Superconductivity in Th-Nb composites

Loren Frederick Goodrich

Iowa State University
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SUPERCONDUCTIVITY IN THORIUM-NIOBIUM COMPOSITES

Iowa State University

Ph.D. 1980

University Microfilms International

300 N. Zeeb Road, Ann Arbor, MI 48106
18 Bedford Row, London WC1R 4EJ, England
Superconductivity in Th-Nb composites

by

Loren Frederick Goodrich

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Physics
Major: Solid State Physics

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1980
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LIST OF SYMBOLS

$T_c$ - Critical temperature

$H_c$ - Critical field

$H_0$ - Critical field at zero temperature

$t$ - Reduced temperature

$H_a$ - Applied magnetic field

$\lambda$ - Penetration depth

$N$ - Subscript denoting normal state

$S$ - Subscript denoting superconducting state

$e$ - Subscript denoting electronic calibration

$g$ - Subscript denoting lattice contribution

$C$ - Heat capacity

$\gamma$ - Sommerfeld constant

$\Theta$ - Debye temperature

$\Delta$ - Energy gap

$V_{hk}$ - Electron-phonon interaction

$\xi$ - Coherence distance

$V$ - BCS coupling constant

$N_e(0)$ - Electron density of states at the Fermi surface

$N_e(E)$ - Electron density of states
\( \phi_0 \) - Flux quantum

\( \psi_s \) - Superconducting wave function

\( F \) - Free energy

\( \kappa \) - Landau-Ginzburg parameter

\( H_{c1} \) - Lower critical field

\( H_{c2} \) - Upper critical field

\( K \) - Kernel

\( b \) - Extrapolation length

\( K_{S,N}^{-1} \) - Decay length

\( I_C \) - Critical current

\( J_C \) - Critical current density

\( J_{cpb} \) - Pair breaking critical current density

\( f_L \) - Lorentz force per unit length

\( P_v \) - Pinning force per unit volume

\( \lambda_e \) - Rod spacing of eutectic

\( d_f \) - Niobium rod or filament diameter

\( R_i \) - Zone rate

\( \rho_{eff} \) - Effective resistivity

\( \rho_{rem} \) - Remnant resistivity

\( d_w \) - Diameter of wire sample
\( C_p \) - Specific heat

\( C_{\text{add}} \) - Heat capacity of addenda

\( C_H \) - Field component of addenda heat capacity

\( \Delta C \) - Jump in the heat capacity at S-N transition

\( H_E \) - Flux entry field

\( H_{C3} \) - Surface critical field

\( H_K \) - Upper critical field using Kramer's scaling law
INTRODUCTION

Superconductivity

Since the discovery of superconductivity, the interest and intrigue of this phenomenon has persisted and there has been a steady flow of new discoveries. In 1911, Onnes (1) discovered that the resistivity, $\rho$, of mercury wires dropped by at least several orders of magnitude in a 0.01 K temperature range near a critical temperature, $T_c$, of 4.3 K. Within the error of the experiment the resistivity dropped to zero and hence the phenomenon was called superconductivity. Onnes (2) also showed that a magnetic field, $H$, would destroy the effect and mapped out the phase boundary separating the superconducting and normal phases. It was found that the critical field, $H_c$, was given by,

$$H_c = H_0 (1 - t^2),$$

(1)

where,

$$t = T/T_c,$$

(2)

and $T$ is the temperature and $H_0$ is the critical field at zero temperature.

In 1933 Meissner and Ochsenfeld (3) showed that some elements show full flux expulsion as well as zero resistivity in the superconducting state. In this so called Meissner state, an applied magnetic field, $H_a$, decays exponentially with distance, $x$, near the surface of the sample,
where $\lambda$ is one of the characteristic lengths, the penetration depth, of a superconductor. Further work by London and London (4, 5) has shown that $\lambda$ is on the order of

$$\lambda = \frac{mc^2}{4\pi ne^2},$$

where the mass $m$, charge $e$, and concentration $n$ are that of an electron and $c$ is the speed of light. Typically $\lambda = 50$ nm for most bulk superconductors.

With Meissner's discovery of flux expulsion it became clear that the superconducting-normal phase change was reversible and the rules of equilibrium thermodynamics could be applied. The specific heat of a normal metal, $C_N$, (the subscript $N$ denotes the normal phase) at low temperatures is given in the Debye approximation as,

$$C_N = C_{eN} + C_{gN} = \gamma T + \zeta(T/\Theta)^3,$$

where the subscript $e$ denotes the electronic contribution and $g$ denotes the lattice contribution to the specific heat. The Sommerfeld constant, $\gamma$, is proportional to the density of electronic states of the Fermi surface, $\Theta$ is the Debye temperature and $\zeta$ is a numerical constant for all
metals. Experiments (6, 7) have shown very little change in the lattice at $T_c$ so it is expected that for the superconducting specific heat

$$C_S = C_{eS} + C_{gS}, \quad (6)$$

where $C_{gS} = C_{gN}$ and the subscript $S$ denotes the superconducting phase. Hence one can separate the electronic specific heat and obtain the essential thermodynamic information about the superconducting state from

$$C_{eS} = C_S - C_N + \gamma T. \quad (7)$$

In 1954 Corak and Satterthwaite (8) used this technique to show that $C_{eS}$ was of the form

$$C_{eS}/\gamma T_c = \alpha_1 e^{-\beta_1/T}, \quad (8)$$

where $\alpha_1$ and $\beta_1$ are constants. This indicated a well-defined energy gap, $2\Delta$, at low temperatures. Direct measurement of the gap by infrared absorption (9) and electron tunneling (10, 11) confirmed the existence of a gap given approximately by

$$2\Delta = 3.52 \ k_B T_c, \quad (9)$$

where $k_B$ is Boltzmann's constant.
At the same time these fundamental experiments were being done, Bardeen, Cooper and Schrieffer (BCS) (12) developed a microscopic theory of superconductivity for a homogeneous material. In this theory new pairing correlations are made possible by an attractive coupling such as the electron-phonon interaction, \( V_{hk} \), and the electron gas is unstable to the formation of pairs of electrons with equal and opposite momenta, the so-called Cooper pairs. A fundamental distinction, then, between a superconductor and a normal metal is that this pair-wise occupation of states (rather than random occupation as in a normal electron gas) makes more effective use of the phase space available for electron-phonon scattering and the free energy is lowered by transforming to the paired state.

Detailed calculations (12) show that it is energetically favorable to mix normal state wave functions of different momenta \( (hk) \) over a range of momentum, \( \Delta k = k_B T_c / v_F \) and this leads to a real space wave packet having dimension

\[
\xi = \frac{\hbar v_F}{2 \pi k_B T_c},
\]

where \( \hbar = h / 2\pi \) is Planck's constant divided by \( 2\pi \) and \( v_F \) is the Fermi velocity. This second characteristic length, \( \xi \), which gives the size of the Cooper pair wave function, is called the coherence distance. The BCS theory also indicates that the transition temperature is given by

\[
k_B T_c = 1.14 \frac{\hbar \omega_q}{e} e^{-1/N_e(0)V},
\]
where $\omega_q$ is the Debye phonon frequency, $N_e(0)$ is the density of state at the Fermi surface of the normal metal and $V$ is the magnitude of the matrix element $V_{hk}$. In addition it gives an energy gap confirming equation 9 and an energy, $E$, dependent density of states $N_e$ given by

$$N_e(E) = \frac{N_e(0)E}{\sqrt{E^2 - \Delta^2}}$$

in good agreement with experiment. Four years after the BCS theory, the essential pairing idea was shown to be correct by the flux quantization experiments of Doll and Nabauer (13) and Deaver and Fairbank (14), which showed that flux trapped by a superconductor comes in quanta, $\phi_0$, (fluxoid) of size

$$\phi_0 = \frac{hc}{q},$$

where $q$ is $2e$, the charge of a pair of electrons rather than a single electron.

Another useful theory of superconductivity is the phenomenological theory of Ginzburg and Landau (GL) (15). This theory has provided a very general framework for understanding superconductivity in environments where the superconducting wave function, $\psi_S$, has some variation in space. In this theory the free energy, $F$, is expanded in a power series with appropriate added terms for the kinetic energy, $\frac{1}{2m}(-ih\nabla - \frac{2eA}{c})\psi_S^2$. 
and magnetic energy, $H^2/8\pi$,

$$F_S = F_N + \alpha |\psi_S|^2 + \beta/2 |\psi_S|^4$$

$$+ \frac{1}{2m} |(-i\hbar \nabla \frac{2eA}{c})\psi_S|^2 + H^2/8\pi,$$

(14)

where $\vec{A}$ is the local vector potential, $\alpha$ and $\beta$ are constants. Minimizing this free energy with respect to $\psi_S$ and $A$ gives the basic GL equations for the spatial variation of the wave function and magnetic field. Using these basic ideas, Abrikosov (16) found that there are at least two different types of superconductors depending on the relative magnitudes of $\xi$ and $\lambda$. The ratio of these two characteristic lengths is defined as $\kappa$, the Landau-Ginzburg parameter, $\kappa = \lambda/\xi$. If $\lambda/\xi < 1/\sqrt{2}$, one finds a solution similar to BCS with a spatially uniform $\psi_S$ and a full Meissner effect. These are called Type I. If $\lambda/\xi > 1/\sqrt{2}$, solutions to the GL equations have a different form and the superconductor is nonstable to the formation of a fluxoid lattice in which vortices of flux quanta enter the sample on a triangular array and form the so-called mixed state. These are called Type II superconductors. Essmann and Träuble (17, 18) first showed the existence of this state by decoration techniques and Schelten et al. (19, 20) and Cribier et al. (21) mapped the magnetic field distribution using neutron scattering. The response of a typical Type II superconductor to an applied magnetic field is to show $B = 0$ inside the specimen up to some lower critical field, $H_{c1}$, where it is favorable for vortices to enter the sample. Above this field, $B$ increases from zero gradually with increasing $H$ and eventually $B = \mu_0 H$ at an upper
critical field, \( H_{c2} \). In this vortex or mixed state between \( H_{c1} \) and \( H_{c2} \) the wave function \( \psi_S \) will approach zero in the core of a vortex, which is about \( 2\xi \) in diameter, over a characteristic length \( \xi \). In addition, the magnetic fields will be a maximum in the core of the vortex and decay away with a characteristic length \( \lambda \). The characteristic fields are given approximately by (22),

\[
H_{c1} = \frac{\phi_0}{2\pi\lambda^2},
\]

and,

\[
H_{c2} = \frac{\phi_0}{2\pi\xi^2}.
\]

The purpose of the work reported here was to study the proximity effect in bulk samples of superconductor-normal metal composites having cylindrical geometry. Both the equilibrium properties such as specific heat and \( T_c \), as well as dynamical properties such as critical currents, are of interest. From the values of \( T_c \) we wish to test simple GL predictions for cylindrical geometry. From the specific heat we hope to get a rough measure of the value of the pair potential in the normal metal. The critical current should give us information about the vortex pinning forces at a super-normal boundary.
Proximity Effect

In this research, our primary interest was focused on changes in the superconducting wave functions which occur at a superconductor-normal metal boundary. The electron-phonon interaction can give rise to very long range correlation in time but the interaction takes place over a very limited range in space of about 0.8 to 1.0 nm. This means that the electron density of states, $N_e(0)$, times the BCS coupling constant, $V$, can change over atomic dimensions. It is of central interest to know how $\psi_S$ changes as a result of the abrupt change in $N(0)V$. This so called proximity effect is the phenomenon that occurs when a normal metal, $N$, is in good electrical contact with a superconductor, $S$. Fundamental to this effect is that superconductivity in a bulk material is characterized by an electron pair correlation, with an associated coherence distance, $\xi_S$, typically of order $10^{-6}$ to $10^{-7}$ m, and this correlation will extend a similar distance into a normal metal in contact with a superconductor. There are several theories of the proximity effect involving the nonlocal nature of superconductivity and thus the spacially dependent pair potential $\Delta(\mathbf{r})$.

A fundamental experiment to observe this effect is the measurement of the $T_c$ of superposed thin films of a normal metal and a superconductor. The qualitative behavior is that a superconducting film, of thickness $D_S$, less than or on the order of $\xi_S$, will have its $T_c$ lowered by the superposition of a normal metal and this lowering should be independent of normal metal thickness, $D_N$, for $D_N$ larger than a coherence distance. One of the first proximity effect theories was that of Cooper (23),
which is a simple model that is still useful within its valid limits. The basis of this theory is that the electron pair correlation introduces a nonlocality into the electron pair wave function, so that the pairs sample an effective attractive potential, which is simply the spatial average of the potentials on the two sides of the interface. The effective coupling constant, $[N_e(0) V]_{\text{eff}}$, of the superimposed films is then,

$$[N_e(0) V]_{\text{eff}} = \frac{D_S [N_e(0) V]_S + D_N [N_e(0) V]_N}{D_S + D_N}, \quad (17)$$

where the subscript $N$ refers to the normal metal and $S$ to the superconductor. Then, the BCS $T_C$ formula becomes,

$$T_C = 1.1400 \xi_D \exp\{-[N_e(0) V]_{\text{eff}}^{-1}\}. \quad (18)$$

Within the range of $D_S$ and $D_N$ much less than $\xi_S$, this model gives reasonable agreement with experiments and is referred to as the Cooper limit.

The proximity effect theory of deGennes - Guyon (24, 25) proceeds in a more basic manner by generalizing the Gor'kov (26) Green's function treatment of superconductivity to the case of a position-dependent electron-electron interaction and thus a spatial variation in the pair potential, $\Delta(r)$. The self-consistent integral equation for $\Delta(r)$ is,

$$\Delta(r) = \int d^3r' K(r, r', T) \Delta(r'), \quad (19)$$
where $K$ is the kernel with a range of the coherence length $\xi$. In the dirty limit this is given by,

\[
\xi(T) = \left(\frac{\hbar v_F \ell}{8\pi k_B T}\right)^{1/2},
\]

(20)

where $v_F$ is the Fermi velocity and $\ell$ the electronic mean-free-path. This theory is valid only for small $\Delta(\bar{r})$ dirty systems ($\ell \ll \xi$) and near $T_C$ of the superimposed NS film.

For the NS sandwich the kernel equation becomes a one-dimensional equation, which deGennes showed that the boundary conditions on $\Delta(x)$ at the interface were,

\[
\frac{\Delta_N(0)}{N_{eN}(0) V_N} = \frac{\Delta_S(0)}{N_{eS}(0) V_S},
\]

(21)

and

\[
\frac{\xi_N^2}{V_N} \frac{d}{dx}\left[ \frac{\Delta_N}{V_N} \right]_0 = \frac{\xi_S^2}{V_S} \frac{d}{dx}\left[ \frac{\Delta_S}{V_S} \right]_0.
\]

(22)

These boundary conditions show that $\Delta(x)$ can be discontinuous at the boundary, but the pair wave function is continuous across the interface. An important parameter is the extrapolation length, $b$, which is defined by the logarithmic derivative of $\Delta_S$ as,

\[
b = \frac{\Delta_S}{\xi_S} \frac{d}{dx} \frac{\Delta_S}{\xi_S},
\]

(23)
at the interface. The solution to the one-dimensional kernel equation in the superconductor is (24),

\[ \Delta_S(x) \propto \frac{\cos K_S(x + d_S)}{\cos K_S d_S}, \tag{24} \]

where \( K_S \) is given approximately by,

\[ K_S^{-1} = \left( \frac{\hbar v_{FS} \xi_S}{6\pi k_B T} \right)^{1/2} \left( \frac{2}{\ln(T_{cs}/T)} - 1 \right)^{1/2}. \tag{25} \]

\( K_S^{-1} \) reduces to the Ginzburg-Landau coherence length near \( T_{cs} \). In the normal metal the solution is approximated for \( x \gg K_N^{-1} \) by,

\[ \Delta_N(X) \propto \exp(-K_N x), \tag{26} \]

where,

\[ K_N^{-1} = \left( \frac{\hbar v_{FN} \xi_N}{6\pi k_B T} \right)^{1/2} \left( 1 + \frac{2}{\ln(T/T_{cn})} \right)^{1/2}. \tag{27} \]

Within this approximation, referred to as the one frequency approximation, \( K_N^{-1} \) is the decay length of the Cooper pairs into the normal metal. In the special case of \( V_N = 0 \), \( K_N^{-1} \) reduces to \( \xi_N \) and boundary condition, equation 21, requires \( \Delta_W(X) \) to be zero.

