MASTER

HEAT CAPACITY OF AMORPHOUS AND
DISORDERED Nb_3Ge THIN FILMS

N. A. H. K. RAO

**Solid State and Low Temperature
Physics Group**

SCHOOL OF PHYSICS AND ASTRONOMY

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HEAT CAPACITY OF AMORPHOUS AND
DISORDERED Nb₃Ge THIN FILMS

A THESIS
SUBMITTED TO THE FACULTY OF THE
GRADUATE SCHOOL OF THE
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BY
NAVALGUND ANANT HEMANT KUMAR RAO

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ABSTRACT

HEAT CAPACITY OF AMORPHOUS AND DISORDERED Nb_3Ge THIN FILMS

Heat capacity measurements on 1000-1500Å thick amorphous Nb_3Ge and granular Al films have been carried out using an ac technique. The major goal of the experiment was to study the effect of thermal fluctuations, both above and below the superconducting transition temperature T_c , in dirty, short mean[#]free path materials.

T_c for Nb_3Ge films prepared by sputtering, were typically on the order of 2.6K. Heat capacity was measured between 1K and 4.5K. The total heat capacity of the calorimeter for $T \gg T_c$ can be adequately represented by an electronic and a lattice term. For $T \ll T_c$ the data is consistent with the variation in the heat capacity of the film as predicted by the BCS theory. Since we were only interested in looking for changes in the heat capacity near T_c , no attempt was made to determine the absolute value of the heat capacity of the film. By carrying out a consistent fit to the data both above and below T_c , we were able to determine uniquely, the thermodynamic transition temperature T_{BCS} . By subtracting the extrapolated value of the fit from the measured heat capacity, close to T_{BCS} , we could determine the excess heat capacity both above and below T_{BCS} , which represents deviations from the mean field behavior.

ABSTRACT (continued)

Above T_{BCS} , the excess heat capacity is consistent with the Hartree approximation for a film in the intermediate regime between two and three dimensions. The width parameters, determined from a fit to the theory, increase linearly with the normal state sheet resistance of the film R^N , and agree with the Hartree predictions within 50%. Below T_{BCS} , the excess heat capacity shows a broad bump in some of the films. The nature and the physical origin of this bump is not clear at the present time.

With increasing sheet resistance R^N , the Nb_3Ge films showed an increasing temperature difference between T_{BCS} and the temperature where the film's resistance goes to zero. We have proposed that the evidence of finite resistance below the thermodynamic transition temperature T_{BCS} , indicates that perhaps a Kosterlitz-Thouless type of phase transition is taking place in our high sheet resistance films, which involves the binding and unbinding of vortecies at a temperature T_{2D} below T_{BCS} . The data is in quantitative agreement with the current theories on such a topological phase transitions in superconductors.

In Part II of the thesis we discuss the low temperature resistivity measurements on some dilute Pd(Fe) alloy films. For the concentration of Fe studied (below .3 at.%) these alloys are known to undergo a ferromagnetic phase transition below 7K. The resistivity, $\rho(T)$ begins to drop below T_C .

ABSTRACT (continued)

A similar behavior was seen in our films. However the change in resistivity due to the magnetic transition $\Delta\rho_m$ varied from sample to sample. It was found to be from 0.2 to 100 times larger than that is seen in bulk alloys of similar Fe concentration. When ever $\Delta\rho_m$ was large, the coefficient of the T^2 term for $T > T_c$ (believed to be due to electron-paramagnon scattering in host Pd) was also found to be large compared to that in bulk alloys. We do not understand the reason for such a behavior at the present time.

CONTENTS

	Page
ABSTRACT	i
TABLE OF CONTENTS.	iv
LIST OF FIGURES.	vi
LIST OF TABLES	viii
I. INTRODUCTION	1
II. FLUCTUATION HEAT CAPACITY: THEORY	8
(i) Mean Field Theory	8
(ii) Mean Field Theory with Fluctuations	9
(iii) Hartree Approximation	14
(iv) Screening Approximation	17
(v) Fluctuations in an Inhomogeneous	
Superconductor.	21
(vi) Previous Experimental Work.	26
III. KOSTERLITZ-THOULESS PHASE TRANSITION	30
IV. FLUCTUATION CONDUCTIVITY	39
V. EXPERIMENTAL PROCEDURE	43
(i) Sample Preparation.	43
(ii) ac-Temperature Calorimetry.	47
(iii) ac-Calorimeter Design and	
Thermometry	52
VI. ac HEAT CAPACITY MEASUREMENTS.	63
(i) Electronics	63
(ii) Measurement Procedures.	71

CONTENTS (continued)

	Page
VII. DATA AND ANALYSIS	77
(i) Heat Capacity of Al films	77
(ii) Heat Capacity of Nb ₃ Ge films	85
(iii) Kosterlitz-Thouless Phase Transition	109
(iv) Fluctuation Conductivity	123
VIII. CONCLUSION.	130
REFERENCES.	134

PART II

Low Temperature Electrical Resistivity

Measurements on Dilute Pd(Fe)

Alloy Thin Films

I. INTRODUCTION.	139
II. THEORY.	141
(i) Fisher and Langer Theory	141
(ii) Some Properties of Pd and Pd(Fe)	
Alloys	145
(iii) Review of Previous Experimental Work	150
III. MATERIALS AND METHODS	156
(i) Sample Preparation	156
(ii) Data Acquisition	160
IV. RESULTS AND ANALYSIS.	162
V. DISCUSSION.	175
REFERENCES.	180
ACKNOWLEDGEMENTS.	184

LIST OF FIGURES

Figure

- 1 Specific heat in the screening approximation from Ref. 22.
- 2 Specific heat in the screening approximation from Ref. 28.
- 3 H-T phase diagram for a superconductor undergoing a Kosterlitz-Thouless phase transition from Ref. 10.
- 4 Block diagram of the model for ac heat capacity technique.
- 5 Calorimeter.
- 6 Experimentally measured thermocouple emf, $E(T)$, for the Au(Fe) vs. Cu thermocouple.
- 7 Electronics.
- 8 Interface and online data acquisition.
- 9 C/T vs. T^2 for Al film SPAL-9.
- 10 C_{ex} vs. T for sample SPAL-9.
- 11 C/T vs. T^2 for sample Nb_3Ge -4.
- 12 C/T vs. T^2 for sample Nb_3Ge -6.
- 13 C_{ex} and R vs. T for sample Nb_3Ge -3.
- 14 C_{ex} and R vs. T for sample Nb_3Ge -4.
- 15 C_{ex} and R vs. T for sample Nb_3Ge -6.
- 16 C_{ex} vs. T for $T > T_{BCS}$ for sample Nb_3Ge -2.
- 17 C_{ex} vs. T for $T > T_{BCS}$ for sample Nb_3Ge -3.
- 18 C_{ex} vs. T for $T > T_{BCS}$ for sample Nb_3Ge -4.
- 19 C_{ex} vs. T for $T > T_{BCS}$ for sample Nb_3Ge -6.

LIST OF FIGURES (continued)

- 20 τ_0 vs. $R_{\square}^N$ for Nb_3Ge films.
- 21 C_{ex} and R vs. T for samples Nb_3Ge - 4, 6 and 3.
- 22 T_R/T_{BCS} vs. $R_{\square}^N$.
- 23 $R/R(4.2)$ vs. T in the tail region of resistive transition for sample Nb_3Ge -6.
- 24 $\ln(R/R(4.2))$ vs. T in the tail region of resistive transition for sample Nb_3Ge -6.
- 25 $\ln(R/R(4.2))$ vs. T for sample Nb_3Ge -6.
- 26 $\ln(\Delta R/R(4.2))$ vs. $\ln H$ for sample Nb_3Ge -6.
- 27 $(\sigma_N/\sigma_{\text{ex}})$ vs. T for sample Nb_3Ge -6.
- 28 $(R(T)/R_{\square}^N)$ vs. T for sample Nb_3Ge -6.

LIST OF TABLES

Table

- I Sputtering conditions during Nb_3Ge film preparation.
- II Estimates of γ and β for the components of the calorimeter.
- III Physical parameters for Al films.
- IV Comparison of least square fit results to heat capacity data of Nb_3Ge -4 sample.
- V Fitting parameters for the low and high temperature fit and the Hartree fit to the excess heat capacity of Nb_3Ge films.
- VI Results of fit to the excess conductivity of Nb_3Ge films.

I. INTRODUCTION

The study of phase transitions is one of the most fascinating areas of condensed matter Physics, which has attracted attention of many scientists in the past decade. There are many different kinds of phase transitions. Examples, to name a few are, the liquid-gas, ferromagnetic-paramagnetic, superfluid, and superconducting transitions. New transitions are being added to the list as time goes by. The transitions are all very different if one considers the details of the interactions involved. Yet they have a lot in common, in their aspect of qualitative change; a small shift in temperature or some other parameter suffices to trigger a spectacular change. One is able to go from an ordered state to a disordered state and vice-versa merely by changing the temperature. Thermodynamically the reason lies in the free energy $F = U - TS$, which is minimized by the state of thermodynamic equilibrium. There is competition between energy U (which favors order) and the entropy S (which favors disorder). A rise in temperature tilts the balance towards entropy and disorder. To distinguish between the two phases one defines an order parameter that has a nonzero value in the ordered phase and is zero in the disordered phase. In general an order parameter with a non-zero value corresponds to the breaking of a symmetry. For a superconductor, the order parameter is complex. Therefore it has two components

and can be described in terms of its amplitude and phase.

