This shows that the ratio $H_{c3}/H_{c2}$ is quite sensitive to the orientation of the sample with respect to the field. Secondly, when the field is parallel to the large face of the sample, the resistive transition shows a sharp discontinuity at $H_{c2}$ followed by a more or less gradual rise to the normal resistance as $H_{c3}$ is approached.

As the transport current is decreased, the sharpness of the change in resistance at $H_{c2}$ diminishes and the return to the normal resistivity takes place more gradually. As a consequence, for small transport currents the value of $H_{c2}$ and $H_{c3}$ and their ratio is not well defined.

In the present measurements, Fig. 26 shows the $V$ vs. $H$ characteristics for the niobium sample for three different values of the transport current in both parallel ($\theta = 0^\circ$) and perpendicular ($\theta = 90^\circ$) field. Due to the misalignment of the sample with respect to the field direction, and because of the small current density, the two critical fields $H_{c2}$ and $H_{c3}$ are not well-defined. By examining the change of the slope $\frac{dV}{dH}$, one can only speculate about the critical fields to be $H_{c2} = 6536 \pm 350$ Oe and $H_{c3} = 9632 \pm 350$ Oe. However, when the power dissipation is measured as a function of the applied
field, striking features appear in the heating versus magnetic field curves of figure 27 (for the geometry of \( H \) parallel to the large face of the sample). There appears at all values of the transport current a sharp break in the slope of the curve at two very well-defined values of \( H \) which one can easily identify as the critical fields \( H_{c2} \) and \( H_{c3} \). Thus one finds \( H_{c2} = 6364 \pm 172 \) Oe, \( H_{c3} = 9030 \pm 172 \) Oe and \( H_{c3}/H_{c2} = 1.42 \pm 0.04 \). This is a remarkable property which can be used to measure \( H_{c2} \) and \( H_{c3} \), since measurements of \( H_{c3} \) have been notably difficult and the results ambiguous. It is not known what mechanism leads to this discontinuity, but it could be due to the change in the specific heat at \( H_{c2} \) and \( H_{c3} \). The discrepancy between the above value of the ratio \( H_{c3}/H_{c2} = 1.42 \pm 0.04 \) and the theoretical value of 1.69 is due in our opinion to sample misalignment effect and is not fundamental.
CHAPTER V

CONCLUSION

The present study indicates that the mixed properties of the thermal conductivity \( K_m \), in a niobium sample of intermediate purity \((\ell/\xi_0 \sim 1)\), are still in qualitative agreement with the dirty limit \((\ell/\xi_0 \ll 1)\) theory of Caroli and Cyrot\(^{12}\) inasmuch as \( K_m \) increases linearly as \( H \) approaches \( H_{c2} \). This linear behavior extends over an appreciable range of mixed state. The slope \( \partial K_m/\partial H \) varies with temperature much faster than predicted by theory and this behavior seems characteristic of samples departing from the extreme dirty limit.

The parameter \( \chi_1(t) = H_{c2}(t)/2 H_c(t) \) is found, in agreement with other investigators, to increase with decreasing temperature much faster than expected from theory.

The temperature dependence of the minimum in the mixed state is thought to imply - in addition to the monotonic decrease of \( K_gm \) with increasing magnetic field - a nonmonotonic variation of \( K_{es} \), viz. a decrease of the electronic conductivity upon entry in the mixed state followed by an increase as \( H \) approaches \( H_{c2} \). This is strongly supported by the data of Muto \textit{et al.}\(^4\). The scattering mechanism responsible for this behavior of \( K_{em} \), though it can be conjectured to be scattering by flux lines, merits further investigation.

The irreversible heating and its field and temperature dependence in the magnetocaloric measurements can be explained qualitatively in terms of the pinning force per unit volume \( \alpha_c \) by comparing with the
The magnetocaloric effect can be used to calculate the thermodynamic quantities in the mixed state and confirms Gorter's criterion \(^{27}\) that no flux jump should occur when the enthalpy \(\Delta E\) in the mixed state is smaller than its corresponding value in the normal state.

Comparison with magnetization measurements confirms that the two critical fields \(H_{c1}\) and \(H_{c2}\) can be measured accurately from magnetocaloric measurements. The temperature dependence of \(h^*\) and \(x_1(t)/x_1(1)\) are in agreement with other investigators and with the thermal conduction measurements and are found to increase with decreasing temperatures much faster than expected from theory. This deviation from the theory also depends on the impurity content and the structural defects content of the sample.