Another treatment of the proximity effect was that of Werthamer (27), which extends the theory of deGennes and obtains a complete solution for \( \Delta(\vec{r}) \) and \( T_c \). By transforming the self-consistent integral equation
for $\Delta(\mathbf{r})$ into a differential equation and including the proper boundary conditions, he was able to make a one to one correspondence between the superposed film problem and the quantum mechanical problem of the energy levels and wave function of a particle in a one-dimensional potential well. The assumptions of his idealized model of the film sandwich were that the two metals are identical in the normal state, that is they have the same $V_F$, $N(0)$, $\rho$ and $\theta$. All of the differences between the two metals were assumed to be contained in the BCS electron-electron interaction parameter $V$, which was taken to be a uniform constant throughout a given metal. The following relations were derived by Werthamer,

$$
\chi (\xi^2 S^2) = \ln \left( T_{CS}/T_{CNS} \right), \\
\chi(-\xi^2 N^2) = \ln \left( T_{CS}/T_{CNS} \right), \\
N_S \xi^2 S \tan (K_S d_S) = N_N \xi^2 N \tanh (K_N d_N)
$$

where

$$
\chi (z) = \psi(z/2 + 1/2) - \psi(1/2),
$$

and

$$
\psi(z) = \Gamma^\prime(z)/\Gamma(z).
$$

(28)

$\psi(z)$ is the digamma function. The combined deGennes - Guyon - Werthamer theory agrees quite well with the existing $T_C$ data and gives a quantitative picture of the spatial dependence of the pair potential in the proximity effect. A more complete discussion of these theories and comparison with experimental data is given by Clarke (28).
Critical Currents

For many practical applications of superconductivity it is desirable to put very large currents through a superconductor and still retain the $\rho = 0$ behavior. Materials such as NbTi and Nb$_3$Sn, which are widely used for commercial application, are Type II materials in which the onset of losses is governed by the pinning of vortices. It is generally thought that grain boundary pinning is the dominant mechanism in these materials but the values of critical current, $I_c$, are always found to be much lower than predicted from GL considerations (22). In this work we would like to study the strength of pinning at superconductor-normal metal boundaries.

Ideally the critical current, $I_c$, is defined as the current above which there is energy loss in the electrical transport of current. Of particular importance is the critical current density, $J_c$, which puts limits on the commercial applications and economies of superconductors. The theoretical existence of an upper limit to the current density, $J_{cpb}$, can be shown (22) to be on the order of $10^7$ A/cm$^2$ for a very thin film using the GL theory. For a current density above $J_{cpb}$, there is no solution to the superconducting wave function, except the trivial solution of zero, which is the normal state solution. This limit is,

$$J_{cpb} = \frac{4e\psi_0^2}{3\sqrt{3}} \frac{n_s}{m \xi(T)} \approx \frac{en_S \Delta_0(T)}{mv_F}$$ (29)

where $\psi_0$ is the amplitude of the wave function and $\Delta_0(T)$ is the pair potential in zero field and zero current, $n_S$ is the superconducting electron pair density and $e/m$ is the charge over mass of an electron.
This critical current density is referred to as the pair breaking current density. It can also be shown that the maximum current density associated with the shielding currents of the Meissner state for type I superconductors is on the order of this $J_{cpb}$. For type II materials, the maximum field that the superconductor is in the Meissner state is $H_{cl}$, which is lower than $H_C \sim H_C/\kappa).$ Therefore, $J$ does not get as large as $J_{cpb}$ before the magnetic flux enters the sample. This $J_{cpb}$ is only achieved with transport currents for very thin samples which exclude magnetic flux from the interior of the sample through surface pinning. Type I superconductors have limited application because of their low critical fields; therefore, most of the interest in in type II materials which have high $H_{c2}$ values.

The theory of critical currents is not well-developed at this time, because the problem becomes very complex when vortices are allowed within the sample. An in depth treatment of this subject is beyond the scope of this work and can be found elsewhere (29) but a brief description of the subject is appropriate here. When a transport current is put through a superconductor, the magnetic field will enter in the form of isolated vortices once $H_{cl}$ and the surface free energy barrier (22) is overcome. If these vortices were free to move within the superconductor under the influence of the Lorentz force the superconductor would not be lossless. Thus, $J_C$ would be limited by the flux entry.

The central concept of the theory of critical currents is force balance in the mixed state. Anderson (30) and Gorter (31, 32) gave the first explanation of very high $J_C$ in $\text{Nb}_3\text{Sn}$ (33) by suggesting that the $I_C$
was reached when the Lorentz force on the vortices balanced by vortex pinning forces due to inhomogeneities within the superconductor. They assumed that the Lorentz force per unit length, $f_L$, on each vortex would be,

$$f_L = \vec{J} \times \phi_0$$  \hspace{1cm} (30)$$

where $\vec{J}$ is the local mean current density and $\phi_0$ is the quantized fluxon. This assumption was later verified by deriving the driving force rigorously using a thermodynamic approach (34, 35). This expression, however, can not be derived by simply averaging the microscopic Lorentz force on the super-electrons that form the vortex. The interaction of a single vortex with an inhomogeneity can, in most cases, be calculated. A simple summation, however, over all of the pinning centers does not give the correct total pinning force. The summation of these single interaction has to take into account the elastic interaction of the vortex lattice with the pinning center array. The mechanism of flux flow is thermally activated motion of the flux line lattice, aided by the Lorentz force, over the energy barriers arising from the pinning effect of the inhomogeneities. These pinning centers can be grain boundaries, precipitates, strains, dislocations and other lattice defects or boundaries between two materials with different superconducting properties. These interactions are in general temperature dependent, because the energy barrier and the size of the vortex are temperature dependent. Reference 30 presents models of these pinning interactions and summation schemes.
The critical state model or Bean-London model (36, 37, 38) is a useful macroscopic model of the critical state equation for the local equilibrium of vortices in terms of a local average pinning force. This pinning force can have any value up to a maximum in any direction, thus magnetic hysteresis is important. This leads to a maximum $J$, or flux density gradient, given by the critical state equation,

$$\mathbf{B} \times (\nabla \times \mathbf{A}) = \mathbf{B} \times \mathbf{J}_c = P_V(B),$$

(31)

where $B$ and $H$ are local values and $P_V(B)$ is the maximum of the average pinning force per unit volume. This model assumes that when the current or field is changed, shielding currents are induced on the surface of the specimen up to a maximum density, $J_c$. When $J_c$ is reached, the current density remains constant, and flux penetrates deeper into the material, where more shielding currents are induced. The local value of $J_c$ may depend upon the local microstructure and flux density. This will give a critical flux profile for a specimen with a transport current, which advances toward the center. When the flux profiles meet in the center of the specimen, annihilation of the opposite sense vortices will occur and a steady state flow of vortices into the sample will ensue. The rate of vortex motion and thus the voltage drop will depend upon the viscous force on the flux lattice. The resulting resistivity is referred to as the flux flow resistivity. As a practical matter the experimental measurement of $I_c$ is limited by the minimum voltage that the apparatus can defect, but the voltage rises rapidly with currents above the actual
critical current and the application of the critical state model is very insensitive to the voltage criterion (29). A typical voltage criterion is $10^{-5}$ to $10^{-7}$ volts which corresponds to a flow of about $10^9$ vortices per second between the contacts.

An analytic solution of the critical state equation is possible for certain geometries with some approximations (39). In the case of zero field $I_C$ and if $\mu_0 H = B$, the critical state equation for a circular wire is,

$$
\frac{d B}{d r} + \frac{B}{r} = \frac{\mu_0 P_v(B)}{B},
$$

(32)

If $\mu_0 P_v(B) = \alpha_2$, a constant and the boundary condition at the surface is the flux density is in equilibrium with the external field, $I_C$ is given by,

$$
I_C = \frac{2\pi a^{3/2}}{\mu_0} \left( \frac{2}{3} \alpha_2 \right)^{1/2},
$$

(33)

where $a$ is the radius of the wire. This can be algebraically manipulated to give,

$$
J_C d^{1/2} = \frac{2\sqrt{2}}{\mu_0} \left( \frac{2}{3} \alpha_2 \right)^{1/2},
$$

(34)

where $d = 2a$. The condition that $\alpha_2 = \text{constant}$ is equivalent to $J_C$ proportional to the inverse of $B$. Equation 34 shows $J_C$ is only dependent
upon the wire diameter, \( d \), within the assumption of \( \alpha_2 = \text{constant} \). Other analytic solutions of the critical state equation have been solved using 
\[ J_c = \beta_2 B^n \] 
(40), where \( \beta_2 \) and \( n \) are constants. These solutions give \( J_c \) as a function of the wire diameter also.

**Directional Solidification of Eutectics**

To measure pinning force associated with superconductor-normal metal boundaries, it was decided to use bulk samples of eutectic alloys which grow with a rod structure of superconductor in a normal matrix. The phase diagram of Thorium-Niobium (Th-Nb) shown on Fig. 1 (41) is typical of a class of eutectic alloys. In this alloy, a Th-rich phase and a Nb-rich phase solidify simultaneously from the liquid giving a two phase structure which can take on a variety of morphologies. If the material is quenched, typically one phase forms very small grains in the matrix of the second phase and a random mixture results. If, however, the heat flow is carefully controlled, the phases can be made to grow in large grain regular patterns of rods or platelet structures. The dominant factors determining the morphology are the surface free-energy of the alloy and the relative amounts of the two constituents present. A full discussion of the kinetics of the formation of these eutectic structures may be found elsewhere (42), but a discussion of a few of the parameters that govern this growth and the particulars of Th-Nb will be given here.

Carlson et al. (43) determined the phase diagram for Th-Nb, which shows a eutectic composition of about 8 weight percent Nb and a eutectic temperature of 1435°C. The solid solubility also was determined to be about 0.1 weight percent Nb in Th and less than 0.1 weight percent Th in Nb.
A very common way to produce a composite structure with a specific geometric pattern throughout the sample is directional solidification, in which the material is solidified in such a way that the solid-liquid interface has a unidirectional motion. When the solid-liquid interface moves slowly in one direction, in a steep temperature gradient, the resulting morphology for Th-Nb is a regular rod eutectic structure (37) with two phases, a Nb rich phase and a Thorium rich phase. The Nb rich phase locally forms an array of rods with a nearly regular hexagonal pattern having the axis of these rods aligned with the solidification direction. The matrix between this array is the Th rich phase. The rod spacing, \( \lambda_e \), and the diameter, \( d_f \), are determined by the diffusion rate in the liquid and the rate at which the solid-liquid interface moves, \( R_i \). \( \lambda_e \) is inversely proportional to the square root of \( R_i \) and if the rod structure were a perfect hexagonal array, the relationship between \( d_f \) and \( \lambda_e \) would be,

\[
\lambda_e = 3.1 \ d_f
\]  

(35)

for Th-Nb. Typical values of \( d_f \) are 518 nm for \( R_i = 10 \ \mu m/s \) and 116 nm for \( R_i = 200 \ \mu m/s \).

The particular advantage of the Th-Nb eutectic was that the structure could be mechanical reduced in size by standard wire drawing techniques. This allows the possibility of studying the properties of the model composite as the dimensions of the components are reduced. Of particular
concern is reducing the physical dimensions of the superconducting component, Nb, to dimensions comparable to the coherence length of the superconductor. Full details of sample growth are given in Pedersen's (44) Master of Science thesis.
EXPERIMENTAL APPARATUS AND MEASUREMENT METHODS

Sample Preparation

The Th-Nb eutectic samples were prepared by Pedersen (44) in the form a 0.32 or 0.48 cm diameter wire at least 25 cm long. This material and a zirconium getter button were placed on a water cooled copper crucible in a conventional nonconsumable arc melting apparatus. The system was pumped, flushed with argon and back-filled to slightly more than an atmosphere of pressure with argon gas. A high frequency arc was used to establish an ionized path for the direct current arc, so that the transfer electrode would not have to touch the sample to start the direct current arc.

First, the zirconium was melted in one of the depressions of the copper crucible to getter the argon atmosphere and remove traces of oxygen and nitrogen. Then the sample material components were melted together in a long finger shaped depression in the copper crucible. The solidified sample was then flipped out of this depression with the flexible mount tungsten electrode and remelted without opening the system to air. Remelting insured good mixing of the sample. The sample was then swaged to form a cylinder with the desired diameter for directional solidification of either 0.32 or 0.48 cm. A Material Research Corporation zone refiner (EBZ-93) was used to directionally solidify the eutectic alloy. In this work the directional solidification process will henceforth be called zoning. A cut with edges parallel to the wire diameter was made close to one end of the sample to facilitate mounting.
in the apparatus. The two pieces of the wire were then mounted in the zone refiner by clamping each end of the sample so as to leave a small gap, less than 0.08 cm, between the parallel cut edges. Mounting the wire in two pieces insures that the mount will not put any stress on the sample and the gap allows for thermal expansion of the material when a section of it is heated to its melting temperature. Both ends of the sample were connected to the positive electrode of the zone refiner through these two clamps. A circular negative electrode filament was concentric around the axis of the wire and could be moved at a controlled rate along the length of the wire, at rates ranging from 1 µm/s to 200 µm/s. Electron beam heating was used to melt the sample and with the adjustment of the accelerating voltage, the emission current and thus the power to the sample could be controlled. First, the gap in the wire was melted together and the power adjusted to keep a molten zone as the filament was moved along the wire. The resulting solidification of the eutectic alloy, out of the moving molten zone, gave a directionally solidified regular rod eutectic structure as described earlier.

A factor which tended to cause irregular growth of the eutectic structure was poor temperature control of the molten zone due to a lack of a sensitive feedback system. Because there are small changes in the thermal heat leak and changes in alloy composition, power adjustments were required. Difficulty in controlling these factors change the length of the molten zone and this disturbs the dynamics which locally gives a different solidification rate and irregular rod structure results. In picking lengths of the zoned wire for samples, these lengths were avoided.
Critical current samples were selected from the best sections of the zoned wire, 0.32 cm in diameter and drawn, with standard drawing dies. This was the smallest diameter wire that could be zoned by this method without having a molten zone that would be too long to be self-supporting in the gravity field (45, 46). Small diameter wires were needed for the critical current measurement to avoid the current transfer length problems and to keep current values within the current supply limit, 600 amperes.

A swager was used to point the wire when drawing diameters larger than 0.06 cm and a 6% (volume) perchloric acid - methyl alcohol electrolytic polishing method (47) was used for pointing the smaller diameters. Pointed sections of the wire were not used for samples since the swaging action greatly distorts the regular eutectic structure. A dry graphite lubricant (Crown 8078, Crown Industrial Products Co.) was found to work satisfactorily as a drawing lubricant for this alloy but this lubricant had one disadvantage. It would work into the surface of the alloy and could not be removed with chemicals or electrolytic polishing. The graphite embedded surface was abrasively removed in a special materials handling room's exhaust hood with grid 600A silicon carbide abrasive paper or crocus cloth (3M products).

To anneal the samples the graphite was removed, and the samples electropolished and placed in tantalum tubes. The tantalum tubes and a type K thermocouple were mounted on a stainless steel rod which was inserted into an electric furnace (Multiple Unit, MK-3024). A high vacuum pumping unit (National Research Corp.) was connected to the end of the quartz tube. The system was outgassed at a low temperature, then taken
to the annealing temperature where it was held by a temperature controller (PSCR-27-208, West Instrument Corporation) which sensed the temperature of the furnace with a thermocouple. The temperature of the sample could be monitored using the thermocouple mounted with the sample. Intermediate anneals were generally not necessary for drawing the wires from the zoned diameter to the smallest wire diameter of 0.013 cm. A sample with a zoning rate of 45 μm/s gave some trouble in drawing due to a combination of bad drawing dies and more oxygen impurity in the sample making intermediate anneals necessary. Annealing the wire at the final sample diameter was found to be necessary for the critical current measurement.