According to Landau¹, when the order parameter exhibits a discontinuity at the transition, one has a first order phase transition. When there is no such discontinuity, the transition is second-order. In a second-order phase transition, as one approaches the transition temperature T_c , the difference in the entropy of ordered and disordered phases goes to zero. Therefore it does not cost the system much entropy to fluctuate from one state into the other. For example, if one is approaching T_c from above (in the disordered state), then close to T_c the fluctuations lead to the appearance of locally ordered regions which persist for a certain length of time. One may define for such fluctuations a correlation length ξ , which measures their mean extension, and a correlation time τ which measures their mean life time. Both ξ and τ increase as one approaches T_c , and one enters a region strongly dominated by fluctuations, known as critical region. The correlation length ξ governs the static critical phenomena, while τ governs the time-scale of the dynamic ones. One can also define the order parameter correlation function that carries information about the spacial and temporal variation of the order parameter (fluctuations). The fourier transformation of these microscopic correlations $\Gamma(k, \omega)$, can be probed directly in some experiments, like neutron scattering in magnetic transitions or pair tunnelling in superconductors².

By measuring the wave vector and frequency dependence of the susceptibility (in a generalized sense) of the system, one can get all the information about the spacial and temporal variations of the order parameter.

Close to critical point of a second-order or higher-order transition, certain physical quantities appear to diverge with a power law in temperature with critical exponents that are not integers. Such singular behavior implies that the thermodynamic quantities and correlation functions are nonanalytic functions of their variables. In such circumstances the usual perturbation methods, which are Physicist's favorite tools are not applicable. Singular behavior demands a special procedure, such as, the renormalization group techniques. Such techniques are valuable because they are free from any perturbation theory.

The most fascinating aspect of phase transitions is that, even though they appear complex in nature they show some very simple characteristics. The various kinds of phase transitions mentioned earlier are very different from each other in the details of their interactions. All those systems undergoing most varied kinds of transitions, can be assigned to a small number of classes, each specified by a certain set of values of the exponents. The observed universal (i.e. independent of materials) character of the divergence suggests that only large scale behavior, not the detailed microscopic interactions, is relevant in a correct theoretical description. One also observes that some very

simple relations, called scaling laws exist between various critical exponents.

At first glance, the superconducting phase transition appears to be fundamentally different from the other higher-order transitions. A mean field or Landau type of theory works very well even close to T_c . The type of critical behavior that is observed in fluids and magnetic systems is not seen in superconducting transitions. It was Ginsburg³ who made it clear that the difference between the superconducting transition and the other transitions had to do with the size of the coherence length and did not involve any other fundamental feature of the superconducting transition. An estimate of the reduced temperature region ϵ_0 about T_c where the mean field theory breaks down and fluctuations become important is given by⁴,

$$\begin{aligned}\epsilon_0 &= [\xi^3(0) \cdot \Delta C / k_B]^{-2} && \text{(Three-dimensions)} \\ &= [\xi^2(0) \cdot \Delta C \cdot d / k_B]^{-1} && \text{(Two-dimensions)}\end{aligned}$$

where k_B is Boltzman constant,

ΔC is the mean field specific heat jump at T_c and $\xi(0)$ is the zero temperature coherence length. $\xi(0)$ in pure superconductors is by far the largest, being on the order of several thousand angstroms. This makes the critical region in superconductors extremely narrow, on the order of 10^{-12} K. On the other hand in magnetic systems and liquid He⁴, $\xi(0)$

is 1 to $10 \text{ \AA}^0$. Therefore the critical region is very large and mean field theory fails near T_c .

This has created a challenge for the experimentalists to find ways to widen the critical region in superconductors in order to study systematic departures from mean field theory. One can achieve this in a dirty superconductor, characterized by a short mean free path ℓ and a smaller $\xi(0)$. One can also achieve this by reducing one or more of the dimensions below the fundamental length of the problem, $\xi(0)$. Estimates of the critical region for Nb_3Ge films turns out to be on the order of 10^{-3} .

A lot of work has gone into the study of the fluctuation conductivity in amorphous and granular materials with short mean-free paths which are nearly two-dimensional. However, fluctuation heat capacity measurements have been sparse because of the technical problems involved. Because the effects are small in bulk systems, one needs to measure heat capacities of thin films which usually constitute a small fraction of the total heat capacity of the calorimeter. The high resolution needed to measure small changes in heat capacity due to fluctuations forces one to use unconventional techniques. Therefore, final results and conclusions are dependent on the technique and various parameters. We have measured the fluctuation heat capacity and conductivity of amorphous Nb_3Ge and granular Al films, about $1000 \text{ \AA}^0$ thick. We have attempted to achieve high resolution using an ac.

technique to measure heat capacity. The results are clean in the sense that they are not subjected to data fitting with a large number of parameters in order to extract the fluctuation contribution.

Kosterlitz-Thouless phase transition:

Kosterlitz and Thouless⁵ presented arguments in favor of a different kind of phase transition. The definition of long range order is not based on the behavior of a two-point correlation function. It can be referred to as topological long-range order. For a two-dimensional neutral superfluid at low temperatures vortices and antivortices are bound in pairs. Above a characteristic temperature T_{2D} , they disassociate into free vortices. At this transition Nelson and Kosterlitz⁶ have established a universal relationship between T_{2D} and the superfluid sheet density. Experiments on superfluid ⁴He films have apparently confirmed this prediction^{7,8}.

The reason for the existence of the predicted vortex-antivortex pairs is intimately connected with the fact that in such films the interaction energy between vortex pairs depends logarithmically on the separation between them.

Pearl⁹ has shown that vortex pairs in thin superconducting (i.e. charged superfluid) films have a logarithmic interaction energy out to a characteristic distance $\lambda_{\perp} = \frac{\lambda^2}{d}$ where λ is the London penetration depth. $\lambda_{\perp}$ for a dirty

type II superconductor can be very large, nearly macroscopic. The situation in a superconductor becomes analogous to the He^4 films. Doniach and Huberman¹⁰ have investigated the possibility of such a transition in superconductors. Beasley et al.¹¹ have derived a simple relationship for $T_{2D} < T_c$ which depends only on the sheet resistance R . If such a transition could occur in a superconductor, one would see a finite resistance below BCS transition temperature T_c due to free vortices. The resistance would go to zero as $T \rightarrow T_{2D}$ because the vortices will condense into a paired state. The temperature region below T_c where one would see a finite resistance, increases with increasing R . The resistance is also sensitive to magnetic field in this region. Our amorphous Nb_3Ge films have very large values of $\gamma_{\perp}$ and we do see evidence for a Kosterlitz-Thouless transition in these films. The details of the theory as applied to superconductors will be discussed later.

II. FLUCTUATION HEAT CAPACITY: THEORY

(i) Mean Field Theory (M.F.T.)

We will consider the Landau-Ginzburg (G-L) Theory,¹² which describes a superconducting system very well. The theory predicts a complex order parameter $\psi(r) = |\psi(r)|e^{-i\phi(r)}$. The average value of $\psi(r)$ is zero above T_c and nonzero below. $|\psi(r)|^2$ can be identified with the density of superconducting electrons. The superconducting free energy relative to the normal free energy density is expanded in terms of $|\psi(r)|^2$ for small $\psi(r)$, as

$$F_s(\bar{r}) = a(T)|\psi(\bar{r})|^2 + \frac{b(T)}{2}|\psi(\bar{r})|^4 \dots \dots \dots (1)$$

We have not considered here external fields and fluctuations.

To find the most probable value of $|\psi|$, which will minimize F_s , we

set $\frac{\delta F_s}{\delta |\psi|} = 0$ and require $\frac{\delta^2 F_s}{\delta |\psi|^2} > 0$. $|\psi| = 0$ minimizes F_s for

$a(T) > 0$ and $|\psi|^2 = -\frac{a(T)}{b(T)}$ for $a(T) < 0$. Since we wish $|\psi|$ to be

zero above T_c and nonzero below, we set $a(T) = a' \left(\frac{T - T_c}{T_c} \right) \cdot b(T)$ is slowly varying and we can approximate it by a constant. When one derives G-L theory from BCS¹³, one can identify a and b with other parameters of the system as follows,

$$a(T) = \frac{\hbar^2}{2m^*} \cdot \frac{1}{\xi^2(0)} \cdot \epsilon \quad (2a)$$

$$b(T_c) = b = 0.098 \frac{\hbar^2}{2m^*} \cdot \frac{1}{\xi^2(0)} \cdot \frac{1}{(k_B T_c)^2} \quad (2b)$$

where

$$\epsilon = \frac{T - T_c}{T_c}$$

$\xi(0)$ is the zero temperature coherence length, and k_B is the Boltzmann's constant, m^* is the effective mass of the charge carriers which is $2m$, where m is the electron mass. We can then calculate the entropy density $S = -\frac{\delta F}{\delta T}$ and the specific heat $C = T \cdot \left(\frac{\delta S}{\delta T}\right)$ just above and below T_c . Mean field theory predicts a discontinuity in the specific heat at T_c is given by,