The flux flow measurements and the corresponding power dissipation confirm the non-linear nature of the flux flow resistance for small current densities and the power dissipation is found to be of the form \(P = VI\). Because of the non-alignment \(^{100}\) and the magnitude of the current density, \(H_{c2}\) and \(H_{c3}\) can not be found accurately but the heat dissipation measurements in the present work reveal sharp discontinuity which allows a precise determination of the ratio \(H_{c3}/H_{c2}\). The mechanism responsible for this discontinuity merits further theoretical and experimental investigations.
EXPERIMENTAL DETAILS FOR MAGNETOCALORIC MEASUREMENTS

The sample, a monocrystal rod, inside a vacuum calorimeter was clamped in a brass sample holder which itself was screwed into a copper post extending up into the liquid helium bath. The temperature of the sample could be raised up to 10°K with the brass sample holder acting as a thermal resistor between sample and heat sink. Two heaters of constantan wire No. 40 were wound, one on the sample covering most of the sample surface and the other on the sample holder. The heater on the sample holder was used to raise the temperature of the sample in the range 4.2°K to 10°K and also to drive the sample normal thermally after each field cycle to eliminate the trapped flux. The sample heater was used to establish a thermal gradient along the system to measure the thermal conductivity of the system. A 50Ω, 1/10 W Allen-Bradley carbon resistor was glued on the sample and was used for the temperature measurement. The thermometer was calibrated against the vapor pressure of liquid helium in the temperature range of 1.3°K to 4.2°K and against a calibrated germanium thermometer in the range 4.2°K to 9°K.

At each fixed temperature of the sample, the magnetic field was swept at the rate of 5.73 Oe per second. The corresponding change in the temperature of the sample was measured indirectly by measuring the change in the resistance of the carbon thermometer which for a fixed current showed as a change in the electrical voltage. This change in voltage was recorded on the Brown recorder and from the slope of the thermometer the corresponding change in
temperature $\Delta T$ was calculated. This $\Delta T$ was in error due to the magnetoresistance of the thermometer. Therefore the magnetoresistance of the carbon thermometer was measured for the same temperature at different values of the magnetic field and determining on its sign was added to or subtracted from the magnetocaloric signal $\Delta T$. To convert the change in temperature $\Delta T$ to the corresponding power dissipation $\dot{Q}$, the thermal conductivity of the system was measured. This was achieved by heating the sample through the sample heater so that the temperature of the system was raised to about $\Delta T'$ such that $\Delta T' = \frac{\Delta T_{\text{MAX}}}{2}$. Knowing the applied heat $Q_{\text{app}}$ and the corresponding change in temperature $\Delta T'$ the ratio $r = \frac{\dot{Q}_{\text{app}}}{\Delta T'}$, a characteristic of the system, was calculated. This ratio was used to compute the magnetocaloric power dissipation $\dot{Q}$ by the relation $\dot{Q} = r \Delta T$. 
APPENDIX II

EXPERIMENTAL DETAILS FOR MAGNETIZATION MEASUREMENTS

The magnetization measurement was made by the standard heat pulse ballistic method. A coil of copper wire No. 45 with about 500 turns was wound on the niobium rod along its length so that when the sample was mounted, the direction of the magnetic field was at right angle to the sample axis and along the axis of the coil. The sample was clamped in a brass sample holder which itself was screwed into a copper post extending up into the liquid helium bath. A heater of constantan wire No. 40 was wound on the sample holder to drive the sample normal thermally by raising its temperature above the critical temperature. The sample was placed in a vacuum.

The coil was calibrated at liquid nitrogen temperature by connecting the coil to a ballistic galvanometer. At a fixed value of the magnetic field, the magnet was suddenly turned off. The corresponding deflection of the ballistic galvanometer, which is proportional to the total change in magnetic flux through the pickup coil, was measured and from a series of such measurements a calibration was obtained.

To measure the magnetization at any fixed temperature, the magnetic field was set at a certain value, and then the sample was driven normal thermally by a heat pulse. The corresponding deflection of the ballistic galvanometer was noted. Since $B = H + 4\pi M$, where $B$ is the field inside the sample, $H$ is the applied field, and $M$ is the magnetization, the deflection was a measure of $-4\pi M = H - B$. From the calibration the value of $-4\pi M$
corresponding to the deflection was calculated. For the next magnetization point at the same temperature, the magnetic field was first turned down to zero before the heat pulse was turned off to avoid any trapping of the magnetic flux. This method was followed for all field values from $H = 0$ to $H = H_{c2}$. As the measurement was made in a field transverse to the axis of the cylindrical sample the demagnetization factor was determined by normalizing the slope of $-4\pi M$ vs $H$ for $H < H_{c1}$ to the slope 2 and the corresponding $-4\pi M_{\text{eff}}$ vs $H$ was calculated.
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