Critical Current and Resistivity Apparatus

A block diagram of the experimental apparatus in the critical current, $I_c$, measurement configuration is given in Fig. 2. The critical current was measured using a four probe method in the helium bath with the sample located between the poles of a 1.5 T (Systron - Donner Alpha) magnet with flat 30 cm pole faces. In this arrangement, $I_c$ could be measured in the temperature range of 4.2 to 1.5 K. The lower temperature was limited by the conductance of the pumping line and the pumping speed of a large roughing pump balanced against the boil-off rate of the dewar and the 500 ampere vapor cooled leads (American Magnetics) that were used to conduct the current into the dewar. The pressure of the helium bath was controlled by a manostat in the pumping line and the vapor pressure was measured with a 0-800 mm Hg differential gauge and a 0-50 mm Hg absolute pressure gauge (both gauges were Wallace-Tiernan). The resulting temperature control and measurement accuracy was about 0.01 K.
The magnetic field was measured with a Hall probe which was calibrated against a rotating coil gaussmeter (Rawson, type 720) which was calibrated using the nuclear magnetic resonance of the proton (48). The Hall probe current was adjusted to give a 50 mV/T hall voltage versus magnetic field relation. This relation was linear over the whole field range within the measuring accuracy of 0.5% and used to monitor the magnetic field at the center of the pole faces. The voltage connections to the \( I_c \) sample were made within a 10 cm diameter circle centered on the pole faces of the magnet where the field profile was uniform and constant to 1%. A power supply was programmed for constant Hall probe current to a stability of 0.1%. This current could be monitored with a digital voltmeter measuring the voltage across a 1 \( \Omega \) shunt in series with the Hall probe current. The magnet power supply was controlled by a ramp generator which allowed the magnetic field to be increased, decreased or held at a field constant to 0.5%.

Sample currents above 5 amperes were supplied by a 600 ampere power supply or by a series pass transistor battery supply. The circuit diagram of the series pass transistor battery power supply is given on Fig. 3. Approximately 9 m of welding cable was used to connect the high current supply to a 0.1 m\( \Omega \) shunt and the vapor cooled leads on the top of the cryostat. The resistance of the welding cable was about 2.2 m\( \Omega \) and the total resistance of the current path in the dewar with a superconducting sample was about 0.3 m\( \Omega \). For the lower sample current ranges a 5A Kepco and the power output (0 - 0.3A) and low current output (0 - 5mA) of the ramp generator were used in order to have a reasonably small zero offset.
current and current control. A 0.1 Ω standard resistor was used as a shunt for the 0 - 5A and 0 - 0.3A ranges and a 10 Ω standard resistor was used for the lowest sample currents. The ramp generator mentioned above was used to ramp the sample current with time, for the other power supplies in a voltage control mode. This is a natural means to protect the sample when $I_c$ is exceeded, since the resistance of the sample in the normal state adds enough resistance, 1 to 100 mΩ, to the current circuit to drop the current by a considerable amount. Another sample protection mechanism was built into the ramp generator. This used the retransmit pot on the sample voltage sensing axis of the X-Y recorder to shut the ramping voltage to zero when the recorder reaches a preset level.

A nanovoltmeter was used to measure the sample voltage with the meter output, filtered with a low pass tunable filter (Frequency Devices, 730BT-1) and input to the Y-axis of the X-Y recorder. The filtering of the nanovoltmeter output was necessary because the meter was operated at a rather high sensitivity, typically 10 µV, and the small third harmonic of the 60 Hz noise of the current supplies and magnet caused a low frequency beating with the second harmonic of the 94 Hz mechanical chopper of the nanovoltmeter. The amplitude of the resulting 8 Hz signal was small enough, typically less than a few percent, that the amplifier was not saturated and good consistent reading could be made between ranges. However, filtering the output of the nanovoltmeter gave a better trace on the X-Y recorder and caused a lot less wear on the balance potentiometer. The voltage across the appropriate shunt resistor was the input to the X-axis of the recorder. In this configuration, traces of sample voltage as
a function of current could be made of fixed temperature and magnetic field.

Figure 4 is a block diagram of the experimental apparatus in the configuration for measuring the normal state resistivity of the sample. There are only a few changes from the \( I_c \) configuration. The sample current was set at a constant value from a 0 - 50 mA constant current supply with a 10 \( \Omega \) shunt or from a 0 - 2A or a 0 - 50A power supplies with 0.1 \( \Omega \) shunt. The voltage across the shunt was measured with a digital voltmeter. Input for the X-axis of the recorder was the Hall probe voltage. By ramping the magnetic field up, a trace of sample voltage versus magnetic field could be made with constant current and temperature. A digital voltmeter was connected to the Y-axis input to get a more accurate sample voltage reading.

Critical Current and Resistivity Measurement

A major problem in the \( I_c \) measurement was the development of low resistance ohmic contacts to the sample. Thorium has a very stable oxide which is not easily removed by conventional chemical means. A wide range of soldering techniques and fluxes were attempted but this approach did not yield reliable results. Pressing a clean sample between clean indium contacts, on the other hand, gave reasonably low resistance junctions and reproducible electrical contact. Typically 50 to 100 \( \mu \Omega \) total contact resistance was found for joints on a 0.025 cm diameter wire and 10 to 40 \( \mu \Omega \) for a 0.05 cm diameter sample. This pressing technique was used throughout this work.
In this experiment, the critical current samples were approximately 32 cm long sections cut from the drawn wire. After the graphite lubricant was removed from the sample, a 9 cm length on each end was lightly electropolished to give a very clean surface for making current contact.

Figure 5 is a sketch of the sample holder. Current leads were soldered to each end of the sample holder, with voltage leads connected to the sample in the center section of the holder. The ends of the sample holder consisted of a 13 strand multifilamentary Cu-NbTi cable (Magnetic Corporation of America) soldered with high temperature solder (Pb-2.5 wt% Ag) into a grooved copper bus bar (0.63 cm x 0.95 cm x 10 cm) with a thin copper plate on top to totally enclose the cable. A layer of pure indium was soldered to the top of this copper plate and served as half of the indium soldered to one side of it was the pressure plate for the other half of the indium clamp. A "U-shaped" brass clamp with six #8-32 brass screws fits around each end of the sample holder, with the screws forcing the pressure plate down into the ends of the sample and bus bar.

The voltage connections to the sample were made in the center section of the sample holder. This section has a polyethylene tube fastened with GE7031 varnish (General Electric) to a split brass bar. A thin bakelite spacer electrically isolated the two ends and a bakelite plate (0.63 cm x 1.9 cm x 10 cm) held the two ends of the sample holder together. The size of the tubing was selected to fit closely over the sample. The top half of the tubing was cut off for short lengths in several sections to allow the liquid helium to flow into the tubing and for sample voltage connections to be made. Two small brass bars with indium soldered to one
side were screwed into the bakelite support of the sample holder, making the indium pressure voltage connections to the sample.

The sample holder was designed to electrically isolate the center section of the sample and yet give a relatively strain free support over the whole length of the sample. Sources of strain were the differential thermal contraction between the sample and holder and the unrestricted motion of the sample under the Lorentz force. The polyethylene tube restricts the motion of the sample and electrically isolates the sample. The magnetic field was directed such that the Lorentz force was into the sample holder, thus the sample holder balanced this force and the sample was not strained. The differential thermal contraction between the sample and brass support was small enough that the slack and limited freedom of motion would keep the sample in a relatively strain free environment. This sample holder assembly was mounted on the bottom of the critical current cryostat which consisted of vapor cooled current leads and voltage wires that fit into the system described earlier.

The $I_c$ measurements were made by ramping the sample current and tracing the sample voltage as a function of sample current on a X-Y recorder. These traces were made at fixed bath temperature and constant magnetic field. Voltage traces were made at a sensitivity of 10 µV full scale on the Y-axis, resulting in a precision of ± 0.05 µV. The characteristic shape of the voltage-current traces is given in Fig. 6. The normal resistance line would have a voltage of 100 µV at 0.024 A, which corresponds to a resistivity of $0.51 \times 10^{-6}$ Ω cm. The sample voltage was constant, with a peak-to-peak noise was less than 0.05 µV, until a
certain current was reached, then the voltage would rise sharply, typically 10 μV for a 5% change in current. The critical current was defined as the current at which the effective resistivity of the sample was $1 \times 10^{-12}$ Ωcm or the sample voltage was 0.1 μV, which ever was the higher voltage. For all samples the resistivity criterion was used for the low magnetic field data. The field at which the crossover occurred depended on the temperature and the sample, but typically it was around 0.1 T.

For some of the samples the voltage-current traces were reversible even up to relatively large voltages, 100 μV, and did not depend on the current ramp rate. This was important because contact heating could cause an apparent lower $I_c$ through the heating, raising the temperature of a section of the sample to a level that the critical current at this higher temperature was reached. A few samples would quench from the superconducting state to the normal state from a very low or undetectable voltage. This would indicate that a section of the sample other than that between the voltage contacts went normal and caused a thermal runaway, quenching the entire sample. There are two possible causes for the sample going normal. The first is that locally there is enough heat generated by the flux flow to cause a thermal runaway and the other is the contact heating is enough to cause the sample of the contact to initiate a thermal runaway. Power calculations of the contact heating and flux flow could be made for each magnetic field. This was used to determine if contact heating was a problem. All of the samples that exhibited contact heating problems, exhibited this only for the lower magnetic fields. Samples not having contact heating problems would have
relatively constant flux flow power, at thermal quench, for all magnetic fields.

For samples with diameter larger than 0.1 cm, current transfer in the multifilamentary superconductor (49) was a problem in attempts to measure the critical current of the samples with diameters larger than 0.1 cm. This was due to the flux flow voltage profile of the outer filaments of a multifilamentary superconductor necessary in order for the current to be transferred through the normal matrix to the inner filaments of the composite conductor. Ekin et al. (50) experimentally evaluated the resulting current-transfer effect and lengths. The effect was an apparent sample resistivity which depends on the resistivity of the matrix and the distance between the current and voltage contacts, which scales with the wire diameter. A typical value for the effective resistivity was $1 \times 10^{-12} \ \Omega \text{cm}$ for a separation distance between current and voltage contacts of 60 times the wire diameter for a matrix resistivity of $2 \times 10^{-6} \ \Omega \text{cm}$. My observation was the same effect with an effective resistivity close to the values calculated in reference 49. All of the samples reported in this work had effective resistivities in the superconducting state of less than $1 \times 10^{-13} \ \Omega \text{cm}$.

An upper limit of the effective resistivity, $\rho_{\text{eff}}$, of the sample in the superconducting state was determined for zero applied magnetic field. As mentioned earlier the sample voltage was constant until the critical current was reached. This constant, typically less than 0.2 $\mu$V, was not zero and was proportional to the current ramp rate and would reverse if the current ramp direction was reversed. This suggests that this voltage
offset was due to the time-varying current caused on electromotive force in the sample voltage loop according to Faraday's law of induction. This effect was minimized by reducing the area of the sample voltage loop, but the offset was always detectable. If the current ramp rate was not linear with time, as was the case for the battery power supply, the trace would have a slope. By making voltage current traces at a slow ramp rate up and at the same rate down or by plotting points with the current slowly drifting, an upper limit of $\rho_{\text{eff}}$ was measured to be approximately $2 \times 10^{-14}$ $\Omega$cm for all of the samples to be measured.

The Nb filaments in the directionally solidified composite were believed to be relatively continuous. A measure of this was the remnant resistivity of the composite in the superconducting state. As Davidson et al. (51) developed a relationship of the remnant resistivity, $\rho_{\text{rem}}$, of a distributed parallel array of superconducting filaments of length $L$, diameter $d$, and separation $s$, in a normal matrix. This relationship was,

$$\rho_{\text{rem}} = \frac{\rho_0}{f_s} \left( \frac{d^2}{L^2} \right) \ln(s/d),$$  \hspace{1cm} (36)

where $\rho_0$ is the resistivity of the matrix and $f_s$ is the volume fraction of the material that is superconducting. Using the measured upper limit on the effective resistivity in the superconducting state for Th-Nb of $2 \times 10^{-14}$ $\Omega$cm and ignoring the proximity effect, within the approximations of this relationship the average length of the filaments would be greater than $2.4 \times 10^4$ d.
The normal state resistivity was measured by plotting the sample voltage as a function of the applied magnetic field, with the sample current held constant. The output of the nanovoltmeter across the sample was input to the Y-axis, with the Hall voltage on the X-axis of the X-Y recorder. A digital voltmeter was connected to the Y-axis input to get a more accurate sample voltage reading. This voltage was read at every 0.1 T interval and the resulting voltage was approximately linear with magnetic field when the sample was in the normal state. The slope of this linear relationship was due to sample magnetoresistance and had a value of approximately 0.02% $\rho_N^p/T$ for all samples. The normal state resistivity, $\rho_N$, was taken to be the extrapolated zero field value.

Transition Temperature Apparatus

The apparatus used to measure the transition temperature was a helium dewar with a mutual inductance bridge and associated electronics. A block diagram of the electronics is given on Fig. 7. The mutual inductance bridge was balanced without a sample. With the sample in one of the matched secondary coils the off-balance signal goes to a dual phase lock-in detector and the inductance phase was input to the Y-axis of a X-Y recorder. The input to the X-axis was the voltage across a germanium resistance thermometer, with a constant thermometer current.

The helium dewar cryostat consisted of a vacuum can with mutual inductance coils, heater and thermometer around an externally accessible sample space. This sample space would be pressurized with helium gas and the pre-cooled sample on a probe, would be inserted in one of matched secondary coils. During the sample space pressurization, some helium
will condense and when this space is pumped the sample temperature would be reduced to about 1.3 K. After all of the liquid helium in the sample space was pumped away, the pressure was reduced to about 0.01 Torr of helium exchange gas which keeps the sample and thermometer at about the same temperature. The sample space heater, with ramp control, was used to raise the temperature above the helium bath temperature.

Transition Temperature Measurement

The transition temperature was determined from the recorder trace of the off-balance of the mutual induction bridge as a function of sample temperature. The magnitude of the change in the off-balance is proportional to the volume that the oscillating magnetic field of the sample coils is excluded from. By measuring a superconductor of known volume, the off-balance signal was calibrated per unit volume of superconductor. This depends upon the shape and size of the sample because of the finite length of the secondary coils and the demagnetization factor of the sample. For similar shaped and sized samples, however, this calibration was useful. The accepted definition of the transition temperature from this measurement is the temperature that the magnetic field is excluded from half of the volume (52).

The temperature trace of the mutual inductance bridge off-balance was made by first pumping on the liquid helium in the sample space, then warming the sample above its transition temperature. By adjusting the heater current ramp rate, the rate of temperature increase could be controlled. There was a temperature difference between the thermometer and the sample, but this was accounted for by cycling the temperature
down through the transition and taking an average of the curves taken in each direction. With small rates of change in temperature, the temperature shift between these two curves would be on the order of 0.02 K. The off-balance of the background was constant on the scale of these samples, except for a small transition around 7.2 K. This was thought to be due to some solder in the area of the mutual inductance coils and could be subtracted from those transitions that would span this temperature.