$$\Delta C = 10.2 N(0) k_B^2 T_c$$

(ii) Mean Field Theory with Fluctuations

Following Ferrell¹⁴ we will consider the equation (1) above T_c but now we will include the effects of fluctuations. As a result, the order parameter can now take on finite value in a certain region of the system. Therefore $|\psi(\vec{r})|$ will have finite spatial variation above T_c . This is taken into account by adding

a gradient term $C|\nabla\psi(\vec{r})|^2$. Neglecting the fourth order term in $|\psi(\vec{r})|$. The free energy density becomes,

$$F_S = a'\epsilon|\psi(\vec{r})|^2 + C|\nabla\psi(\vec{r})|^2 + \dots \quad (3)$$

where

$$C = \frac{\hbar^2}{2m}$$

$$\psi(\vec{r}) = \sum_k \psi_k e^{i\vec{k} \cdot \vec{r}}$$

If we calculate the thermal average of $|\psi_k|^2$ by weighting the fluctuations according to the free energy which is associated with them¹⁵, we get,

$$\langle |\psi_k|^2 \rangle = \frac{2m^*}{\hbar} \frac{k_B T}{\left(k^2 + \frac{1}{\xi^2(T)} \right)} \quad (4)$$

where

$$\xi(T) = \left[\frac{\hbar^2}{2ma(T)} \right]^{\frac{1}{2}} = \frac{\xi(0)}{\sqrt{\epsilon}} \quad (5a)$$

$$= \frac{0.85 (\xi_0 \ell)^{\frac{1}{2}}}{\sqrt{\epsilon}} \quad \text{for } \ell \ll \xi_0 \text{ (dirty material)} \quad (5b)$$

where ξ_0 is the BCS coherence length. We will consider only the dirty-limit case which is appropriate for amorphous Nb_3Ge and Al .

From equation (4) it is clear that Fourier components describing variations in distance less than $\xi(T)$ come in with reduced weight. This means that we are emphasizing only the

slowly varying long wavelength fluctuations of the order parameter.

If we consider the order parameter correlation function defined as,

$$g(\bar{r}, \bar{r}') = \langle \psi^*(\bar{r}) \psi(\bar{r}') \rangle$$

—> where $\langle \rangle$ signifies thermal average, $g(\bar{r}, \bar{r}')$ only depends on relative coordinates $(\bar{r} - \bar{r}')$. Therefore we will replace it by the relative coordinate $\bar{r}$. Going through all the integrations, one can show that,

$$g(\bar{r}) = \frac{\sum_{\bar{k}} \langle |\psi_{\bar{k}}|^2 \rangle}{k} e^{i\bar{k} \cdot \bar{r}} \quad (6)$$

From equation (4) we know that

$$\langle |\psi|^2 \rangle = \frac{\sum_{\bar{k}} \langle |\psi_{\bar{k}}|^2 \rangle}{k} \quad (7)$$

In order to calculate the specific heat we start with the free energy which has the $\langle |\psi|^2 \rangle$ term in it and differentiate it twice with respect to T . Therefore from equation (6) it is clear that short range correlations $g(r)$ with $r \rightarrow 0$, are dominant in determining the fluctuation heat capacity.

Ferrell has calculated the fluctuation heat capacity of a two-dimensional film (film thickness $d \ll \xi(T)$) in the dirty limit.

$$\frac{C_{ex}}{\Delta C} = 0.6 \frac{1}{k_F^2 \ell d} \epsilon^{-1} \quad (8)$$

where k_F is the Fermi wave vector, ℓ is the electron mean free path and ΔC is the mean field (or BCS) jump in specific heat at T_c .

In the case of Nb_3Ge films, $d \approx 1000 \text{ \AA}$ and $\xi(0) = 30 \text{ \AA}$.

Therefore we are in a situation intermediate between two-dimensions and three-dimensions. The two-dimensional result given above has to be corrected. Going back to equation (7) we note that the sum is to be carried over all the $\vec{k}$'s allowed by the boundary conditions on $\psi(\vec{r})$. If we apply the condition that the normal derivative of ψ be zero at the boundaries of the film of thickness d , width w and length L , the allowed wave vectors are restricted to those having components given by,

$$k_x = \frac{N_x \pi}{d}, \quad k_y = \frac{N_y \pi}{w}, \quad k_z = \frac{N_z \pi}{L} \quad (N_x, N_y, N_z = 0, 1, 2, \dots)$$

From equation (4) we note that the contribution from $\langle |\psi_k|^2 \rangle$ goes down as $\frac{1}{k^2}$ for large k . Normally in a film $w, L \gg d$. Therefore as

k_y and k_z are very small compared to k_x , and k_x contribution is dropped from the summation in a two-dimensional case. The k_x contribution can be included by first integrating over $k_y - k_z$ plane, for a fixed value of k_x and then summing contributions of all such planes. The effect of this is to simply multiply the final result by,

$$G(T) = \sum_{N_x=0}^{\infty} \frac{1}{\left(1 + \frac{N_x^2 \pi^2 \xi^2(T)}{d^2}\right)} = \frac{1}{2} \left[1 + \frac{d}{\xi(T)} \coth \frac{d}{\xi(T)} \right] \quad (9)$$

Therefore the fluctuation heat capacity of a film in the intermediate region is given by,

$$\frac{C_{ex}}{\Delta C} = 0.6 \frac{1}{\left(k_F^2 d\right)} \cdot \epsilon^{-1} \cdot G(T) \quad (10)$$

we can define a width parameter $\tau_0 = 0.6 \frac{1}{\left(k_F^2 d\right)}$. Aslamazov and Larkin¹⁶ obtained results for three-dimensional case, along with their calculation for fluctuation conductivity. They did a microscopic calculation but did not extend their results to the two-dimensional case.

In arriving at the result given by equation (10), we have kept only the $|\psi|^2$ term in the free energy and added a gradient term to introduce the effect of fluctuations. Equation (10) shows that C_{ex} diverges at T_c . This is because we have neglected the $|\psi|^4$ term. Therefore, the above results are valid only far away from T_c .

Before concluding this section one should note that in order to evaluate the integral in equation (7), we have introduced a cut off ususally called the "Debye cutoff." This simply introduces a constant term which can be absorbed in the renormalization

of T_c . The validity of equations (8) and (10), can be estimated by considering where the non-linearity $\sim b|\psi|^4$ becomes important. According to Ferrell¹⁷, this occurs when

$$\xi(T) \leq \xi_c \equiv 1.7 \left(\frac{\hbar^2}{2m} \right)^2 \cdot b \cdot k_B \cdot T_c$$

This also implies

$$\frac{C_{ex}}{\Delta C} \leq 0.1.$$

(iii) Hartree Approximation

In this section, we will consider the theories that go beyond the free fluctuation theory of the previous section. We now want to go one step further and include the $|\psi|^4$ term in our calculations. Gunther and Gruenberg¹⁸ have taken such an approach and we will consider their results here.

Including the quartic term, the free energy can be written as,

$$F(\psi) = \int d\vec{r} \psi^*(\vec{r}) \left[a(T) + \frac{b}{2} |\psi(\vec{r})|^2 - \frac{\hbar^2}{2m} \cdot \nabla^2 \right] \psi(\vec{r})$$

$a(T)$ and b have been identified in the previous section. The Hartree approximation consists of replacing $|\psi|^4$ in the fourth order term as follows¹⁹.

$$|\psi|^4 \rightarrow 2\langle |\psi|^2 \rangle^2 - \langle |\psi|^2 \rangle^2$$

The free energy in Hartree approximation becomes,

$$F(\psi) \rightarrow F_H(\psi) = \int d\vec{r} \psi^*(\vec{r}) \left[a(T) + \sigma - \frac{\hbar^2}{2m} \nabla^2 \right] \psi(\vec{r}) - \frac{V\sigma^2}{2b} \quad (11)$$

where V is the sample volume and the self-energy σ is determined self-consistently by the following equation,

$$\sigma \equiv b \langle |\psi(\vec{r})|^2 \rangle = \frac{b}{V} \sum_{\vec{k}} \langle |\psi_{\vec{k}}|^2 \rangle$$

or

$$\sigma = \frac{bk_B T}{V} \sum_{\vec{k}} \left(a + \sigma + \frac{\hbar^2 k^2}{2m} \right)^{-1} \quad (12)$$

When one compares equation (12) with equation (4) of the previous section, it is clear that one can define a new coherence length $\xi(T)$ which is different from $\xi(T)$ of free fluctuation theory since it now contains the self-energy term σ in addition to $a(T)$. Thus,

$$\xi(T) = \left[\frac{\hbar^2}{2m(a(T) + \sigma)} \right]^{\frac{1}{2}} \quad (13)$$

After computing the sum (or integral) in equation (12), one can calculate the optimal free energy and finally the heat capacity.

For a two-dimensional system ($\xi(T) > d$), the sum in equation (12) can be converted into an integral which can be readily evaluated. After some algebra one can write the self-consistency equation as,

$$\eta = \varepsilon + \tau_0 \ln [1 + (q_c \xi(0))^2 / \eta] \quad (14a)$$

where

$$\eta = \xi^2(0)/\xi^2(T) \quad (14b)$$

and τ_0 is the width parameter.

$$\tau_0 = \frac{1}{(k_F^2 \ell d)} \quad (15)$$

q_c is the Debye cutoff necessary to evaluate the integral in equation (12). For a dirty superconductor q_c is on the order of inverse mean free path, ℓ^{-1} .