Heat Capacity Apparatus

The same cryostat and pumping systems were used for both the thermometer calibration and heat capacity measurement. Only the thermometers, sample, sample holder and electronics needed to be changed for these two experiments. The cryostat was a standard helium 3 apparatus similar to that described in reference 53, so a brief description of the cryostat will suffice here. The body of the cryostat was made up of several thin wall stainless steel pumping lines which connected the vacuum can on one end to the pumping line manifolds on the top plate of the cryostat. The cryostat was inserted into a pair of concentric glass dewars, a liquid nitrogen outer dewar and a liquid helium inner one. The isolation vacuum of the vacuum can was pumped by a diffusion pump with a small fore pump and the pressure was read using a cold cathode ionization gauge. A $^4$He pot and a $^3$He pot are inside the vacuum can, supported by their respective stainless steel pumping lines. $^4$He could be condensed in the $^3$He pot by pressurizing it with $^4$He gas and causing condensed liquid to reflux between the pumping line in contact with the $^4$He bath and the $^4$He pot. The
The 4He pot, located above the 3He pot, was sufficiently decoupled from the helium bath surrounding the vacuum can by the length of the thin wall stainless steel pumping line to be pumped to less than 1 K by a large rough pump. The thin wall stainless steel 3He pumping line was thermally anchored to the top of the 4He pot and extended below the bottom of the 4He pot. The thermal anchor at the 4He pot allowed the 3He to condense and reflux between this point and the 3He pot, thus condensing in the 3He pot. The length of thin wall stainless steel pumping line decoupled the 3He and 4He pots enough so that pumping on the condensed 3He with a diffusion pump backed with a small fore pump allowed a temperature of 0.29 K to be reached. Typically, the 3He pot could be operated from 0.29 to 1 K for more than 8 hours and left below 1 K overnight without recondensing the 3He. An experimental support frame and electronic terminal strip was fastened to the bottom of the 3He pot with a cylindrical copper can surrounding it to provide an isothermal shield for the sample area. Electronic connections were made at an equipment rack and were coupled to an epoxy (Emerson & Cuming, Inc., Stycast 2850 GT) vacuum feed through the cryostat top plate and the top of the vacuum can. The cryostat wires were #30 AWG manganin or copper wires in the helium bath and #30 or #36 AWG manganin wires in the vacuum can depending upon the power level required. These wires were thermally anchored in the helium bath at a terminal strip. In the vacuum can they were anchored with GE7031 varnish to the 4He pot and 3He pot before they were connected to the sample terminal strip inside the isothermal shield.
In the thermometer calibration experiment four germanium resistance thermometers, GRT, (Honeywell: GRT 99, GRT 665, and Cryo Cal, Inc.: GRT 267, GRT 4645) were intercalibrated in the temperature range of 0.29 to 77 K in zero applied magnetic field and calibrated in the range of 0.4 to 10.4 K with magnetic fields up to 2 T. The temperature in a magnetic field was held constant by monitoring the relatively field independent (54) value of a capacitance thermometer, CT, (Lake Shore Cryotronics, Inc., CT 245). Typical field dependence for this type of CT was reported in reference 54, for 1.5 < T < 4.2. The change in capacitance was ±1 mK, in magnetic fields up to 14 T. A block diagram of the electronics used in the intercalibration experiment is given on Fig. 8. The four GRT's and the CT were mounted in a copper block and suspended in an experiment support frame on the cryostat described earlier. A 10 cm length of #20 copper wire thermally connected the copper block to the bottom of the $^3$He pot. A constant direct current could be selectively put through each germanium thermometer, one at a time. Another switch was used to select the GRT voltage or 100 Ω standard shunt resistor voltage which would be monitored. The 1000 Ω standard shunt resistor voltage in the thermometer current circuit, with the above 100 Ω, was connected to the auxiliary position of a potentiometer. The selected voltage was connected to the input of the potentiometer and the off-balance was fed to a null detector. With these connections both the thermometer current and voltage were potentiometric measurements. The temperature of the $^3$He pot was sensed with a carbon resistance thermometer, CRT, (Speer Carbon Co., 470 Ω, 1/2 watt) which was fastened to the $^3$He pot with GE7031 varnish. The
resistance of the CRT was sensed by an a.c. Wheatstone bridge in a standard three wire configuration (53). A temperature controlling heater power supply for the $^3$He heater, operating with the bridge off-balance, was used to control the $^3$He pot temperature. The resistive phase output of the lock-in detector was connected to channel 2 of a strip chart recorder. A capacitance bridge was used to measure the capacitance of the CT and the quadrature phase output of the lock-in detector was connected to channel 1 of the strip chart recorder. The CT was approximately linear with temperature below 20 K with a sensitivity of 200 to 250 pf/K. The least count of the capacitance bridge was 0.1 pf, but the lock-in output gave a sensitivity of about $\pm$ 0.1 mK. A 2 T superconducting magnet was mounted around the vacuum can with the sample area in the $\pm$ 1% uniformity field region. The magnet current could be set by monitoring the voltage across a shunt resistor and locked into a persistent mode by the magnet controller power supply.

The heat capacity apparatus was designed to operate from 0.48 to 15 K, in magnetic fields of zero to 1 T. The basic apparatus was similar to the thermometer calibration apparatus except for changes in sample, sample holder and electronics. The heat capacity measurements were made with the usual pulse heating method. The only additional complications were the correction for the GRT calibration in a magnetic field, compensation for the rather large radioactive self-heating of the thorium in the sample ($\sim$50 nW) and the rather small sample mass. The magnetic field calibration of the GRT, as described in a later section, was used for the high magnetic field heat capacity data and was checked in both the sample
and addenda data runs using the CT mounted on the isothermal shield. In
order to compensate for the large radioactive self-heating power of the
sample, a heat leak wire (~38 cm of #44 copper wire, 0.005 cm diameter)
was connected between the sample holder and thermal shield. The size and
length of this copper wire was calculated assuming a tolerable tempera­
ture gradient between the shield and the sample of 0.1 K at the lowest
temperature and the experimentally measured radioactive self-heating
power of Th (55) which was 12 nW/gm. The resulting temperature gradient
was about 0.15 K at the lowest temperature and the radioactive self-
heating power of this sample was estimated at 50 nW compared to the 30 nW
calculated using the result of reference 55.

A photograph of the heat capacity sample holder and experiment
support frame is shown on Fig. 9. A sketch of the sample holder is
shown on Fig. 10. A thin copper sheet (0.023 cm thick) was formed and
silver soldered together with a 0.32 cm diameter by 1.6 cm long cylindri-
cally shaped space for GRT 4645 and a 0.48 cm diameter by 2.2 cm long
cylindrical shaped space for the Th-Nb heat capacity sample. This copper
sheet acts as the support for the thermometer and sample as well as a
high thermal conductivity medium. Copper wires were put through small
holes on the ends of the cylindrical shaped regions to hold the compo-
nents, which were thermally anchored with N-grease (Apiezon), in place and
to serve as tie points for the sewing thread used to mount the assembly in
the supporting frame of the $^3$He stage of the cryostat. Thermal anchors
for the thermometer, heater and heat leak wire were made with seven
3.2 cm lengths of #30 copper wire fastened with GE7031 varnish to the
copper holder. The thermometer thermal anchors ensure that the thermometer would be at the temperature of the sample holder (56). The four thermometer leads were soldered with low melting point solder (40% Cd - 60% Bi eutectic alloy) to the ends of four thermal anchors and four, 9 cm lengths of 0.005 cm diameter Pt-8% W wire were soldered with the same solder to the other ends of these four thermal anchor wires. These Pt-8% W wires were the low thermal conductivity (57), electrical connections to the terminal strip on the support frame of the 3He stage of the cryostat. The copper heat leak wire was soldered to one end of a thermal anchor and the other end of the heat leak wire was bolted to the support frame of the 3He stage. The sample heater consisted of a 80 cm length of 0.00254 cm diameter Pt-8% W wire, which was bifilarly and distributively wound around and fastened with GE7031 varnish to the sample holder. The low melting point solder was used to solder the ends of the heater to two thermal anchors. Each heater current lead soldered to the other end of the thermal anchor had a 1.3 cm length of 0.005 cm diameter Pt-8% W wire in series with a 7 cm length of #36 copper wire (diameter 0.0127 cm) which had its far end soldered to the terminal strip on the support frame of the 3He stage. One of the heater voltage leads (9 cm length of 0.005 cm diameter Pt-8% W) was soldered with the current lead at the thermal anchor point and the other was soldered at the terminal strip mentioned above.

The heater design was crucial to the accuracy of the heat capacity measurement, therefore the factors considered in the design will be mentioned here. The first consideration was the working range and re-
solution of the constant current supply and voltmeter available for use in the heater circuit. A high stability (1 part in $10^4$) constant current supply in the range of a few microamps to a few milliamps and a 5 1/2 digit, digital voltmeter with a least count of 1 microvolt were used. With this choice, a heater resistance of approximately 1000 $\Omega$, which would give an experimental precision of the order of 0.01%, was used. Another factor was making the current leads long enough to give a thermal impedance which was much greater than the heat leak impedance. Some of the electrical power generated during a heat pulse in the current leads will flow into the sample holder and the rest, except for the energy needed to warm the lead wires to the new equilibrium temperature, will flow to the terminal strip. If the heat pulse was taken symmetrically around the equilibrium point between the sample and terminal strip, the of heat flowing in each direction should be equal to the first approximation. Therefore, by making the current lead resistance approximately the same for each end of the heater and measuring the voltage from one end of the heater at the sample holder to the other end of the current lead, the heat generated in the leads will be approximately compensated (58). It was still important to make the lead resistance as small a percentage of the total resistance of the heater as possible. The heater resistance was measured as 1032.9 $\Omega$ and each lead resistance was adjusted to be approximately the same, 4.2 $\Omega \pm 3\%$ at room temperature. This makes the total lead resistance about 0.8% of the heater resistance. Using the lead compensation method the accuracy of the power of the heat pulse should be good to better than 0.1%. 
A block diagram of the heat capacity electronics is given in Fig. 11. The shield temperature control and magnet circuits were the same as described earlier in the thermometer calibration experiment. CT 245 was mounted on the isothermal shield and measured with the same electronic as above. GRT 4645 was mounted in the sample holder and used as the heat capacity thermometer. Standard shunt resistors of 100 and 1000 Ω, in series with the thermometer current, were used to set the current, which was stable to 1 part in $10^4$ over a time span of several hours. Potentiometer inputs of shunt voltages and thermometer voltage in the forward and reverse current directions were selected with a switching system in the current supply. This switching system would also change the direction of the potentiometer current when the thermometer current was reversed. This allowed the ground on the low side of the potentiometer detector to stay in the same place relative to the rest of the detector circuit, thus avoiding ground loop problems. The detector output was put through a low pass filter and connected to channel 1 of a strip cart recorder. With the potentiometer calibrated against a standard voltage cell, the potentiometer off-balance on the strip cart recorder was used to measure the thermometer voltage and thus determine the thermometer resistance and from the calibration infer the temperature. As mentioned earlier, the sample heater was wound on the sample holder. The constant current supply for the heater was switched during the heat pulse from a 1000 Ω dummy load to the sample heater and back to the dummy load at the end of the pulse. A digital timer measured the duration of the pulse. A digital voltmeter was used to measure the heater voltage during the pulse and to
measure the heater voltage and current after the pulse so that the heater resistance could be calculated. Another digital voltmeter monitored the dummy load voltage to aid in setting the heater current before a pulse.

The heat capacity controller, shown on Fig. 12, switches the constant current at the beginning of the heat pulse from the dummy load to the sample heater and back to the dummy load at the end of the pulse. The duration of the heat pulse was set with the programmable timer. The programmable timer circuit was provided by the supplier of the chip (Exar Integrated Systems). This gave reproducible time intervals typically to better than 0.05% for consecutive points and 0.1% for points taken over a span of several hours. The programmable timer logic output, buffered and inverted to the appropriate sense, was used to trigger a digital timer and switch the two field effect transistors (FET) switches. One FET switch, in series with the dummy load, had finite resistance (~40 Ω) normally and nearly infinite resistance (>20 MΩ) during the heater pulse. The other FET switch, in series with the heater and heater shunt resistor, had finite resistance (~40 Ω) during the heater pulse and nearly infinite resistance (>20 MΩ) otherwise. The advantages of this controller were: 1) the FET switches gave bounceless current switching, 2) the reproducible time intervals was used to determine if heater switching or timing was erroneous, 3) the preset time interval was used to calculate the heater power to give the temperature change desired, 4) the automatic heater shut-off allowed the operator to concentrate on recording the heater voltage and balancing the potentiometer during the short heater pulses. One problem was discovered with this system and was later shown to be
due to a timer trigger bounce. This happened for less than 2% of the points and was easily detected by the half second delay in re-triggering the timer from the otherwise reproducible to 0.05% pulse duration.

Thermometer Calibration

Each of the four GRT's in this thermometer calibration had a previous calibration as part of some other experiment. The purpose of this calibration was to use these calibrations to calibrate these thermometers over the complete temperature range, 0.29 to 77 K, of the $^3$He cryostat and to extend the calibration to magnetic fields up to 2 Tesla in the temperature range of 0.4 to 10 K. Before the intercalibration, all four thermometers were dipped into a liquid helium dewar at least 12 times and measured with the Cryobridge described in reference 59 to check their reproducibility at 4.18 K. A summary of this dipping data is listed on Table 1. The reproducibility of the thermometers was determined by plotting the thermometer resistance, $R$, as a function of temperature for each dip from room temperature to 4.18 ± 0.02 K. The temperature of each dip was determined by a reproducible calibrated GRT. Ideally the resulting $R(T)$ plot would be linear over this small temperature range, with the range of scatter from this linearity, $\Delta T$, representing the reproducibility. One thermometer, GRT 15519, was found to have an open current lead. Another thermometer, GRT 4644, seemed to change calibration by a definite amount so that the resistance was either 93.8 or 99.9 $\Omega$ at 4.18 K, which corresponds to an apparent change in temperature of ~0.3 K. This thermometer would go back and forth on different dips with no pattern
Table 1. Summary of thermometer dipping data

<table>
<thead>
<tr>
<th>Serial Number</th>
<th>R(\Omega) T=4.18K</th>
<th>Number of dips</th>
<th>ΔT(mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRT 99</td>
<td>8681</td>
<td>20</td>
<td>0.9</td>
</tr>
<tr>
<td>GRT 267</td>
<td>36.6</td>
<td>20</td>
<td>4.5</td>
</tr>
<tr>
<td>GRT 665</td>
<td>66.2</td>
<td>12</td>
<td>0.4</td>
</tr>
<tr>
<td>GRT 1280</td>
<td>23.5</td>
<td>24</td>
<td>10.5</td>
</tr>
<tr>
<td>GRT 4645</td>
<td>93.4</td>
<td>20</td>
<td>0.5</td>
</tr>
<tr>
<td>GRT 15358</td>
<td>619</td>
<td>12</td>
<td>1.6</td>
</tr>
</tbody>
</table>
and it also gave values of 96.9 and 99.5 Ω on some occasions. This emphasizes the value of this dipping step. The range of ΔT was 0.4 mK to 10 mK for the six GRT's dipped.

The GRT 4645 was used as the standard thermometer, ST, over its entire calibration range 0.9 to 77 K for reasons that will be presented in a later section. This thermometer was calibrated and self-heating effects determined earlier by Anderson and Swenson (59). GRT 665 had a low temperature calibration by both Wollan (60) (0.06 to 0.85 K) and Sample (61) (0.14 to 5.4 K). These two calibrations had a rather systematic difference of 2 to 5 mK over their over-lap range. GRT 665, with the calibration from Sample's data, was used as the low temperature ST because of its over-lap with GRT 4645. The calibration relation, T(R), was obtained by fitting the data with the standard form (62, 63),

\[
\ln T = \sum Q_j (\ln R)^j .
\] (37)

The fitting procedure would minimize the sum of

\[
\frac{(T - T_{calc})^2}{T^2},
\] (38)

where the subscript calc corresponds to the calculated value from the fit equation. Typically, the best fits were of 7th to 9th order for three temperature range; 0.9 - 6.5, 4.0 - 21, 16 - 78. These ranges give sufficient over-lap so that the ranges joined smoothly with temperature differences between ranges of less than 0.1 mK and slopes differences of
less than 0.1%. The root-mean-square deviation, RMSD, which was calculated using the standard form,

\[ \text{RMSD} = \left( \frac{\sum_{i=1}^{M} (T(i) - T_{\text{calc}}(i))^2}{\sum_{i=1}^{M} 1} \right)^{1/2}, \]  

(39)

where \( M \) was the number of points and the subscript calc denotes the calculated value of \( T \) from the fit relation. The values for the RMSD in Anderson's calibration were; 0.075, 0.17, and 1.3 mK for the low, middle and high temperature range respectively. It should be mentioned here that the emphasis of sample's calibration of GRT 665 was below 2 K and there were only 14 of these 96 points above 2 K. The scatter in the data above 2 K was on the order of 10 mK and two points around 4.2 K had \( (T - T_{\text{calc}}) \) of -10 and +18 mK. The scatter in the data below 1 K was on the order of 1 mK. The RMSD for this calibration was 4.1 mK. The self-heating effects of GRT 4645 were determined by Anderson and they were similar to the general self-heating effects presented in reference 59. When a GRT is operated with thermometer voltage of 2 mV, the general rule is that the self-heating effects will be \( \approx 0.1 \) mK at 10 K and \( \approx 0.3 \) mK at 30 K. This voltage criterion tends to make the self-heating effects decrease with decreasing temperature and for this reason the present calibration was performed with constant current over definite intervals such that the thermometer voltage always was between 1 and 2 mV. The self-heating effects of the thermometers in this calibration were checked
at one temperature and gave results similar to reference 59. The experimental situation did not lend itself to this type of measurement so a complete study was not made.

To take the zero field calibration points, the $^3$He pot and shield temperature were controlled to a set resistance value of the CRT and the CT and ST were monitored. The thermometer block would drift into equilibrium with the $^3$He pot and when this equilibrium was established to the precision of the ST or within the thermal noise level, the voltage across each thermometer was measured with a potentiometer. The ST was measured at the beginning and end of each calibration point, with the average temperature assigned to the data point. Each calibration point took several minutes and the initial and final temperature, in general agreed to the precision of the ST. These were 0.05 mK at 1 K, 0.3 mK at 4 K, 1 mK at 10 K and 2 mK at 20 K. After each point, the set resistance values of the CRT was changed so as to change the temperature by about 5 percent of the absolute temperature and when control and thermal equilibrium were re-established another data point was taken.

As the experiment was designed, there were some temperature control problems for temperatures above 30 K because of the large heat capacity of the thermometer block and below 0.9 K because the thermal coupling between the $^3$He pot and the thermometer block was rather weak. In the temperature range of 0.9 to 30 K, the temperature control was within the precision of GRT 4645 as mentioned earlier. For temperatures above 30 K, the time constant for the thermometer block to reach equilibrium with the shield were on the order of hours so a correction for the drift toward
the equilibrium was made. The drift was assumed to be a constant with time and the calculated temperature assigned to each thermometer. The drifts were between 15 and 35 mK, so with this correction was on the order of the measurement uncertainty which was \( \approx 5 \) mK in this temperature range. At temperatures below 1 K, the thermal conductivity of the link and the heat capacity of the thermometer block became sufficiently small that changes in power input to the thermometer block changed the temperature. These power changes were due to measuring the various thermometers with different power levels, small mechanical vibrations and a.c. noise heating in the thermometer circuit which changes for different thermometers and ground position in switching. Later, in the heat capacity experiment, the a.c. noise was traced to an a.c. sputtering apparatus in an adjacent laboratory, which was picked up by the unshielded lead wires in the glass dewar. This problem caused the resulting temperature uncertainty to be larger than the measurement resolution. An estimate based on capacitor response during the calibration points and shifts from beginning to end of a calibration point would put the worst case uncertainty at \( \approx 0.5 \) mK.

The capacitance thermometer, which was used to maintain constant temperature while the magnetic field was changed for the calibration of the GRT's as a function of \( H \) and \( T \), showed rather substantial changes in calibration on cycling to room temperature as shown on Fig. 13. The data show a slight upward curvature, but straight lines were drawn through the data for reference. These curves, for temperatures in the range of 3.9 to 4.3 on four different cool downs are representative of temperature
below 20 K. The shifts are approximately 52 to 120 mK between cool downs. During a given cool down, over periods of several weeks when the temperature did not exceed 20 K, the capacitor calibration was retained to \( \pm 3 \) mK. This, of course, has been reported previously (64, 65) and it means that a CT is not useful as a thermometer unless it is calibrated every run, as was once done for carbon thermometers. The slight temperature rises, typically 0.1 to 0.2 K, which occur between the field points, due to the eddy current heating, may have caused some temperature shifts on the order of a few tenths of a millikelvin due to the inherent precision limit of a CT.

Another important feature of the CT was the equilibrium time. When the temperature of the calibration block was changed and re-established by the GRT, the CT would, for the most part, track this change with the GRT's to an accuracy of a few mK, but it would continue to drift for several minutes at a rate of several mK per hour after the calibration block had reached a constant temperature according to the GRT's. After this initial aging, the drift rate would decrease to a value on the order of 1 mK/hr. or less. The magnitude and direction of these drifts depended upon the thermal history of the CT. The more the temperature was changed before the observation, the larger the drift and the drift direction was toward the former temperature. These isothermal aging effects have been reported, to some degree, before (64, 65) but the lower drift rates observed here remained after the initial cool down and annealing at a higher temperature had removed the large initial drift rates as reported in the references. For the purpose of this experiment this simply
meant that some patience was required in taking the data and this did limit the absolute accuracy of the magnetoresistance measurement. If a CT were to be used as the thermometer in a specific heat experiment, however, this equilibrium time might limit the rate of which measurements could be made.

The magnetoresistance of the four GRT's was measured in the temperature range of 0.4 to 10.5 K in fields up to 2 Tesla. To make a measurement, the temperature was held constant by monitoring the CT and recording the resistance of each GRT at magnetic fields of 0.0, 0.2, 0.4, 1.0, 2.0 and 0.0 Tesla. The time necessary to make the resistance measurements, change the field, let the eddy current heating effects decay and regain temperature control at each field value was between 2 and 4 hours depending upon the particulars of the cooling power and heat capacity at each temperature. When the zero magnetic field temperature was measured at the end of the sequence, the temperature drift of the CT could be determined. The typical drift was less than 1 mK with the worst case drift of 4 mK at 0.4 K. The effects of this drift will be given later.

Heat Capacity Measurement

The heat capacity measurements were made with the usual pulse heating method. A natural progression of this measurement was to start at the lowest temperature and move up in temperature with temperature increments of approximately 5%. When the measurement was to be made in a magnetic field, the field was taken from zero to the set field on a virgin sample of the lowest possible temperature. The eddy currents induced by the ramping the magnetic field would raise the temperature of
the sample but all of the low field measurements were made with the magnetic field set below 0.7 K. This kept the magnetic flux trapped in the sample to a minimum.

Each heat capacity data point was taken with the $^3$He pot and shield held at a constant temperature by the CRT controller. The off-balance voltage of the CRT controller was displayed on channel 2 of the strip chart recorder and the control was better than 0.05 mK (0.005%) at 1 K and 2 mK (0.02%) at 10 K. The potentiometer off-balance GRT voltage was recorded on channel 1 of the strip chart recorder at a sensitivity of 2 or 6 μV/in, depending upon the thermometer sensitivity. A correction was made for the heat gained by the sample during the heat pulse, in warming toward the shield before the shield temperature was reached and the heat lost by the sample during the heat pulse, in cooling toward the shield temperature after the shield temperature was exceeded. This correction was made by extrapolating the sample temperature drift before and after the heat pulse and defining the initial and final temperatures of the heat pulse at the midpoint in time of the heat pulse. A simple geometric construction would show that this averages the heating and cooling rates regardless of these relative sizes. However, an attempt was made to have the magnitude of the warming and cooling rates equal, in order to minimize the temperature drift rate and thus maximize the precision in that regard. The duration of most of the heat pulses was set at approximately 10 seconds for the sample run and 4 seconds for the addenda run. The choice of these times was determined by the rate that the temperature of the sample or addenda changed with time and the
ability of the operator to read and record the heater voltage and bring
the potentiometer back on scale before the end of the heat pulse. The
heater power was adjusted for most of the data, to change the temper-
ature, $\Delta T$, by 2 to 3 percent. This choice was governed by a trade-off
among $\Delta T$, the change in CRT voltage, $\Delta V$, the rate of temperature drift,
$\frac{dT}{dt}$, and the temperature difference between the shield and the specimen
$\Delta T_{ss}$. As $\Delta T$ is increased, $\Delta V$ would increase to give higher precision,
but as $\Delta V$ increases the potentiometer detector sensitivity would have to
be decreased because $\frac{dT}{dt}$ before and after the pulse is proportional to
$\Delta T_{ss}$ and thus the overall precision is limited. The opposite limit,
decreasing $\Delta T$, has additional factors: the precision of the shield con-
trol, the electrical noise in the thermometer circuit and the thermal
noise of the sample or addenda which limit the precision. The choice of
the relatively small percentage $\Delta T/T$ also makes the approximation, of
assigning the calculated heat capacity to the average of the initial and
final temperature, a good one.

A test was performed to determine if the heat capacity measurement
technique was relatively independent of heater power, pulse time dura-
tion, initial conditions, timer malfunction, different cool downs, and
the magnitude of the temperature change. Figure 14 is a plot of $C/T$
versus $T^2$ for the sample run in zero magnetic field, for three different
cool downs which spanned a two month time period. A straight line was
drawn through two of the points of cool down #2 as a reference line,
because the data in this temperature region lie approximately on a straight
line. As mentioned earlier, the normal data point was taken with a pulse
duration, $\Delta t$, of 10 seconds for the sample run and 4 seconds for the
addenda run, with the heater power adjusted to give $\Delta T/T$ equal to 2 to 3%
and with a warming drift toward the shield before the pulse, $(dT/dt)_i$ and
an approximately equal cooling rate toward the shield after the pulse
$(dT/dt)_f$. All of the points on Fig. 14 were taken in this normal way,
except for points labeled C, D, and E. This small temperature interval
was representative of the whole temperature range, with cool down #1 and
2 in agreement to within 0.2% and an apparent shift of approximately 0.5%
between the first two cool downs and the last. All points labeled A
through E were taken with the same CRT setting and thus the same shield
temperature on the same day. Between the data points the shield temper­
ature was changed to set up the desired initial conditions. The data
point labeled A was the control for cool down #3, with $\Delta T/T = 2.4\%$ and
$(dT/dt)_i = -(dT/dt)_f$. Data point B had an incorrect timer reading because
of the timer trigger bounce problem described earlier. When the time dura­
tion of the point was corrected to the reproducible time, the resulting
data point was $B'$, which was within 0.1% of the third cool down results.
However, all data points that had this problem were discarded out of
principal. Data point C was taken with $\Delta T/T = 2.2\%$ and $(dT/df)_i$ of
point C approximately equal to $(dT/dt)_f$ of point A. This point agreed
with the third cool down results to within 0.1% and demonstrates the data
taking technique to be relatively independent of initial conditions. Data
point D was taken with the same $\Delta t$ as A, but with the power adjusted so
that $\Delta T/T = 9.6\%$, approximately four times that of A. The initial con­
ditions of point D were adjusted so that the temperature of the data point
would be near that of point A, with \((dT/dt)^i \approx -(dT/dt)^f\). These two points; A and D, are in agreement to within 0.1\%, showing that the technique was relatively independent of heater power and percentage change in temperature. Data point E was taken with \(\Delta T/T \approx 2.5\%\) and a pulse duration of approximately 40 seconds, four times that of A. This point was approximately 0.35\% below the expected result. This small discrepancy was due to the extrapolation approximation not being able to account for all of the heat lost and gained from the shield during the long heat pulse. This emphasized the need to make \(\Delta t\) as small as possible in order to minimize the amount of temperature change that has to be accounted for by this approximation. With the normal technique, the maximum rate of cooling or warming, before or after a data point was approximately 0.1 mK relatively independent of temperature from 0.5 to 10 K. This arises because of the set value of \(\Delta T/T\), the temperature dependence of the heat capacity of the sample and the temperature dependence of the thermal conductivity of the heat leak wire have a cancelling effect. The typical percentage of \(\Delta T\) accounted for by the extrapolation approximation was \(\sim 6\%\) at 0.5 K, \(\sim 2.5\%\) at 0.8 K, and \(\sim 0.2\%\) at 10 K.

As mentioned earlier, the radioactive sample made it necessary to use a heat leak wire rather than a heat switch for the thermal connection between the shield and the sample. The thermal conductivity of the heat leak wire could be measured by holding the shield at a constant temperature and allowing the sample to come to equilibrium with the shield and recording the GRT equilibrium temperature. Then a known constant power was put through the sample heater, with the shield still held at the same
original temperature. When the sample reached a new equilibrium temperature, the GRT reading was recorded and the difference between the initial and final temperature defined as $\Delta T$. As a check to determine if the shield temperature hadn't drifted, the heater power was turned off and the sample would return to the zero heater power equilibrium, to within a resulting calculation error of $\sim 0.5\%$. The power, $P$, in the normal thermal conductivity equation was just the heater power and the difference in the stead state thermometer power, within the approximation that all other powers, such as the radioactive self-heating and mechanical motion remain constant over this measurement. The other power inputs only cause the equilibrium sample temperature to be above the shield temperature by the amount determined by a separate thermal conductivity equation. The measured combination of $P/\Delta T$, for the first cool down, was approximately 0.64 $\mu$W/K at 0.5 K and 7.0 $\mu$W/K at 4.0 K. For all of the other runs $P/\Delta T$ was approximately 0.35 $\mu$W/K at 0.5 K and 3.3 $\mu$W/K at 4.0 K. The temperature dependence of $P/\Delta T$ was approximately linear in this temperature range and there was a systematic difference between the last four cool down of $\pm 5\%$ at 4 K. This was thought to be due to some coils of the coiled heat leak wire touching each other or a different amount of residual gas in the vacuum can. The thermal conductivity was also independent of magnetic field, at least to 0.4 Tesla, to the precision of this measurement. Using an estimation of the temperature dependence of the quantity $\Delta P/T$ and the lowest equilibrium sample temperature and shield temperature, the radioactive self-heating was estimated as 50 nW. If the sample was isolated from the shield, as in a
heat switch arrangement, this radioactive self-heating would cause the sample and addenda to warm at a rate of approximately 1.9 mK/s at 0.5 K and 0.54 mK/s at 0.8 K. This would have made it very difficult to take data below 1 K and was the reason for using the heat leak wire, which gave maximum warming and cooling rates of 0.1 mK/s over the range of 0.5 K to 10 K.

The magnetoresistance of GRT 4645 was checked in the heat capacity measurement by the same technique as the calibration, except the CT 245 was mounted on the shield and the temperature difference between the sample and shield was assumed to be independent of magnetic field. The difference between the calibration run and the heat capacity run, at 1.0 Tesla, was 1.2, 1.4, and 5.9 mK at temperatures of 4.3, 6.4, and 10.5 K respectively. This represents a minor change in the magnetoresistance effect and may have been caused by this different technique and assumptions, so no further correction was made. An additional magnetoresistance calibration point was taken at 15 K to better cover the range of magnetic field data.
RESULTS AND DISCUSSION

Sample Quality

The microstructure of directionally solidified Th-Nb was a nearly hexagonal array of Nb rods in a Th matrix. The eutectic composition was about 7.07 weight percent Nb, which has approximately 9.4% of the total cross-section area or volume Nb. At the zoned diameter, the approximate number of Nb rods per square millimeter was 0.5, 2.0 and 9.0 million for zoning rates of 10, 45 and 200 μm/s respectively. If the array was perfectly hexagonal, the center to center distance, \( \lambda_e \), would be given by equation 35. Four scanning electron microscope (SEM) micrographs are shown on Fig. 15. Each of these was taken of the cross-section surface, either normal to the surface or at a tilt angle of about 30° to give a perspective view. The surface was prepared by mechanical polishing the surface and chemically etching the Th away with 1 part water and 1 part HNO₃ with a small amount of sodium hexafluorosilicate (Na₂ Si F₆) catalyst. Figure 15a was a SEM micrograph of a sample at the zone diameter (0.32 cm) which had been tilted to give a perspective of the 0.32 μm diameter Nb rods (Nb was the lighter tone). The Nb rods are normal to this cross-section surface and ran in the same direction as the directional solidification which was along the axis of the wire. Figure 15b, c and d were taken after this wire was drawn to a diameter of 0.046 cm. Uniform area reduction would give a 46 nm Nb diameter for this reduction. The diameter of the drawn Nb was estimated at 50 ± 20 nm, which agrees with uniform area reduction within the resolution of the SEM. Figure 15b was an end-
on, normal to the surface, view of the wire. Because of the large aspect ratio, length to diameter, the deep etched Nb filaments have fallen together in bundles of several hundred filaments. The drawing process does not seem to have greatly disturbed the filaments in that they seem to come from all of the surface area and are separate from each other. Figure 15c was a tilted perspective which better illustrates the nature of the bundling and individual filaments. Figure 15d was taken directed at the same part of the sample as c, but with the magnification change by a factor of 10. This still only shows a small section of the sample, but this was characteristic of the cross-section and gives some indication of the uniformity of the sample.