The result of the calculation is that the excess heat capacity rises continuously over a temperature range on the order of several times the width parameter τ_0 going from zero to a value Δc given by the bulk specific heat discontinuity in the absence of fluctuations.

$$\bar{c}(T) = \frac{c_{ex}(T)}{\Delta c} = \left[1 + (\xi(0)/\xi(T))^2 / \tau_0 \right]^{-1} \quad (16)$$

One has to solve equation (14) for η and then use it in equation (16) to calculate excess heat capacity. τ_0 and T_c are the two parameters.

If we are in an intermediate range between two-dimension and three-dimension, then the summation in equation (12) has to be modified in a similar way as discussed in the previous section. After carrying out the calculations, equation (14a) is then of the form:

$$\eta = \epsilon + \tau_0 G(T) \ln \left[1 + (q_c \xi(0))^2 / \eta \right] \quad (17)$$

where $G(T)$ is defined by equation (9), except that $\xi(T)$ is now evaluated in the Hartree approximation and is given by equations (14a) and (14b).

It is clear from equation (17) that this change has the effect of introducing a temperature dependent width parameter. In the dirty limit, this will change equation (16) for the excess heat capacity to,

$$\bar{c}(T) = \frac{C_{ex}(T)}{\Delta C} = \left[1 + (\xi(0)/\xi(T))^2 / (\tau_0 G(T)) \right]^{-1} \quad (18)$$

In the free fluctuation theory $\eta = \epsilon$ and in the limit $\epsilon \gg \tau_0$ the above expression reduces to the free fluctuation result of the previous section (equation 10). We will compare our experimental results on the excess heat capacity due to fluctuations in Nb_3Ge films with the above expression.

(iv) Screening--Approximation

In the previous sections we have considered a perturbative type of approach to the problem. In the free fluctuation theory we completely neglect the interaction of the fluctuations. In the Hartree approximation we treat this interaction in the lowest order. Perturbation theory cannot be used for treating interactions as the individual Feynmann diagrams diverge badly. Ma²⁰ first introduced the concept of using renormalization group

techniques to the problem of an n -parameter field in a d -dimensional space. Ferrell and Scalapino²¹ first used the $\frac{1}{n}$ expansion technique and calculated the specific heat of a superconducting film²². They predicted a peak in the heat capacity over and above the Hartree approximation heat capacity. We will outline their calculations and then give the results.

They generalize the Ginzberg-Landau formalism to an n -component field (n is the number of components of the order parameter, $n = 2$ for a superconductor), and write the free energy density as,

$$F[\psi(\vec{r})] = \frac{1}{2} \sum_{i=1}^n \left[(\nabla \psi_i)^2 + \psi_i^2 \left\{ \epsilon + (2n)^{-1} \sum_{j=1}^n \psi_j^2 \right\} \right] \quad (19)$$

distance r and ϵ have been scaled by $\xi(0)$ and τ_0 respectively. $n \rightarrow \infty$ is the Hartree limit where the component ψ_i is acted upon by an effective interaction averaged over all the other components. The coefficient of ψ_i^2 defines the inverse coherence length κ by,

$$\begin{aligned} \kappa^2 &= \epsilon + \lim_{n \rightarrow \infty} \left(n^{-1} \sum_{j=1}^n \langle \psi_j^2 \rangle \right) \\ &= \epsilon + G(0) \end{aligned}$$

$G(0)$ is a correlation function which has the Ornstein-Zernike form. In two-dimensions $G(0) = (2\pi)^{-1} \ln \frac{q_c}{\kappa}$. Therefore the self-consistent equation for κ is the same as the one we considered in the previous section.

For finite n , the last term in equation (19) represents the interaction of the fluctuations. In analogy with the plasmon problem they introduce a screened interaction given by ^{23, 24},

$$V = n^{-1} + n^{-1}\pi n^{-1} + n^{-1}\pi n^{-1}\pi n^{-1} + \dots = \frac{-n^{-1}}{(1 + \pi n^{-1})}$$

The bare interaction is $1/n$ and π is an irreducible polarization associated with the fluctuations. They calculate the lowest order contribution π_0 , consisting of closed loops composed of two fluctuation propagators. The contribution of the polarization graphs to the free energy are found by summing over ring diagrams. Without going into the details we show the results of such a first-order screening approximation for $n = 2$ in figure 1 (from reference 22). The temperature axis needs some clarification.

$$\tau = \frac{(T - T_c)}{T_c * \tau_0} + \Delta\tau_n \text{ where } \tau_0 \text{ is width parameter and } \Delta\tau_n \text{ is an } n\text{-}$$

dependent temperature shift, or temperature renormalization, related to the Debye cutoff. It can be seen that the screening approximation differs significantly from the Hartree approximation ($n \rightarrow \infty$). They demonstrate that there should be a definite peaking of the heat capacity, rising up to 30% of the BCS jump. Bray and Rickayzen²⁵ have used the screening approximation to treat the fluctuations beyond Hartree approximation. Even though there calculations are less illuminating than the $1/n$ technique, they also predict a similar peaking in the heat capacity.

FIG. 1. Specific heat C of a two-dimensional Ginzburg-Landau model versus reduced temperature τ . C is normalized to unity as $\tau \rightarrow -\infty$. The curve labeled " ∞ " shows the specific heat per component of an n -component model in the Hartree limit, $n \rightarrow \infty$. The curve labeled "2" shows the first-order screening approximation for $n=2$. The difference between the two curves is $\frac{1}{2}\delta C$, the screening correction, and is shown by the bottom curve. The Feynman graph shown in the upper right-hand inset is a typical ring diagram included in the screening correction.

Fig. 1 (From Ref. 22)

(v) FLUCTUATIONS IN AN INHOMOGENEOUS
SUPERCONDUCTOR

So far we have considered the theoretical predictions for the fluctuation heat capacity of a homogeneous superconducting film characterized by a uniform T_c over the whole sample. Now we ask what happens if the sample has a certain distribution of T_c 's which is a consequence of a geometric inhomogeneity.

One can incorporate such a model within the framework of the Ginzburg-Landau formalism. Simánek^{26, 27} has done such a calculation. The variation in T_c is taken into account by considering the coefficient of the $|\psi|^2$ term to be spatially varying. The free energy is then of the form,

$$F = \int d^2\bar{r} [a(\bar{r}, T)|\psi|^2 + c|\nabla\psi|^2] \quad (20)$$

where $a(\bar{r}, T) = a_0(T) + \delta a(\bar{r})$. The coefficient of a_0 is that of a homogeneous system. $\delta a(\bar{r})$ is the spacial fluctuation proportional to $\delta T_c(\bar{r})$. Note that Simánek does not consider the $|\psi|^4$ term. He assumes a spectral density function $S(q)$ of the δa fluctuations, which is constant for $q \leq 1/\lambda$ where λ is the frozen-in disorder, and zero otherwise. One also has an additional parameter $\langle \delta^2 T_c \rangle$, the mean square fluctuations of T_c . Detailed calculations then show that the inverse square of the coherence

length κ^2 is modified in the same manner as in the Hartree approximation of section (iii).

$$\kappa^2 = \frac{\epsilon}{\xi(0)} + \frac{T_{2m}}{d\hbar^2 \Lambda} \Sigma(0, T)$$

where Σ is the lowest order contribution to self-energy that is calculated treating fluctuations in δa as perturbations. The heat capacity $\sim \frac{1}{\kappa^2} \left(\frac{\delta \kappa^2}{\delta T} \right)$ has two terms. One is proportional to

$\frac{1}{\kappa^2} = \epsilon^{-1}$ and the other is proportional to $\frac{\delta \Sigma}{\delta T}$ which diverge at a different temperature given by T_c^* as $(T - T_c^*)^{-\frac{1}{2}}$.

The results can be summarized as follows:

1. Far away from T_c (average) the system will behave like a homogeneous superconductor with free fluctuations, i.e., $C_{ex} \sim (T - T_c)^{-1}$.

2. At a certain cross-over temperature $t_{cr} = (T_c^* - T_c)/T_c$, the system will exhibit gaussian random behavior and the heat capacity will diverge as $\sim (T - T_c^*)^{-\frac{1}{2}}$ where T_c^* is lower than T_c but is related to T_c , through the parameters λ and $\langle \delta^2 T_c \rangle$.

3. At some point this theory will fail. Simánek calculates this cross-over by estimating the importance of $|\psi|^4$ term.

It turns out to be identical to that of a homogeneous superconductor. Therefore this theory is only useful in the tail region of the fluctuation heat capacity.

Bray²⁸ has developed a theory of inhomogeneous superconductors using the $\frac{1}{n}$ expansion technique of Scalapino et al.,²² which we have considered in section (iv).

Bray has used only one parameter g in his calculations, where $g = [\lambda/\xi(0)]^2 <\delta^2 T_c> / T_c (\Delta T_c)$ as a measure of the amount of inhomogeneity in the system. His approach was to take $n = \infty$ limit of the homogeneous system as starting point and to use perturbation theory to compute corrections to order $1/n$ and to order g . Since this approach goes beyond the Hartree approximation, the results do not show any divergence and should be valid closer to T_c . In fact he goes even further than reference 22 and presents a self-consistent calculation which is expected to be more reliable than the simple perturbation theory for not too small values of $1/n$ and g .

The final results are very complicated and messy, therefore it will not serve any purpose to reproduce them here. Instead we reproduce the plotted curve from the self-consistent approach. From Bray's calculations it is clear that the g order contribution to the heat capacity due to inhomogeneity is negative in the region where a peak due to order $(1/n)$ contribution was previously predicted. Therefore when one adds the $O(g)$ and $O(1/n)$ corrections to the Hartree heat capacity, the peak disappears for $g \geq 1$. For $g = 2$, we can see that the width of the transition is broadened and the heat capacity approaches

FIG. 8. Specific heat of the two-dimensional GL model according to the self-consistent approach, with $n=2$, for three values of g . For $g \geq 1$ the peak associated with the $g=0$ curve disappears so that the specific heat resembles qualitatively the Hartree result labeled C.

Fig. 2 (From Ref. 28)

asymptotically the limiting value of 1. The meaning of τ is the same as explained earlier.

Bray has also shown that g can be related to the variation in T_c with concentration of an alloy,

$$g \sim 14 c(1 - c) \left(\frac{n}{n_A} \right) \left(\frac{T_c}{\mu} \right) \left(\frac{d \ln T_c}{dc} \right)^2$$

where c is the concentration of one component, n_A is the number of atoms per unit volume, μ is the fermienergy ($k_B = \hbar = 1$). It has been assumed throughout that $\lambda \ll \xi(0)/\sqrt{(T - T_c)}$ and $\lambda \gg d$. However the opposite limit, $\lambda \ll d$ and/or $\lambda \gg \xi(0)/\sqrt{(T - T_c)}$ (long range fluctuations in T_c) will not wipe out the peak in the heat capacity.

(vi) PREVIOUS EXPERIMENTAL WORK

Experimental measurement of fluctuation heat capacity have been very sparse. Perhaps the main reason is the difficulties in resolving small changes in the heat capacity and separating the heat capacity of a film from that of the substrate.

One of the early measurements of fluctuation heat capacity on bulk Ta and Sn was done by Cochran.²⁹ Transitions were only about 5mK wide. He attempted to fit the data to free fluctuations with a Gaussian distribution of T_c 's.

Barnes et al.³⁰ have measured the heat capacity of an extreme type-II superconducting alloy Ti - 16 at .% Mo. According to Lee and Shenoy³¹, the effective dimensionality of the sample can be changed from 3 to 1 by the application of magnetic field. Barnes et al.³² later reanalyzed their data based on reduced one-dimensional fluctuation theory in Hartree approximation. Bray³³ later showed that a screening approximation gave better agreement of experiment with theory. Thouless³⁴ did an exact calculation of the critical fluctuations of a type-II superconductor near the upper critical field. Measurements of pure bulk Nb by Farrant and Gough³⁵ are in excellent agreement with this theory.

Zally and Mochel^{36, 37} measured fluctuation heat capacities of amorphous $\text{Bi}_x\text{Sb}_{1-x}$ films by an ac technique. Films that they studied, ranged in thickness from $150\text{\AA}$ to $1350\text{\AA}$. Two-dimensional excess heat capacities due to fluctuations were observed in both $800\text{\AA}$ and $1350\text{\AA}$ thick films, the only samples for which quantitative data was available. The films were flash evaporated onto cold substrates held at 4K. It is rather surprising that they found good agreement with the two-dimensional free fluctuation theory covering as much as 60% of the BCS jump. One would have expected the free fluctuation theory to break down and show divergence before that. No peaking in the heat capacity was observed. Zally and Mochel did not make an independent measurement of the coherence length $\xi(0)$. For amorphous Bi, $\xi(0) \approx 80\text{-}90\text{\AA}$, for amorphous BiSb, $\xi(0)$ would probably be even smaller. With this order of magnitude of $\xi(0)$ they should not have observed two-dimensional fluctuation behavior except very close to T_c , at least in $1350\text{\AA}$ thick film and probably in the $800\text{\AA}$ film as well. Gunther and Gruenberg¹⁸ showed that the data for the $1350\text{\AA}$ film was in excellent agreement with the two-dimensional Hartree approximation. According to their theory, the width parameter τ_0 is proportional to the sheet resistance of the film, (the sheet resistance $R_{\square} = R \frac{w}{l}$ where R is the resistance of the film and w and l are width and length respectively). With the $800\text{\AA}$ film there is also similar agreement of the data with the Hartree calculation, however the fitted value of τ_0 is smaller.

than that of the 1350Å thick film even though R_c was larger for the 800Å film. This makes one wonder whether the agreement of experiment and theory is fortuitous. Zally and Mochel³⁷ evaporated the films onto the center of a thin glass bubble used as a substrate. The substrate forms the bottom of a copper can which is filled with liquid helium prior to evaporation and is later on pumped out. There may be problems in this experiment with adsorbed layers of He^4 contributing to the heat capacity for $T > T_c$ as the heat capacity does not vary simply as $\gamma T + \beta T^3$. The data in this regime must be fit to a fourth order polynomial in T . The results of the background subtraction, needed to determine the excess heat capacity due to fluctuations, can be very sensitive to the quality of fit for $T \gg T_c$. Zally and Mochel do discuss the sensitivity of the excess heat capacity extracted from the fit to the data for $T \gg T_c$. They were apparently able to create a peak in the excess heat capacity by choosing an appropriate background but only at the cost of letting the heat capacity drop to zero 0.1K below T_c . Such an analysis detracts from the credibility of the results of the experiment.

Goldman and Solinsky³⁸ have measured the heat capacity of 1000Å granular Al films. They used the resistive transition of the film as its own thermometer. The results indicate a rise in the heat capacity near the lower end of the transition where the film resistance became zero. The rise was several

times higher than the BCS jump. The temperature width of the rise (or a peak in one sample) was on the order of 5mK. They did not carry out any quantitative analysis of the data. This method has the advantage that $\frac{dR}{dT}$ is large in the region of the film's resistive transition and can serve as a good thermometer. One does not need a separate thermometer which will add more heat capacity. The sample is in excellent thermal contact with the thermometer. The disadvantage is that one can take data only in a limited temperature range near T_c . Therefore one cannot do a quantitative analysis with the data obtained in this fashion.

No other work on fluctuation heat capacity of thin films has been reported to the author's knowledge. The previous history illustrates the difficulties involved in doing such experiment and the difficulty in extracting meaningful data from the total heat capacity.

III. KOSTERLITZ-THOULESS TRANSITION

Kosterlitz and Thouless⁵ have predicted an entirely new type of phase transition in neutral superfluids, xy models and two dimensional solids which has been called a topological phase transition. In two dimensional superfluid films, for example, at low temperatures the system would have bound vortex-antivortex pairs. At higher temperatures the dissociation of these pairs leads to a transition. The existence of such bound pairs is intimately connected with the fact that in such films the interaction energy between vortex pairs depends logarithmically on the separation between them. In their original discussion Kosterlitz and Thouless also pointed out that for a charged superfluid (superconductor) such arguments could not be carried through, because for large separations the interaction energy between the two vortices with opposite circulation falls off as r^{-1} instead of increasing as $\ln r$, where r is the distance between the vortices.

As pointed out by Beasley, Mooij and Orlando¹¹, there is a regime in superconductors for which the interaction energy is logarithmic. They recalled the calculations of Pearl⁹ on the properties of quantized vortices in superconducting films. His results show that in films, distant regions are electromagnetically coupled through free space, while in bulk samples, regions are

screened from each other by free electrons. The pair interaction energy U_{ij} between two vortices is given by,

$$U_{ij} = \left(\frac{\phi_0}{2\pi\lambda} \right)^2 d \left[\ln \frac{\lambda}{r_{ij}} + \ln \frac{4\lambda}{d} - \gamma \right], \quad r_{ij} \ll \frac{2\lambda^2}{d} \quad (21a)$$

$$= \left(\frac{\phi_0}{2\pi} \right)^2 \frac{1}{r_{ij}}, \quad r_{ij} \gg \frac{2\lambda^2}{d} \quad (21b)$$

where λ is the bulk London penetration depth of the material of the film, d is the film thickness, ϕ_0 is the flux quantum ($\frac{\hbar c}{2e}$) and r_{ij} is the distance between the vortices. The transverse penetration depth, $\lambda_{\perp} = \lambda^2/d$, characterises the separation distance, below which the logarithmic interaction between the pairs is dominant.

For a dirty superconductor $\lambda(T)$ is given by³⁹,

$$\lambda(T) = \frac{1}{\sqrt{2}} \left[\frac{mc^2}{4\pi ne^2} \right]^{\frac{1}{2}} \left[\frac{\xi_0}{1.33\lambda} \right]^{\frac{1}{2}} \left[\frac{T - T_c}{T_c} \right]^{-\frac{1}{2}} \quad (22)$$

where m and n are the electronic mass and density respectively, ξ_0 is the BCS coherence length and λ is the mean free path. Beaseley, Mooij and Orlando¹¹ noticed that in thin, high sheet resistance superconducting films $\lambda(T)$ could be large enough so that the vortex interaction energy might be logarithmic thus permitting a topological phase transition to occur.