Dispersive X-ray analysis in the SEM (66) indicated there was some oxygen contamination of the Th from the arc melting and zone refining of the samples. This contamination caused the regular rod eutectic growth to have a cell structure (42) with the ThO₂ precipitating at the cell boundaries. The effect on the Nb rod growth was near the cell boundary where the rods would tend to grow toward the boundary. For the samples reported here, the percentage of the volume of the sample that was contained within the disturbed regions around the cell boundaries was approximately 5% for the 45 μm/s zone and 2 to 3% for the other critical current samples. In the worst case the cell size was 0.2 mm and was not thought to have affected the experimental results greatly.

A detail study of sample uniformity was performed by Pedersen (44) on the heat capacity sample. This sample was prepared and zoned in the same manner as the critical current samples, except the wire diameter was
0.47 cm. A section 2.2 cm long was cut from a rather uniform region of the zoned wire and the ends and one side were mechanically polished, electropolished and examined under an optical microscope for uniformity. The polishing removed most of the oxygen contaminated regions of the sample and left less than 1% of the sample in the cell boundary affected regions. A small piece of undissolved Nb was also removed in the polishing. There were some small diameter Nb rods, \( \sim 0.27 \mu m \) diameter, distributed throughout the sample, but these represent only about 3% of the total Nb. The remainder of the Nb had filament diameters of \( 0.50 \pm 0.02 \) nm as examined on each end of the specimen. A chemical analysis was performed by the Ames Laboratory Analytical Services Group on sections of the heat capacity sample after the measurement. Two determinations of the Nb weight percent were made, 6.83 and 6.86% with estimated uncertainty of 1% of this quantity. One determination of the Th, 93.08 wt%, was made with an uncertainty of 2000 ppm. This was slightly below the original 7.05 wt% Nb which can be explained by the undissolved Nb mentioned above.

Critical Current Density

The goal of the \( J_c \) measurement was to determine if the superconducting-normal interface would serve as effective pinning centers for the vortices. This would be indicated by an increase in \( J_c \) as the Nb filament diameter was decreased, because of an increase in effective pinning centers per unit volume. Samples were drawn from three directionally solidified, 0.317 cm diameter, cylinders of the eutectic material with zoning rates of 10, 45, and 200 \( \mu m/s \), which had initial Nb filament diameters respectively of approximately 518, 244, and 116 nm. The
diameter of the Nb filaments in the drawn samples was determined by assuming uniform area reduction in the drawing process. This assumption was verified to ± 20 nm, the resolution of the SEM. The three different zone rates gave \( J_c \) samples with Nb filament diameters in the range of 116 to 8 nm for wire diameters in the range of 0.10 to 0.013 cm. For a given wire diameter, the three zone rates gave samples with Nb filament diameters which were different by a factor of 4.5. This gave a check of wire diameter and area reduction effects.

The critical current measurement was a very difficult measurement to make because of the inability to solder the sample. Indium pressure contacts gave the lowest contact resistance, but contact heating still affected most of the low field data, especially for wire diameters below 0.025 cm. For this reason some of the data represent only a lower limit of \( J_c \). An operational check was performed to determine when contact heating could be a problem. This involved a measurement of the power across the sample when the sample thermally quenched into the normal state. Contact heating and thermal runaway may have been a problem if the sample power at quench was not approximately the same for \( I_c \) measurements at different applied magnetic field. This test would only indicate when contact heating affected the thermal quench, so the \( I_c \) measurement may have been unaffected even if the sample failed this test, but the degree that the quench was affected indicated the extent of the problem.

The area reduction effect is shown on Fig. 16, which is a plot of \( J_c \) versus inverse wire diameter, \( d_w^{-1} \), in an applied remnant magnetic field of 0.002T for sample drawn from the same zone run, 200 \( \mu m/s \). Samples
were as drawn and annealed, 850°C for 1 hour, after drawn to test diameter. This plot was characteristic of area reduction effects observed for the other samples as well. The area reduction caused an increase in pinning centers per unit volume as the wire was drawn, due to inhomogeneities introduced by drawing. For area reductions greater than 75, a competing factor, lowering $T_C$ of the sample with drawing, wins out and the crossover of the as drawn and annealed samples occurs. Annealing at 850°C for 1 hour proved sufficient to minimize the area reduction effect and the rest of the data will be on samples with this heat treatment.

The $J_C$ proved to be insensitive to Nb filament diameter and only dependent on wire diameter. This suggests that $J_C$ was determined by a critical state model and the pinning force per unit volume was dominated by bulk pinning and insensitive to filament diameter. This is shown on Fig. 17, which is a plot of $J_C$ versus $d_w^{-1}$. Ten of the larger wire diameter samples fall on a smooth curve displaying the wire diameter dependence. The six smaller wire diameter samples, with lower $J_C$ values than a smooth extension of the curve, had contact heating problems and are just lower limits to $J_C$. Four samples that passed the contact heating criterion had $d_w^{-1}$ and zone rates respectively of: 9.8 cm$^{-1}$, 200 μm/s; 20.4 cm$^{-1}$, 45 μm/s; 27.9 cm$^{-1}$, 10 μm/s and 39.8 cm$^{-1}$, 45 μm/s. These points indicated that this smooth curve was a real dependence on wire diameter and not a dependence through contact heating.

The critical state equation for a cylindrical wire in zero applied field, equation 32, gave an analytic solution for $J_C$ inversely proportional to $B$, which gave $J_C d_w^{1/2}$ equal to a constant (equation 34). For the ten
larger wire diameter samples on the smooth curve, this product, $J_c d_w^{1/2}$, had a systematic variation of 43%. A better fit to this data was $J_c d_w^{0.8} = \text{constant}$, which had a variation of $\pm 5.8\%$. Using the results of reference 40, $J_c d^{0.8} = \text{constant}$, implies that $J_c$ was approximately inversely proportional to $B$ to the fourth power. Figure 18 is a full logarithmic plot of $J_c$ versus magnetic field for the four samples which didn't have heating problems. Note that a magnetic field, $H = 10 \text{kOe}$, is the same as $\mu_0 H = 1 \text{T}$. There was no unique power low dependence for these curves, but the region above $0.1 \text{T}$ had a slope of $-3$ to $-4$. The other samples showed similar shaped curves but the lower field data may have been affected by contact heating. The critical state model are inadequate to describe all of the results, but it seems that $J_c$ was determined by a critical state equation. It should also be pointed out that the proximity effect didn't seriously degrade $J_c$ for Nb filament diameter down to 8 nm.

**Thermometry**

The basic temperature scale for the heat capacity measurement was established in earlier experiments in which two germanium resistance thermometers, GRT's, were calibrated against a scale established by constant volume gas thermometry and the susceptibility of paramagnetic salts. Between 77 K and 0.9 K, GRT 4645 was calibrated on the well-documented scale (59, 67) of Swenson and Anderson with an accuracy of 1 mK up to 4.2 K and 4 mK at 20 K. Below 0.9 K the temperature scale was taken from a thermometer, GRT 665, previously calibrated against the magnetic susceptibility of a paramagnetic salt and T-58 over the temper-
ature range of 0.14 to 5.4 K. The purpose of this thermometer intercalibration was to calibrate a total of four GRT's over the temperature range of 0.3 to 77 K, using GRT 4645 and GRT 665, and calibrate the thermometers for magnetic fields up to 2 Tesla in the temperature range of 0.3 to 10 K.

One of the other thermometers, GRT 99, had been calibrated earlier in the range of 1.3 to 13 K and had since been corrected to T-68. A comparison between the calibration of GRT 4645 and GRT 99 illustrates, Fig. 19, the low temperature precision of the intercalibration which was on the order of a few tenths of a millikelvin over this range. Below 2.5 K, an end effect of the calibration of GRT 99 was observed. The two thermometers, GRT 4645 and GRT 665, used in the calibration had a wide range of overlap and they had a small systematic deviation as shown on Fig. 20, with the two scales agreeing to 1 mK just below 1 K. There was a high temperature end effect on the GRT 665 calibration due to an insufficient number of data points and end effect of the curve fitting. Approximately half of this systematic difference arises from the well-established change in the temperature scale between 1958 and 1968, which was approximately linear with temperature. Experience with a large number of thermometers which had shifted calibration, indicates that the linear difference in these two thermometers between 0.9 and 2.6 K was due to one of the thermometers having a small change in resistivity and lead geometry (68). Because GRT 4645 was calibrated most recently and it compared well with GRT 99 and $^3$He vapor pressure measurements, it was presumed to have the better calibration. Fortunately the differences were
small, so the calibration used GRT 4645 above 0.9 K and GRT 665 below 0.9 K. A low temperature, 0.29 - 5.0 K, calibration of GRT 4645 was performed using GRT 665 as the standard. The RMSD of this calibration was 0.44 mK for the 9th order, 81 point fit.

The error in the heat capacity measurement due to errors in the calibration can be estimated (62) by fitting,

\[ T_{\text{meas}} - T_{\text{real}} = \alpha_3 + \beta_3 T, \]  

and getting

\[ \frac{C_{\text{meas}} - C_{\text{real}}}{C_{\text{meas}}} = -\beta_3 + \sigma(T) \frac{\alpha_3 + \beta_3 T}{T}, \]

where the subscripts meas and real correspond respectively to the measured value and the real value, \( \alpha_3 \) and \( \beta_3 \) are fit constants and

\[ \sigma(T) = \frac{d \ln C}{d \ln T}. \]

The low temperature normal state heat capacity is dominated by the free electron term so \( \sigma(T) \approx 1.0 \). In zero magnetic field the sample is superconducting and \( \sigma(T) \approx 2.7 \) better fit to the temperature dependence of \( C(T) \). The fit constant were \( \alpha_3 = 7.40 \times 10^{-3} \) K and \( \beta_3 = -9.21 \times 10^{-3} \) K, giving the correction factors on Fig. 21. These corrections were small, less than \( \pm 1\% \), and the correction was sufficiently uncertain that no correction was made to the heat capacity data presented here.
Thermometer calibrations were made at fields of 0.2, 0.4, 1.0 and 2.0 Tesla on all four thermometers for eight different temperatures in the range of 0.4 to 10.5 K. The magnetic field was along the axis of the cylindrical GRT and in the same orientation as the heat capacity experiment. Typically one would like 50 to 100 data points at each field over this temperature range, but each temperature took 2 to 4 hours depending upon the temperature, so time did not permit this. Fortunately the changes in resistance, $\Delta R$, from the zero field value, $R_0$, were rather small and a smooth function of $T$ on a full logarithmic scale so that the resistance, $R(T, H)$, could be determined from a relatively few points to permit a precision of 0.001 K in the calibration. As shown in Fig. 22, $\Delta R/R_0$ was a relatively smooth function of $T$ at each value of $H$ and intermediate points in temperature could be obtained by Lagrange interpolation of $\log (\Delta R/R_0)$ versus $\log (T)$. These data points were then added to the corresponding zero field value and the total, $R(T, H)$, was fit in the usual way to give calibration coefficients for constant field. Figure 23 is a plot of the apparent temperature change, $\Delta T = T(H) - T(H = 0)$, versus $T$ on a full logarithm scale for magnetic fields of 0.2, 0.4, 1.0 and 2.0 T.

The change in zero field resistance of the GRT due to the CT drift over the data point was the main source of error in the magnetoresistance calibration. As a result of this the lower field data, 0.2 and 0.4 T had more scatter because of the small $\Delta R$, less than 1%. Also, the lower temperature data, below 2 K, were more susceptible to this because of the increased GRT sensitivity and CT drift at these temperature giving a
larger scatter in $\Delta R$. For the magnetoresistance temperature correction, this effect was somewhat cancelled by the GRT sensitivity, leading to a relatively constant calibration uncertainty of 2 mK at 10 K and 4 mK at 1 K for a magnetic field of 1.0 Tesla. A correction was made for the CT drift by assuming that $R_o$ varied linearly with time between the beginning and end of the temperature calibration point. Figure 24 is a plot of $\Delta R/R_o$ versus $H$ on a full logarithm scale for each temperature. It was observed that the data for each temperature, especially the higher temperature data, lie nearly on a straight line indicating the empirical relation $\Delta R/R_o = \alpha_4 H^{\beta_4}$, where $\alpha_4$ and $\beta_4$ were constants. This relation could be used to determine $\Delta R/R_o$ at intermediate fields or to correct the lower field data. The values of $\beta_4$, obtained from fitting the 1 and 2 Tesla data points at each temperature varied systematically between 1.91 at 15 K to 2.24 at 1.4 K. The value of $\beta_4$ at 0.40 K and 0.75 K was 2.11 and 2.13 respectively, which were somewhat lower that the 1.4 K value. It was not known whether this was a real effect or not. This empirical relation was used to correct the 0.4 T data and temperature end points at 0.29, 16 and 17 K were extrapolated by hand to give a better fit over the temperature range of 0.4 to 15 K. The resulting thermometer fit of GRT 4645 in fields of 0.4 and 1.0 T had RMSD values of less than 0.1 mK for all ranges because of the mathematical smoothing of the data. Because the temperature correction in 0.2 T was less than 5 mK at 10 K and 2 mK at 1 K, the correction was not made for fields of 0.2 T or less.

All four GRT's showed similar magnetoresistance effects on $\Delta R/R_o$ versus $T$ at constant $H$ as illustrated on Fig. 25. The data groups are
within a factor of 2 for temperatures above 1 K and a factor of 2.5 below, even though the GRT's had quite different resistances (see Table 1). GRT 99 had a resistance of 34800 Ω at 0.9 K and was not calibrated below that temperature because the resistance was getting too large. On the other hand, the resistance of GRT 267 was only 78 Ω at 0.29 K. GRT 4645 and GRT 665 had resistance values of 7230 and 1500 Ω respectively at 0.29 K. The apparent change in temperature, ΔT, however, were somewhat different, within a factor of 5, depending on the thermometer sensitivity, with the high resistance GRT having the lowest ΔT.