Doniach and Huberman¹⁰ have applied the idea of Kosterlitz and Thouless⁵ to thin-film dirty limit superconductors. They consider thermally excited vortex pairs interacting via a two-dimensional coulomb force. The interaction energy is given by,

$$\begin{aligned}
 U_{ij} &= -2q_i q_j \ln(r_{ij}/\xi) \quad r_0 \leq r_{ij} \ll \lambda_{\perp} \\
 &= 0 \quad r_{ij} \ll r_0
 \end{aligned} \tag{23}$$

where $q^2 = (\frac{\phi_0}{4\pi})^2 \lambda_{\perp}^{-1}$ measures an effective charge for the vortices and ξ is the coherence length which also determines the core radius r_0 .

The effective hamiltonian of a system of vortices in a superconducting film may be written as,

$$H = N\mu_0 + U_0 \left| \sum_i \text{Sgn}(q_i) \right|^2 + \frac{1}{2} \sum_{i \neq j} U_{ij} + H \sum_i m_i \tag{24}$$

where N is the total number of vortices, μ_0 is the chemical potential associated with the vortex core ($\mu_0 = \frac{q^2}{8}$), U_0

is the magnetic energy associated with an excess of vortices of a given sign, which is given by,

$$U_0 = q^2 \ln(R/\xi)$$

where R is the sample size. The third term gives the total pair interaction energy. The fourth term comes from the interaction of an individual vortex with the external field H . M_i is the paramagnetic moment of the i^{th} vortex given by $m_i = m \text{Sgn}(q_i)$ where $m = (\frac{\phi_0}{16\pi}) \frac{R^2}{\lambda_{\perp}}$.

It is assumed that the chemical potential μ_0 is sufficiently large so that there is a dilute gas of vortices. At low temperatures the configurations of least energy are those in which vortices of equal and opposite sign are bound in dipole

pairs. The mean square separation of the vortices making up such a pair, ignoring the interaction between the pairs is,

$$\langle r^2 \rangle = r_0^2 (\beta q^2 - 1) / (\beta q^2 - 2)$$

In this simple approximation the polarizability which is proportional to $\langle r^2 \rangle$ diverges when $\beta q^2 = 2$. This is the signature of a phase transition to a superconducting state at a temperature T_{2D} is given by,

$$k_B T_{2D} = \frac{1}{2} q^2 = \frac{1}{2} \cdot \left(\frac{\phi_0}{4\pi} \right)^2 \cdot \frac{1}{\lambda_{\perp} T_{2D}} \quad (25)$$

The above expression can be solved for T_{2D}/T_c using equation (22) and the expression for electrical conductivity in the free electron model. Beasley et al.¹¹, using the dirty limit theory of superconductivity have shown that this leads to a very simple universal relationship,

$$\frac{T_{2D}}{T_c} = \frac{11830/R_{\square}}{(1 + \frac{11830}{R_{\square}})} \quad (26)$$

where $R_{\square} = \rho/d$ is the sheet resistance of the film, ρ is the normal state resistivity and d is the film thickness. T_c is the BCS transition temperature of the film.

Let us now consider the meaning of such a phase transition and how it might manifest itself in a superconducting system. At temperature $T < T_{2D} < T_c$, and in zero field one would expect a state with bound vortex and antivortex pairs. No free vortices are present and the electrical resistance would be

zero. For $T_{2D} < T < T_c$ the bound pairs break up and the system might be described as a vortex-antivortex plasma. Since unpinned and unbound vortices would be swept across a film by a finite electric current, the sample is expected to exhibit a finite flux flow resistance, decreasing to zero as $T \rightarrow T_{2D}$. In the range $T_{2D} < T < T_c$ one would expect to observe a finite electrical resistance. From equation (26), one can see that the width of this region is a monotonically increasing function of $R_\square$. Therefore the resistance transitions will show increasing broadening with increasing $R_\square$.

Doniach et al.¹⁰ have also calculated the phase diagram and the effects of temperature and applied magnetic field on the resistance behavior of the superconducting film undergoing a Kosterlitz-Thouless or topological phase transition. At $T = 0$, H_{c1} is the field for which the film becomes unstable to the nucleation of a single vortex. At T_{2D} , the vortex pairs of largest separation become unbound and the resulting screening leads to a reduction of H_{c1} to zero for $T > T_{2D}$. As the field is further increased, the superconducting order parameter is reduced to zero at the depairing field $H_{c2}(T)$ and one attains the normal state. The H-T phase diagram is shown in Fig. 7, from reference 10. Phase I has almost no free vortices present and should exhibit zero resistance. Phase II has unbound vortices forming a screened vortex plasma. These vortices will

experience a Lorentz force in the presence of current flow and therefore will be swept across the direction of current flow towards film boundaries giving rise to a finite resistivity $\rho(T, H)$ which can be written as³⁹

$$\frac{\rho(T, H)}{\rho_n} = 2\pi\xi^2 (n_+ + n_-) \quad (27)$$

where $n_{\pm}$ are the densities of the free vortices with paramagnetic moments parallel (+) or antiparallel (-) to the field.

The renormalization of the interactions between pairs due to the other vortices may be described by an effective dielectric constant $\epsilon(r, T)$. This modifies the expression for T_{2D} (equation (25)) to as follows,

$$k_B T_{2D} = \frac{1}{2} \left(\frac{\phi_0}{4\pi} \right)^2 \frac{1}{\lambda_{1D} T_{2D} \epsilon(\infty, T_{2D})} \quad (28)$$

Considering the screening effect in the phase II and following Kosterlitz's general scaling arguments, one can calculate

$$n_+ = n_- = \frac{1}{2} n_{\text{free}} \text{ self consistently in zero field as }^{10},$$

$$n_{\text{free}} = 2\xi^{-2} (e^{-\beta\mu_0})^{\nu(T)} \quad (29)$$

where

$$\beta = \frac{1}{k_B T}, \quad \nu(T) = \frac{1}{(t + \chi t^{\frac{1}{2}})} \quad \text{with}$$

$$t = \left(\frac{T}{T_{2D}} - 1 \right) \text{ and } \mu_0 \approx \mu_0 + \ln \left(\frac{C^2}{\pi} \right).$$

In the presence of an externally applied magnetic field H , there will be a net imbalance $(n_+ - n_-) > 0$ for all non zero fields. This leads to $H_{c1} = 0$ and a finite magnetization μ in the phase II region. The free vortex density $n_{\text{free}} = (n_+ + n_-)$ has to be obtained by solving the following pair of equations self-consistently,

$$M = \pi R^2 n_{\text{free}} \sinh \beta (mH - m_\beta M) \quad (30a)$$

$$n_{\text{free}} = 2\xi^{-2} (e^{-\beta\mu_0} \cosh \beta (mH - m_\beta M)) \quad (30b)$$

where

$$M = \pi R^2 (n_+ + n_-) \text{ and } m_\beta = \frac{q^2}{2} \left[\ln \left(\frac{R}{\xi} \right) - \frac{1}{2} \right]$$

m is the paramagnetic moment of a vortex given by

$$\left(\frac{\phi_0}{16\pi} \right) \frac{R^2}{\lambda_\perp}.$$

$\rho(T, H)$ calculated from the equations (27) and (30), has been shown in the inset of Fig. - 3. It illustrates the strong dependence of resistivity on small magnetic fields in the phase II region.

In summary we see that in dirty-limit Type II superconductors $\lambda_\perp$ can be very large, nearly macroscopic. This leads to a coulomb-like interaction between vortex pairs. The situation becomes analogous to He^4 films where a Kosterlitz-Thouless transition has been reported. Considering the possibility of such a transition in superconductors leads to a simple relationship between T_{2D} and T_c which depends only on $R_\square$. The physical

Fig. 3 (From Ref. 10)

manifestation of the vortex plasma in the temperature region $T_{2D} < T < T_c$ is a finite resistance which depends strongly on externally applied magnetic fields.

IV. FLUCTUATION CONDUCTIVITY

The theoretical and experimental development of the understanding of fluctuation conductivity in superconductors has been very vigorous. The reader can find all the details in the review article by Tinkham³⁹ and the references therein. We will only consider some of the results that are relevant to our work.

Aslamazov and Larkin (AL)¹⁶ calculated the fluctuation contribution to the conductivity using diagrammatic techniques. The AL results arises in the normal state from fluctuations into the superconducting phase in which electrons accelerate without resistance for the duration of the fluctuation. The results can be expressed in a very simple form as follows:

$$\frac{\sigma_{ex}}{\sigma_n} = \frac{g_{AL} R_{\square}}{\epsilon} \quad \text{for } d < \xi(T) \quad (31a)$$

$$\frac{\sigma_{ex}}{\sigma_n} = \frac{g_{AL}}{\sigma_n^2 \xi(0)} \frac{1}{\epsilon^{\frac{1}{2}}} \quad (\text{for } d > \xi(T)) \quad (31b)$$

where σ_n is the normal state conductivity, $R_{\square} = \frac{1}{\sigma_n d}$, d is

the film thickness and $\xi(0)$ is the zero temperature Ginzburg-Landau coherence length. The constant $g_{AL} = \frac{e^2}{16\hbar} = 1.52 \times 10^{-5}$.

It is clear from the previous equations that the fluctuation conductivity in bulk is quite small. For an amorphous

three-dimensional superconductor like Nb_3Ge , $\xi(0)$ can be very small due to the short mean-free-path in these materials. However the normal state conductivity is also reduced. As a result the AL contribution becomes measurable.