Heat Capacity

The heat capacity of a sample of directionally solidified Th-Nb was measured over the temperature range of 0.48 to 15 K, in magnetic fields of 0.00, 0.02, 0.05, 0.1, 0.2, 0.4 and 1.0 Tesla. The sample was cut from a 0.47 cm diameter wire which was zoned at 10.2 μm/s and had approximately 6.845 ± 0.068 weight percent Nb. A section 2.2 cm long was cut from a rather uniform region of the zoned wire and the ends and one side were examined for uniformity as mentioned in the sample quality section. The total mass of the sample was 2.7185 ± 0.0001 gm, so there was approximately 0.1861 gm of Nb and 2.5324 gm of Th in the sample. Because the specific heat, C_p, has been measured previously for both Nb (69) and Th (55), the heat capacity of the composite can be predicted if there were no proximity effect. This is a convenient reference curve which will be referred to as bulk Nb and bulk Th with N and S subscripts to denote the normal and superconducting states.
The total mass of the addenda was 2.3166 gm and had a heat capacity, $C_{\text{add}}$, of approximately 40 to 60% of the total heat capacity for temperatures above 2 K. Figure 26 is a plot of $C_{\text{add}}/T$ versus $T^2$ in zero magnetic field for the low temperature range. $C_{\text{add}}/T$ at high temperature was a smoothly increasing function of $T^2$. The broad spike in $C_{\text{add}}/T$ just below 1 K was thought to be due to the $^3$He exchange gas in GRT 4645 condensing. There was some hysteresis around the condensation spike which was thought to be due to surface absorption of the $^3$He gas or longer thermal equilibrium time constants around this spike. A sharp rise in $C_{\text{add}}/T$ was observed around 0.5 K, where $C_{\text{add}}$ more than doubled in a span of 0.048 K, changing by $2.85 \times 10^{-2}$ mJ/K. Lower temperature addenda data indicated that this rise stopped at about 0.46 K and $C_{\text{add}}/T$ decreased in a linear way with $T^2$, down to the lowest temperature data 0.32 K. Some insight to the possible source of this sharp rise was given by the magnetic field dependence of the addenda. Figure 27 is a plot of $C_{\text{add}}/T$ versus $T^2$ at different magnetic fields. It was observed that the onset of the sharp rise at about 0.5 K was insensitive to magnetic fields up to 1.0 Tesla, but there was a relatively constant shift in $C_{\text{add}}$ for each field with the magnitude of the shift increasing with field. These observations suggest that the sharp rise at 0.5 K was due to a long range magnetic ordering and the shift to higher $C_{\text{add}}$ above this ordering temperature was due to local ordering. The broad spike just below 1 K was unaffected by magnetic field, but the shift of $C_{\text{add}}$ was measurable for the highest field up to 2 K. Regardless of the cause of two structures,
the addenda was subtracted from the total heat capacity data of the sample and addenda.

The low temperature heat capacity, $C$, of a solid can be expanded in a power series in the temperature (70) as,

$$C = \sum_j G_j T^j,$$

where $j = 1, 3, 5, 7, \ldots$. This can be expressed as,

$$C/T = \sum_{i=1}^{L+1} G_i T^{(2i-2)},$$

or

$$Y = \sum_{i=0}^L G_i X^i,$$

where $Y = C/T$ and $X = T^2$. The coefficients of equation 45 can be determined by a least-squares-fitting technique which minimizes $(Y - Y_{\text{calc}})^2/ Y_{\text{calc}}^2$, where the subscript calc denotes the calculated value. This gives a relative weighting factor to the data, which was the experimental reality. This fitting technique was used for both the zero magnetic field addenda data and sample data, except a divergent term was added to the series expansion of the addenda to better fit some temperature regions of the data. For these regions the fit equation was,

$$C_T = \sum_{i=1}^{L+1} G_i T^{(2i-2)}.$$
or

\[ Z = \sum_{i=0}^{L} G_i x_i \]  

(47)

where \( Z = CT \) and \( X = T^2 \). With this fit equation, the minimization was made on \((Z - Z_{\text{calc}})^2/Z_{\text{calc}}^2\), where \( Z_{\text{calc}} \) was the calculated value of \( Z \).

This also gives a relative weighting factor to the fit. The regions of the zero magnetic field addenda data were selected to give reasonable fits, typically 0.3 to 1.6% root-mean-square deviation (RMSD), with sufficient temperature range overlap to give a continuous representation of the addenda without end effects on the fit. The magnetic field dependence of the addenda was fit separately by subtracting the zero magnetic field addenda fit from the field data and fitting this difference, \( C_H \), for each field with the fit equation,

\[ C_H = \sum_{i=0}^{L} G_i T_i \]  

(48)

with the minimization made on \((C_H - C_{H \text{ calc}})^2/C_{H \text{ calc}}^2\). Thus the addenda data was the sum of the zero field addenda fit and the appropriate field fit. Within experimental error the 0.02 and 0.05 Tesla addenda were the same as the zero field addenda, so no field correction was made. It should also be pointed out here that no reasonable magnetoresistance effect on the thermometer calibration would cause this low temperature magnetic field dependent addenda. The magnetoresistance correction was a smooth function of temperature and was, in fact, less of a temperature
correction at the low temperature end. Also, the addenda data for all magnetic fields, in the range of zero to 1.0 Tesla, agreed to an RMSD of 0.5% over the temperature range of 2 to 15 K and the sample data of all fields and temperature above 10 K were with 0.5% of the normal state curve. In spite of the complicated appearance of the addenda, it was reliably fit and subtracted from the total heat capacity to give the sample heat capacity to an accuracy of approximately 2% at 0.5 K, 1% at 1.0 K and 0.5% at 10 K.

Over much of the temperature range, the heat capacity of the sample was fairly close to the predictions based on literature values for bulk Nb (69) and bulk Th (55). The proximity effect made a major contribution only in the region near $T_C$ of Th. Above 5 K, the heat capacity is dominated by the phonon terms and the jump in C at $T_C$ of Nb is rather small. The jump in the heat capacity, $\Delta C$, of the sample as a function of magnetic field can best be shown by plotting the percentage difference between the heat capacity and the normal state, which was a fit to the 1.0 Tesla data, versus temperature, Fig. 28, because less than 7% of the sample weight was Nb. The magnitude of the jump was estimated by drawing a smooth curve through the data below the jump and a straight line through the data in the jump. These values were; 0.225, 0.216, 0.229, 0.267 and 0.129 mJ/K at fields of 0.00, 0.02, 0.05, 0.1 and 0.2 Tesla respectively. A small step of 1.7% was observed in the 0.4 Tesla data but was left off this plot for clarity. The zero field jump was 14% below the expected jump for the Nb alone (69), using the BCS theory and the chemical analysis to determine the number of moles of Nb. The $T_C$ was
defined, as is commonly done (52), as the midpoint of the straight line through the data in the jump. The midpoint temperature of the data taken in other fields were used to determine the critical field curve, \( H_{c2}(T) \), shown on Fig. 29. Also plotted on this figure are \( H_{c2} \) values of pure Nb determined from magnetization data (71). The \( T_c \), \( \Delta C(T_c) \) and \( H_{c2}(T) \) of the Nb in the Th-Nb eutectic were close to bulk Nb properties. The \( T_c \) was slightly depressed because of the proximity effect with the Th. The \( H_{c2}(T) \) curve indicates that the sample had critical field properties like slightly dirty bulk Nb, as might be expected from the Th dissolved in the Nb, a value less than 0.1%. The magnitude of \( \Delta C \) indicates that for the most part only the Nb goes superconducting at \( T_c \). This was supported by the susceptibility measurement of \( T_c \), which shows a rather sharp change in susceptibility at the onset and a tailing to much lower temperatures (but well above \( T_c \) of bulk Th) before the entire sample was in the Meissner state.

Other bulk like properties are illustrated in Fig. 30, which is a comparison of \( C/T \) versus \( T^2 \) for magnetic fields of 1.0 and 0.02 T data with bulk curves. At 1.0 T, the sample was completely normal and the data was within 1% of the sum of normal bulk Th and Nb (55, 69). A rather unexpected result was that the 0.02 T data were so close, within a few percent, to the sum of bulk superconducting Nb and bulk normal Th. These data suggest that, in spite of the proximity effect, this magnetic field, which was above the critical field of bulk Th (72), was sufficient to drive the Th normal. The deviation between these two may have been due to some superconducting Th, but it could only be a few percent, de-
pending upon its $T_c$. There was a temperature region, 0.5 to 0.7 K, over which the sample temperature was erratic in a field of 0.02 T. This was thought to be due to irreversible flux motion in the Th causing sample temperature changes that were noticeable with the low heat capacity at these temperatures. The only other time this behavior was observed was for the low temperature data in 0.2 T which was thought to be due to flux motion in the Nb at these temperatures. These would be consistent with the expected flux entry fields of Th and Nb respectively. A fit to the 1.0 T heat capacity data, $C_N$, gave,

$$C_N = \tau T + \eta T^3,$$

(49)

where $\tau = 6.165 \times 10^{-2}$ mJ/K$^2$ and $\eta = 5.47 \times 10^{-3}$ mJ/K$^4$. Using the mass fraction of each element from the chemical analysis and literature values (55, 69), a comparison can be made between the composite data and the bulk values (see Table 2). The range of values for $\tau$ and $\eta$ were obtained by fitting different temperature ranges, but the best fit to the data are listed. The measured $\tau$ was 1.6% below the computed bulk value, which was within the $+1.6\%$ and $-1.9\%$ uncertainty. Under the assumption that the Th was completely normal in a magnetic field of 0.02 T and that the Nb was completely superconducting, a linear fit to the low temperature, 0.02 T data would give $\gamma_T$. This value was determined to $+0.6$ and $-2.3\%$, which was 1% above the bulk value. Under these same assumptions, the difference between the fit to the 1.0 T data and the 0.02 T data would give $\gamma_N$. The value of $\gamma_N$ was determined to $+14.8$ and $-10.4\%$, ...
Table 2. Normal state heat capacity constants

<table>
<thead>
<tr>
<th>Material</th>
<th>Normal State Heat Capacity Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Th</td>
<td>$\gamma_{\text{bulk Th}} = 4.31 \text{ mJ/mole K}^2$</td>
</tr>
<tr>
<td>Bulk Nb</td>
<td>$\gamma_{\text{bulk Nb}} = 7.80 \text{ mJ/mole K}^2$</td>
</tr>
<tr>
<td>Nb and bulk Th</td>
<td>$\tau_{\text{bulk Nb and bulk Th}} = 6.26 \times 10^{-2} \text{ mJ/K}^2$</td>
</tr>
<tr>
<td>Nb and bulk Th</td>
<td>$\eta_{\text{bulk Nb and bulk Th}} = 5.05 \times 10^{-3} \text{ mJ/K}^4$</td>
</tr>
<tr>
<td>1.0 T data</td>
<td>$\tau(1.0 \text{ T data}) = 6.17 \times 10^{-2} \text{ mJ/K}^2$ $+1.6%$ $-1.9%$</td>
</tr>
<tr>
<td>1.0 T data</td>
<td>$\eta(1.0 \text{ T data}) = 5.47 \times 10^{-3} \text{ mJ/K}^4$ $+3.9%$ $-6.8%$</td>
</tr>
<tr>
<td>Th (0.02 T data)</td>
<td>$\gamma_{\text{Th (0.02 T data)}} = 4.36 \text{ mJ/mole K}^2$ $+0.6%$ $-2.3%$</td>
</tr>
<tr>
<td>Nb ((1.0-0.02) T data)</td>
<td>$\gamma_{\text{Nb ((1.0-0.02) T data)}} = 6.94 \text{ mJ/mole K}^2$ $+14.8%$ $-10.4%$</td>
</tr>
</tbody>
</table>
which was 10% below the bulk value. These results verify the accuracy of the experiment and tend to support the idea that the Th was essentially normal in a magnetic field of 0.02 T.

The heat capacity data taken at low temperature and intermediate fields are shown on Fig. 31. The 0.02, 0.05 and 0.1 T data were very close to each other in this temperature range because there was no change in the flux exclusion from the Nb. The 0.2 T data showed irreversible flux flow and this indicated that flux had entered the Nb at these low temperatures. It should be pointed out here again that the magnetic field was applied to the virgin sample with the sample temperature kept below 0.7 K.

The low temperature, zero magnetic field data are shown on Fig. 32 along with a curve expected for bulk superconducting Nb and bulk normal Th. The data between 2.8 and 4.0 K are within 1% of this expected curve. This figure also shows a bulk BCS superconducting Th curve and model points. The model curve came from a simple assumption that 40% of the Th went superconducting at 2 K and 60% at 1.4 K and that the Th was a BCS superconductor (72). This gives good quantitative agreement with the low temperature data and illustrates the effect of this model on the high temperature behavior.

Figures 33 and 34 show more elaborate extensions of this model in which the Th is assumed to be composed of many regions having different $\Delta(T)$. In this model, one fills the Th space with a collection of cylindrical shells with outer radius of 3.15 times the Nb filament radius with the Nb filament at the center. This Th shell is divided into subshells
each having a $\Delta(T)$ which depends on the distance it is from the Nb rod. To determine the $\Delta(T)$ appropriate to each subshell it was assumed that the superconducting wave function decays exponentially into the Th with decay length, $k_N^{-1}$. The percentage of the Th electrons that are in the superconducting state was proportional to the normalized integral of this wave function. As the temperature decreases, the percentage of the Th electrons in the ground state increases and it was assumed that 5 percent of the Th goes superconducting at each temperature, $T_i$, for which an additional 5 percent of the electrons has fallen into the ground state and that the appropriate $\Delta(T)$ for this subshell has a BCS dependence with a $T_C$ equal to $T_i$. This approximation ignores the effect of the adjacent Nb filaments and doesn't account for all of the volume of the Th, but this will suffice for this approximation. The $\xi$ was given by

$$\xi_N = \frac{\hbar v_F}{2\pi k_B T} \quad \text{(clean)}, \quad \text{(50)}$$

in the clean limit and by equation 20 for the dirty limit, where $v_F = 2.5 \times 10^5 \text{ m/s}$ (73). The temperature dependence of $k_N^{-1}$ was taken from a relation developed in reference 74 in the clean limit and equation 27 for the dirty limit.

The clean limit model, Fig. 33, fits the data better around the peak of the data, but the temperature dependence of $k_N^{-1}$ doesn't have quite the right shape. An approximation to the clean limit dependence of $k_N^{-1}$ is given in reference 74 as
\[ k_N^{-1} = \frac{1}{\xi_N^3} \left[ 1 + \frac{2}{\ln(T/T_{cN})} \right]^{1/2}, \]  

where \( \xi_N \) is in the clean limit. The dirty limit model, Fig. 34, fits the low temperature data better, but the \( \xi_N \) is too short for the high temperature data making the peak too sharp. The resulting model of the qualitative behavior had many variables and short comings, so no attempt was made to fit the data exactly.

At magnetic fields of 0.02 T and higher the heat capacity data show very little evidence that the Th was superconducting. This suggests, as observed by Hsiang and Finnemore in reference 74, that \( k_N^{-1}(T) \) has a magnetic field dependence as well. So relatively low magnetic field suppresses the superconductivity on most of the Th.

The pair potential in the Nb was determined by assuming that only the Nb was superconducting for temperatures above 3.2 K and that it was a constant, throughout the Nb for temperatures below 8.1 K. The first part of this assumption was a result of the observed jump in the heat capacity at \( T_c \) and the heat capacity in zero field modeled as the sum of normal bulk Th and superconducting bulk Nb above 2.8 K within the accuracy of the experiment. The assumption that \( \Delta(T) \) was a constant throughout the Nb involves a spatial averaging. Equation 7 was used to determine \( C_{eS}(T) \), with \( C_S(T) \) the zero field data and \( C_N(T) \) the fit to the normal state data, 1.0 T, evaluated at the temperature of the \( C_S(T) \) data and \( C_{eN} = \gamma_{Nb} T \). Figure 35 is a plot of \( \ln \left( C_{eS}/\gamma_{Nb} T_c \right) \) versus \( T_c/T \), calculated with \( T_c = 9.1 \) K and the BCS theory line for reference. The data
were on the BCS line just below $T_c$ and falls faster with temperature. The BCS line has a slope of about -1.45 for reduced temperatures between 0.6 and 0.3. There is a large uncertainty in the $C_{es}$ data, especially the lower temperature data, because of the small fraction of the sample that was Nb and because the heat capacity at these temperatures is dominated by the lattice terms. The slope of the data on Fig. 35 was determined, with weighting to the higher temperature data, to be $-1.73 \pm 0.15$. This slope is $-\Delta(T)/k_B T_c$ using equation 8 and can be used to obtain $\Delta(0)$ by scaling the temperature-dependent BCS energy gap by a constant factor as suggested by Finnemore and Mapother (75). This gives a value of $(4.2 \pm 0.4) k_B T_c$ for $2\Delta(0)$ of Nb, compared with the values of 3.66 $k_B T_c$ and 3.69 $k_B T_c$ for bulk Nb from references 71 and 69 respectively.

The assumptions used to calculate the pair potential in the Nb are not appropriate for calculating the pair potential in the Th. This can be seen by observing that the Th transition was very broad in temperature, indicating that the pair potential was a strong function of position and temperature in the Th due to the proximity effect. It was, however, instructive to calculate the low temperature $C_{es}$ and make a plot of $\ln \left( C_{es}/\gamma T_c \right)$ versus $T_c/T$, even though the interpretation was not simple. One way to determine the low temperature $C_{es}$ was to use equation 7 with $C_{eN} = (\gamma_{Th} + \gamma_{Nb})T_c$, which enters into equation 8, was taken to be $\gamma_{Th} T_c$ where $T_c$ was that of Th which was between 1.39 K (clean) and 1.375 K (slightly dirty) (72). Figure 36 is a plot of $\ln \left( C_{es}/q_{Th} T_c \right)$ versus $T_c/T$ with $T_c = 1.39$ K and the BCS theory line for reference. The slope of this line was $-1.59 \pm 1\%$ and the slope of the line with $T_c = 1.375$ was $1.61 \pm$
The data lie below the BCS line because some of the Th goes superconducting at a temperature higher than the $T_c$ of Th leading to the shift and an involved interpretation of the slope. As in the model of the low temperature $C(T)$ in zero magnetic field, it can be assumed that each part of the Th will have its own $T_c$ because of the proximity effect and the corresponding $C_{eS}$ will have a BCS like dependence on $T$ with that $T_c$. This leads to an overall exponential dependence but the pair potential in the Th could only be derived from an exact model. If the $\gamma_{Th}T_c$ was replaced by $0.80 \gamma_{Th}T_c$, the data will lie approximately on the BCS line. This implies that the overall dependence was equivalent to 80% of the Th going superconducting at 1.39 K. A more realistic simple model was the two part model described earlier which had 41% of the Th going superconducting at 2.0 K and 59% at 1.4 K. This gave a low temperature $C(T)$ close to the measured $C(T)$ and would also explain the data being shifted lower than the BCS line.

As mentioned earlier, the low temperature 0.02 T data were essentially the sum of normal bulk Th and superconducting bulk Nb with the defined by the 0.02 T data. This leads to another way to calculate the low temperature $C_{eS}$ assuming that the $C_{eS}$ of the Nb was very small at these temperatures. Using equation 7 with $C_N(T)$ being the fit to the 0.02 T data and $C_{eN} = \gamma_{Th}T$. Figure 37 is a plot of $\ln (C_{eS}/\gamma_{Th}T_c)$ versus $T_c/T$ with $T_c = 1.39$ K and the BCS reference line. The slope of this line was $-1.59 \pm 1\%$ and the slope of this line with $T_c = 1.375$ was $-1.61 \pm 1\%$. There were only slight differences between the $C_{eS}$ calculated with the normal state data 1.0 and 0.02 T. This does not prove that the Th was
completely normal at 0.02 T, but rather that the two methods gave consistent results.

Critical Fields

The most unambiguous measurement of the upper critical field, $H_{c2}$, comes from the heat capacity data shown on Fig. 28. The jump in heat capacity, although a small portion of the total heat capacity, was easily measured and was rather close to the results of bulk Nb. If one defines the $H_{c2}$ verse T curve from the midpoint of the jump, as is commonly done (52), one finds the $H_{c2}$ verse T data shown in Fig. 29. For this as zoned 10 $\mu$m/s sample, the $H_{c2}$ data lie somewhat above the bulk Nb line. This means that the Nb in this rod structure was relatively clean with a kappa value close to 1.0 and a mean-free-path on the order of 30 to 50 nm. Hence, the presence of a Th matrix has only a minor effect on $H_{c2}$ of the Nb rods.

Because the heat capacity measurement is difficult to make on a large number of small wires needed for the systematic $J_c$ studies, an attempt was made to determine $H_{c2}$ verse T from 33 Hz susceptibility, $\chi$, data by Finnemore (76). A typical curve taken at 4.2 K is shown on Fig. 38 for a sample drawn to 0.02 cm diameter wire from a sample zoned at 200 $\mu$m/s. This gives an Nb filament size of about 7.7 nm and the sample was annealed at 850°C for one hour. The flux was totally excluded out to a flux entry field, $\mu_0 H_E$, of about 25 mT at which point the $\chi$ rises linearly with $\mu_0 H$ up to about 222 mT. At higher fields the slope increases quickly and the sample becomes completely normal at about 385 mT. Tentatively the critical fields have been marked as shown by the arrows.
This identification of $H_{c2}$ and $H_{c3}$, surface critical field, are not certain from Fig. 38 but there are several clues that these choices are correct. A plot of critical current data of this sample indicated that $H_{c2}$ should be about $\mu_0 H_K = 220$ mT using the scaling law of Kramer (77). In addition a plot, Fig 39, of $H_E$, $H_K$ and $H_{c3}$ for a large range of filament diameters shows that an average $H_{c3}/H_K$ is about 1.7 as predicted by de Gennes (22). The $H_E$ and $H_{c3}$ values were determined from $\chi$ data and $H_K$ from $J_c$ data. Although there is considerable scatter in these results, $\mu_0 H_E$ consistently runs in the 10 to 50 mT range; $\mu_0 H_K$ ranges from 180 to 280 mT; and $\mu_0 H_{c3}$ ranges from 370 to 430 mT. In addition, there does not seem to be large systematic changes in these characteristic fields with the diameter of the filament in the range from 10 to 120 nm. The corresponding fields for bulk Nb are $\mu_0 H_{c1} = 144$ mT, $\mu_0 H_{c2} = 271$ mT and $\mu_0 H_{c3} = 450$ mT, so the critical fields of the composite are not markedly different. On the basis of these results, this tentative assignment seems reasonable.

Transition Temperatures

In composite systems, the transition from the normal to the superconducting state takes place in a manner which differs from a homogeneous superconductor because the pair potential has a spatial as well as a temperature dependence. As shown on Fig. 28, there is a sharp rise in the heat capacity at 9.1 K which has a magnitude very close to that expected for the Nb rods if they were not connected to the Th. The midpoint is somewhat below the bulk $T_c$ for Nb of 9.25 K, an effect which could arise from Th dissolved in the Nb or from residual strain. If $T_c$
of this sample was detected by a 33 Hz a.c. Hartshorn bridge technique, with a measuring field parallel to the axis of the rods, one finds that the sample does not exclude all of the flux until temperature much below 9.1 K. Indeed in the temperature interval of the heat capacity rise, the \( \chi \) falls by only about 10\% a value comparable to the volume fraction of Nb. This indicates that the proximity coupling between the Nb rods through the Th matrix is not strong enough to shield against fields on the order of 0.2 mT until the temperature is approximately 1 K or more below the onset of superconductivity in the rods. For purpose of this discussion, \( T_c \) is defined by the jump in heat capacity, (52), for the Nb rods and is taken to be the point on the susceptibility curves where the percentage change in \( \chi \) is equal to half the volume fraction of Nb in the composite.

As stated previously, this material can be drawn into a fine 0.010 cm diameter wires and the basic structure of the rods remains intact. As the diameter of the Nb rods, \( d_f \), is reduced, \( T_c \) is systematically depressed. There is some variation with different zone rates the dominant factor controlling \( T_c \) is \( d_f \). A common way to describe the depression in \( T_c \) is through the extrapolation length \( b \) introduced by de Gennes (equation 23) to describe changes in the boundary condition on the wave function at the super-normal interface. Using Ginzberg-Landau theory in cylindrical geometry, Clem (78) has derived an expression for \( T_c \) in terms of the bulk transition temperature \( T_{cB} \), the coherence length, \( d_f \) and \( b \) given by

\[
\frac{T_c}{T_{cB}} = 1 - \left( \frac{2\xi}{d_f} \right)^2 u^2,
\]  

(52)
where,

\[ u \tan u = \frac{d_f}{2b} \]  

(53)

Taking the measured values of \( T_c \), \( b \) can be deduced to have the values shown on Fig. 40. At large filament diameters where \( d_f \gg \xi \), \( b = 100 \text{ nm} \) which is comparable to the spacing between rods. As \( d_f \) becomes smaller than \( \xi \), \( b \) becomes very large indicating that the wave function is nearly a constant across the Nb rod. These data, in conjunction with the model calculation (78), confirm the frequently used assumption that the pair potential is essentially constant across samples with \( d_f \ll \xi \). It should be remembered, however, that this discription was done entirely within the phenomenological Ginzberg-Landau-de Gennes-Werthamer approaches and no full theory for \( T_c \) is yet available.
SUMMARY

A very dense array of superconducting filaments, Nb, in a normal metal matrix, Th, can be prepared using directional solidification techniques in conjunction with standard wire drawing procedures. A typical zone melting run at 10 μm/s gives rod shaped morphology with rod diameter of 0.5 μm and a rod spacing of 1.6 μm. Specific heat measurements on these composites indicate an abrupt drop in pair potential at the superconductor-normal boundary as predicted by the de Gennes boundary conditions. Although there is as yet no full theory for superconductivity in these composites, a fit of the zero magnetic field heat capacity data, using the de Gennes - Werthamer proximity effect theory, gives a characteristic decay length of the order parameter, $k_N^{-1}$, which was given approximately by equation 51. This decay length is very sensitive to magnetic field and a field as small as 20 mT will reduce the average pair potential in the Th so that the specific heat shows the Th to be in the normal state to an accuracy of about 2%. 

Critical current samples were drawn from Th-Nb wires solidified at three different rates to give Nb filament diameters in the range of 8 to 116 nm. The critical current density was in the $10^4$ to $10^5$ A/cm$^2$ range for these wires and correlated well with the wire diameter. A critical state model fits the data rather well. The $J_C$ was insensitive to filament diameter in this range which indicates that the superconductor-normal metal boundaries were not the dominant pinning sites. The problems associated with making the $J_C$ measurement on this composite, made it difficult to perform definitive critical current studies.
As the diameter of the filaments decreases, $T_c$ is suppressed in roughly the manner predicted by GL. If an extrapolation length, $b$, defined by equation 23, is derived from the data as a function of filament diameter, it is found that $b$ becomes very large for $d_f < \xi$. This, then, indicates that $\Delta$ is independent of $x$ in this regime, which confirms this frequent assumption.
Figure 1. Th-Nb phase diagram (41)
Figure 2. Block diagram of apparatus used to record V-I characteristics in constant magnetic field
All transistors are mounted on heatsinks. Batteries are 2 V each Gould NAX-1350. All inductors are ferrite beads w/ the indicated number of wire loops. 1, 2, & 3 Power Tech P9501 Transistors (matched). Other transistors are 2N5886's.

Figure 3. Circuit diagram of 600 Amp battery power supply.
Figure 4. Block diagram of apparatus used to record sample voltage as a function of magnetic field at constant current.
Figure 5. Sketch of critical current sample holder (not drawn to scale)
Figure 6. Typical V-I characteristics at four different magnetic fields
Figure 7. Block diagram of apparatus used to measure the critical temperature.
Figure 8. Block diagram of thermometer calibration apparatus
Figure 9. Photograph of experimental stage of $^3$He cryostat with heat capacity sample holder.
Figure 10. Sketch of heat capacity sample holder (not drawn to scale)
Figure 11. Block diagram of heat capacity apparatus
Figure 12. Circuit diagram of heat capacity controller
Figure 13. A plot to illustrate the calibration shift of the capacitance thermometer between different cool downs.
Figure 14. Heat capacity technique test illustrated by plot of heat capacity divided by temperature versus temperature squared.
Figure 15. SEM micrographs of directionally solidified Th-Nb eutectic alloy: a) 8,650X at zoned diameter of 0.32 cm, b,c) 3700X and 7300X respectively, after drawn to diameter of 0.046 cm, d) 730X after drawn to diameter of 0.046 cm (a,c, and d were taken at a tilt angle of about 40° from the normal to the end of the wire)
Figure 16. Area reduction and annealing effects illustrated by $J_c$ versus $d_w^{-1}$.
Figure 17. Critical current data for samples from three different zone runs with critical state model.
Figure 18. Typical critical current versus applied magnetic field
Figure 19. Thermometer comparison between GRT 99 and GRT 4645
Figure 20. Thermometer comparison between GRT 665 and GRT 4645
Figure 21. Effect of temperature scale correction to heat capacity
Figure 22. Magnetoresistance effect of GRT 4645, percent change in resistance versus temperature at constant applied magnetic field.
Figure 23. Magnetoresistance effect of GRT 4645, apparent change in temperature versus temperature at constant applied magnetic field
Figure 24. Magnetoresistance effect of GRT 4645, percent change in resistance versus applied magnetic field at constant temperature.
Figure 25. Magnetoresistance effects of four GRT's, percent change in resistance versus temperature at constant applied magnetic field.
Addenda heat capacity

$0.48 < T < 2.83 \text{K}$

$H = 0.0 \text{ kOe}$

Figure 26. Addenda heat capacity illustrating the low temperature structures in zero magnetic field
Figure 27. Addenda heat capacity illustrating the applied magnetic field dependence.
Figure 28. Percent difference of sample heat capacity data from the normal state versus temperature
Figure 29. Critical field plot of Th-Nb from heat capacity data compared with magnetization data on pure Nb.
Figure 30. Sample heat capacity data taken in applied magnetic fields of 10.0 and 0.2 kOe with bulk data for comparison.
Figure 31. Sample heat capacity data taken in applied magnetic fields of 2.0, 1.0, and 0.5 kOe with 10.0 and 0.2 kOe data for reference.
Figure 32. Sample heat capacity data in zero applied magnetic field with bulk values, BCS Theory and 2 point model.
SAMPLE HEAT CAPACITY $0.48 < T < 4.0$ K

- ZERO FIELD DATA
- MODEL, CLEAN LIMIT

Figure 33. Sample heat capacity data in zero applied magnetic field with bulk values, BCS Theory and clean limit proximity effect model.
Figure 34. Sample heat capacity data in zero applied magnetic field with bulk values, BCS Theory and dirty limit proximity effect model.
Figure 35. The superconducting electrons contribution to the heat capacity for temperatures between 3.2 and 9.3 K, which was attributed to Nb, compared with the BCS Theory with $T_c = 9.1$ K.
Figure 36. The superconducting electrons contribution to the heat capacity for temperatures between 0.48 and 1.4 K with the normal state defined by the 10 kOe data and the BCS Theory for comparison with $T_c = 1.39$ K.
The data

\( T_c = 1.39 \, \text{K} \)

\( 0.48 < T < 1.40 \, \text{K} \)

Normal State = 0.2 kOe data

Figure 37. The superconducting electrons contribution to the heat capacity for temperatures between 0.48 and 1.4 K and the normal state defined by the 0.2 kOe data.
Figure 38. Typical susceptibility data for Th-Nb (75)
Figure 39. Critical field versus diameter of Nb filaments with the high field, open symbol points $H_{C3}$, closed symbol points $H_K$ and low field, open symbol points $H_E$. 

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Figure 40. Extrapolation length, $b$, versus Nb filament diameter.
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ACKNOWLEDGMENTS

The author wishes to thank the following individuals who contributed to the completion of this work: Dr. D. K. Finnemore who provided guidance and advice throughout the course of this research; Dr. J. D. Verhoeven, Mr. E. D. Gibson, Mr. T. E. Pedersen, and Mr. M. A. Noack for their work in sample preparation and SEM studies; Mr. J. E. Ostenson who was a constant source of sound advice; Dr. C. A. Swenson and Mr. M. S. Anderson for their advice on thermometry and experimental technique; Dr. J. R. Clem who provided guidance to this research; To the many fellow graduate students who provided unselfish assistance; And last, but certainly not least, the author wishes to thank his typist, V. L. Grove, for her accuracy and patience and to Dr. A. F. Clark for his understanding during the preparation of this manuscript.