Later Maki,⁴⁰ calculated the effect of superconducting fluctuations on the conductivity of normal electrons. This gave a contribution that was four times larger than AL term in three-dimensions, but it was divergent in one and two dimensions for all temperatures. Thompson⁴¹ introduced a low momentum cutoff, which is a function of a pair breaking parameter, to remove the divergence. The difficulty with this picture is that one has to make an ad hoc assumption about the pair-breaking parameter. Recently Patton⁴² has carefully used impurity averaging techniques in the presence of fluctuations to get a nondivergent solution of fluctuation induced conductivity in one and two dimensions. In the limit of large pair-breaking, the Maki contribution becomes very small compared to AL term. It has been shown that in dirty and amorphous superconductors the pair-breaking parameter could be large enough to suppress the Maki contribution^{42, 44}. Therefore we will not consider this contribution in our work on Nb_3Ge films.

Bulk fluctuation conductivity in amorphous Nb_3Ge has been observed.⁴⁴ However agreement with AL theory is good only close to T_c . Fluctuation conductivity falls off much more rapidly with

increasing temperature than predicted, at temperatures far above T_c . It has been proposed that this is due to the breakdown of the assumptions of the Ginzburg-Landau (GL) theory that the derivative of ψ should vary slowly in space. In the case of dirty superconductors with small $\xi(0) \sim 30 \text{ \AA}$, the higher order correction terms in the GL formalism become important for the case where $q \sim \xi(0)^{-1}$ ⁴⁵.

Recently Ami and Maki ⁴⁶ have re-examined theoretically the fluctuation induced conductivity of dirty Type II superconductors in bulk. They use Feynmann diagrams and consider the dynamic fluctuations as well. They consider three distinct contributions. First is the AL term. The other two are often called anomalous terms as they arise from the scattering of quasiparticles by fluctuations. All the three terms are very difficult to calculate since they involve integration over frequency ω . If they make a static approximation by neglecting the dynamic fluctuations, they recover the AL result expressed as,

$$(\sigma^{\text{AL}})_{\text{st}} = \frac{1}{8\sqrt{2}\pi} \sigma_0 \epsilon^{-\frac{1}{2}}$$

where

$$\sigma_0 = \frac{\pi}{2\sqrt{2}} \frac{e^2}{\hbar} [\xi(0)]^{-1}$$

If they introduce the static approximation for the fluctuation propagator but retain the Bose distribution function in the integral, they get the following expression for the dominant part of AL term,

$$\sigma^{AL} \simeq (\sigma^{AL})_{st} \left[1 - \frac{8}{3\pi} (1.46)\epsilon^{\frac{1}{2}} + \frac{16}{\pi^3} (2.612)\epsilon^{3/2} \right] \quad \epsilon \ll 1 \quad (32)$$

We should note that the above expression is valid only in the immediate vicinity of T_c . However, equation (32) indicates that σ^{AL} decreases much faster than $(\sigma^{AL})_{st}$ as ϵ increases, which is in qualitative agreement with the observed data.

We have seen qualitatively similar behavior in amorphous Nb_3Ge films.

V. EXPERIMENTAL PROCEDURE

(i) Sample Preparation

There are several reasons why amorphous Nb_3Ge and granular Al, were chosen to be the materials used in the study of the fluctuation heat capacity. First, the superconducting transition temperature, T_c for each of these materials is below 3K. At such a low temperature, the substrate contribution to the heat capacity and the addendum contribution can be kept small compared with the film heat capacity. Furthermore, amorphous Nb_3Ge has a very short coherence length ($\xi(0) \approx 30\text{\AA}$) and short conduction-electron mean free path ($l \approx \text{few } \text{\AA}$). As was mentioned in the introduction, this results in a widened critical region. In addition, the amorphous phase is stable at room temperature. This eliminates the need for preparing the films by quench-condensation onto liquid helium cooled substrates to stabilize the amorphous phase. As we will see later, this leads to an important simplification of the calorimeter design.

For granular Al films the zero-temperature coherence length $\xi(0) \approx 2000\text{\AA}$. Therefore, a few hundred Angstrom thick film can still be within a two-dimensional limit in the sense that $d \ll \xi(T)$. However, there is a strong evidence that granular Al is a good example of a random superconductor, a system in

which the superconducting properties are position dependent within the sample. Heat capacity measurements on such films might help to strengthen the theoretical understanding that exists at the present time (see section (v) of chapter II).

We will now consider film preparation techniques in detail. Due to reasons that will become clear later, both the amorphous Nb_3Ge and the Al films were formed on very thin sapphire substrates.

(a). Amorphous Nb_3Ge Films

These films were prepared by cryogetter dc diode sputtering in ultra high vacuum system. The details of the apparatus can be found in Ref. 47. Buitrago has determined a phase diagram of sputter deposited Nb_3Ge films. It represents the phase found in the deposited films as a function of target composition and substrate temperature. Below a substrate temperature of 400°C one obtains an amorphous phase for target compositions in which the Nb/Ge ratio is between 1.85 and 2.75. We used the 2.75 target. The substrate was held near 77K during the deposition.

Typically the system was evacuated to a pressure between 10^{-9} to 10^{-10} torr. It was then back filled with 250μ of research grade Ar. The target was presputtered for 15-30 minutes and then the substrate was exposed by a shutter and the deposition was carried out for a fixed length of time. Another piece of sapphire

substrate was simultaneously exposed to the plasma and used for subsequent thickness measurement by interferometry. The details of film preparation are given in Table I.

(b) Granular Al Films

These films were prepared by vacuum evaporation. The vacuum system used for this purpose was an Ultek system pumped by a 250 liters/sec ion pump, and a Titanium sublimator. Only a dry vacuum pump and a sorption pump were used to evacuate the system below 10^{-3} torr. Therefore the system was free of any oil vapors.

Al (99.999% pure) was evaporated from an Al_2O_3 coated boat. The background pressure achieved before evaporation was typically $2-4 \times 10^{-8}$ torr. In order to produce granular Al films, the evaporation chamber was valved off from the ion pump during the Al evaporation. The presence of oxygen coming from the outgassing of the Al_2O_3 boat helps to achieve granular Al films.^{48,49} The pressure during the Al evaporation as measured by an ion gauge was approximately 10^{-6} torr. The film thickness was monitored on a quartz crystal thickness monitor. The mask used to define the lateral dimensions of the films was kept close to the substrate in order to avoid edge effects.

Table - I

Sample	Background pressure (torr)	Presputtering time (min.)	Argon pressure (micron)	Sputtering current (A)	Sputtering voltage (volts)	Sputtering time (min.)
Nb ₃ Ge-1	7×10^{-10}	10	300	56 → 36	356 - 600	90
Nb ₃ Ge-2	2×10^{-9}	25	250	36	586	260
Nb ₃ Ge-3	5.5×10^{-10}	30	250	34	592	85
Nb ₃ Ge-4	2×10^{-8}	15	250	28.5	587	120
Nb ₃ Ge-5	1.3×10^{-9}	60	250	48	260	100
Nb ₃ Ge-6	5×10^{-9}	30	250	46	385	160

(ii) ac--Temperature Calorimetry

A steady-state technique for measuring heat capacity using ac heating was first introduced by Sullivan and Seidal⁵⁰. This method is very useful for precise measurement of heat capacity changes as a function of an external parameter, like temperature.

Consider the model schematically shown in Fig. 4. A sample with heat capacity C_s is coupled to a thermal bath at temperature T_b by a thermal conductance K_b . A thermometer and a heater with heat capacity C_θ and C_h respectively are coupled to the sample by thermal conductances K_θ and K_h respectively. T_s , T_θ and T_h are the time dependent temperatures of the sample, thermometer and heater respectively. A sinusoidally varying current $I_0 \cos(\frac{\omega t}{2})$ drives a heater of resistance R_0 . The power delivered to the sample is $I_0^2 R_0 \cos^2(\frac{\omega t}{2})$. We can write down three coupled thermal equations for the system. Under the condition that the temperature variations are small, the steady state solution for T_θ is given by,

$$T_\theta = T_b + \Delta T_{dc} + \Delta T_{ac} \cos(\omega t - \alpha) \quad (34a)$$

where

$$\Delta T_{dc} = \frac{Q_0}{K_b} = (\frac{1}{2} I_0^2 R_0) / K_b \quad (34b)$$

and

Figure 4. Block diagram of the model for the ac-heat capacity technique (after Sullivan and Seidel).

$$\Delta T_{ac} = \frac{Q_0}{\omega C} \left[1 + \frac{1}{\omega^2 \tau_s^2} + \omega^2 (\tau_\theta^2 + \tau_h^2) \right]^{-\frac{1}{2}} \quad (34c)$$

The three relaxation times are defined as

$$\tau_s = \frac{C_s + C_h + C_\theta}{K_b} = \frac{C}{K_b}; \quad \tau_\theta = \frac{C_\theta}{K_\theta}; \quad \tau_h = \frac{C_h}{K_h} \quad (34d)$$

If we consider the finite thermal conductivity of the sample in the model, then it adds a time constant to the problem, given

$$\text{by } \tau_{int} = \frac{L^2}{(90)^{0.5} n} \quad (L \text{ is the thickness of the sample and } n$$

is its thermal diffusivity), the expression for ΔT_{ac} becomes,

$$\Delta T_{ac} = \frac{Q_0}{\omega C} \left[1 + \frac{1}{\omega^2 \tau_s^2} + \omega^2 (\tau_\theta^2 + \tau_h^2 + \tau_{int}^2) \right]^{-\frac{1}{2}} \quad (35)$$

The usefulness of this technique can be seen from equation (35). There are two main time constants in the problem. The first one is the effective total internal time constant associated with the heater, thermometer and the sample, given by $\tau_2^2 = (\tau_\theta^2 + \tau_h^2 + \tau_{int}^2)$. The second one is τ_s , the sample-to-bath relaxation time. If a frequency ω can be chosen such that $(\omega \tau_s)^{-2} \ll 1$ and $\omega^2 \tau_2^2 \ll 1$ then $\Delta T_{ac} = \frac{Q_0}{\omega C}$, i.e., the amplitude of temperature oscillations varies inversely with the heat capacity.

Therefore the design of the experiment and the calorimeter should be such that the two time constants τ_s and τ_2 satisfy the

inequality $(\omega\tau_2)^2 \ll 1 \ll (\omega\tau_3)^2$. Then while heating the sample at a frequency f , the amplitude of temperature oscillation, ΔT_{ac} are measured at a frequency $2f$. The heat capacity is then inversely proportional to ΔT_{ac} .

The design of the calorimeter used in these experiments is based on the work of R. Viswanathan and C. Varmazis at Brookhaven National laboratory.⁵¹ Before considering the design in detail, let us consider the requirements for successful ac heat capacity measurements. This will help to explain and justify the choice of materials and thermometers used in this experiment.

(1) It is clear from the discussion in the previous section that it is desirable to achieve as small an internal time constant τ_2 as possible. This means that the substrate material, which contains the film, the heater and the thermometer, in addition to being an electrical insulator, should be a good thermal conductor. Usually insulators are poor thermal conductors. For example, Zally⁵² used thin pyrex glass substrates. He had to evaporate an Indium film onto the substrate in order to increase the thermal conductance within the area covered by the sample film. Sapphire ($\alpha - Al_2O_3$) is an excellent choice as a substrate. At 4.2K its thermal conductivity is almost as good as that of Copper⁵³. Its specific heat is low compared to other materials used in the calorimeter $\theta_D \sim 1042K$ ⁵⁴. It is also available in the form of very thin (.005 cm) substrates.

(2) The main objective of the present work was to measure the small fluctuation contribution to the heat capacity of the film near T_c . The ac heat capacity technique is admirably suited to such a goal keeping this in mind, it was essential to minimize the addendum contribution to the heat capacity from the heater, substrate and the thermometer. A thin film heater evaporated on to the sapphire substrate, minimizes the contribution of the heater to the heat capacity and at the same time establishes good thermal contact between the heater and the sample. Usually it is difficult to minimize the thermometer contribution to the heat capacity. Examples of the thermometer used in the past for such heat capacity experiments have been, wafers machined from Allen-Bradley carbon resistor^{55, 56} and small silicon or Germanium chips^{57, 36}. In the present instance a small thermocouple junction was used as a thermometer. This has the advantage that the contribution to the heat capacity addendum from the thermometer will be small. Following Viswanathan⁵⁸ we used a Au(Fe)-vs. Cu thermocouple as a thermometer for our heat capacity measurements.

(3) All the electrical leads making contact at the substrate were spot-welded, thereby eliminating the need for silver paint or solder, and keeping the addendum as low as possible.

The calorimeter as shown in Fig. 5 has two parts, the substrate with the sample film and Au heater film, and the

thermometer. We will describe their fabrication in detail. The sapphire substrates used in this work were $2.54 \times 1.26 \times .005$ cm in dimensions and were purchased from Insaco Inc. They were polished to a finish of better than one micro inch on both sides.

(iii) ac-Calorimeter Design and Thermometry

The low temperature apparatus that was used in the present work was designed by R. V. Carlson for a pair-tunneling experiments. The details can be found in his thesis⁶⁰. The cryostat consists of an outer copper vacuum can which was immersed in the 4.2K Helium bath. A copper Helium pot was suspended from the upper plate of this can by three stainless steel tubes. This pot could be filled with liquid Helium from the outer bath through a needle valve located at the top of the pot. The Helium in the pot could be pumped to below 1K. This pot was used as the reference thermal reservoir for the heat capacity experiment. The electrical leads (twisted pairs of #36 cu wire) were passed through a room temperature feedthrough at the top of the cryostat and down the inner pumping line. The leads were thermally anchored to the outer 4.2K bath and then to the Helium pot.

The bottom of the Helium pot had holes for threaded screws. Copper rods .64 cm. in diameter and 2.54 cm. long were securely held to the pot using screws. Clean metal-to-metal contact was

achieved for maximum thermal contact. These rods were used for thermally anchoring the leads coming from the calorimeter substrates to the Helium pot (see Fig. 5).

Varmazis⁶¹ et al. found a technique for bonding Au to sapphire. Using this technique, four small pieces 3N purity Au (each piece ≤ 1 mg) were placed on the sapphire substrate at locations where bonding was desired. The substrate was then placed inside a quartz tube in an oven. The oven was heated up to 1400°C for one to two hours and then allowed to cool down to room temperature. During the heating, the Au melts and forms a small bead which bonds very strongly to the sapphire.

After the beads are bonded to the sapphire, the substrate is cleaned in an ultrasonic cleaner and freon vapor degreaser. Then it is held down flat on a clean glass slide using thin strips of masking tape. The substrate is completely covered with thin Al foil except for a small area around each bead. Film of Au approximately 1000 Å thick are then evaporated onto the exposed area around the Au beads. Since the beads form a finite contact angle when bonded to the sapphire, the Au evaporation is done with the direction between the evaporation source and the substrate at an angle with respect to the normal to the surface of the substrate rather than along the normal. In this way, electrical continuity can be established between the evaporated pads and the beads. A few hundred angstrom thick

Figure 5. Schematic of the calorimeter.

Au strip heater is also evaporated between two Au beads. This heater is usually near the end of the substrate and is in the shape of U to reduce any magnetic coupling with other parts of the sample film. The heater resistance is usually on the order of 100 ohms.

Finally, as shown in Fig. 5 the sample film is deposited covering most of the remaining area on the substrate. The mask used is 1 cm. x 2 cm., and it is divided into two areas. One area on the side is a strip 1 cm. by 0.2 cm. The mask is placed on the substrate in such a way that this strip falls right across two remaining Au pads. This separation of the film into two sections by a mask is done, because it is not easy to scratch a Nb_3Ge film. Fig. 5 shows a sketch of the location of the sample film, the heater film and the Au beads on the sapphire substrate. This film strip is used for measuring the resistance transition of the sample. The deposition is carried out as explained in the section (i) of this chapter.

Two .008 cm. diameter Manganin wires, with thin insulation stripped off are spot-welded to the Au beads used for the sample strip. Two .008 cm. diameter bare Cu wires are spot-welded, in a similar fashion, onto the Au beads used for the heater. It is much more difficult to spot weld Cu wire than Manganin wire, because of good thermal conductivity of Cu.

However if the Cu wire is pressed into the form of a thin sheet, the spot welding becomes easier. Attempts to spot weld superconducting wires were unsuccessful. The length of these Cu and Manganin wires was about 2 cm. Fig. 5 illustrates all the details of the sample prepared in this way.

For the ac thermometry, we used a Au = 0.07 at .% Fe vs. Cu thermocouple; .006 cm. diameter Au(Fe) was purchased from the Sigmund Cohen Corporation. The wire comes with a transparent plastic insulation which has to be scratched off with a dull razor before forming a junction. Long pieces of Cu and Au(Fe) wire were cut from the spool and about 2 cm. of insulation on both the wires was stripped off. This portion of the wire was twisted together and brought near an oxygen-butane flame in the presence of a flowing Helium gas. Both Cu and Au melt readily in this flame very beautiful small junctions bead could be formed in this way⁶². The length of Au(Fe) wire was approx. 60 cm. and the Cu wire approximately 90 cm. Two junctions were formed and the Au(Fe) wire was used as a common leg. One junction along with about 20 cm. of both Cu and Au(Fe) wire was tied to a copper rod using lens paper and GE 7031 varnish. This rod was in turn bolted to the Helium pot, thus thermally anchoring one junction to the reference Helium pot. The second junction was spot-welded onto an Au bead bonded on a small piece of

sapphire. The length of Cu wire between the Helium pot heat sink and the junction on the sapphire piece was about 70 cm. and that of Au(Fe) wire, about 40 cm. As we shall see later, it was necessary to have this length in order to achieve a large enough value for τ_S . This length was accommodated inside the can by lightly winding the wires in the form of loops.

Twisted pairs of 35 cm. long and 0.004 cm. diameter superconducting Nb wires were used as leads for the measurement of the sample and the heater resistances. They were heat sunk to a copper rod fastened to the Helium pot. These wires soldered to wires spot-welded to the dots on the substrate. At the Helium pot these superconducting wires were soldered to four Cu wires running up to the top of the cryostat for 4-terminal resistance measurements. The small piece of sapphire with the thermocouple junction on it is attached to the large sapphire substrate by using a small amount (< 1 mg) of Wakefield heat sinking compound.²⁹ The compound was placed between the two pieces and then the pieces were gently rubbed together to remove any air bubbles. The large substrate and the thermocouple junction were left hanging from the Helium pot. The four superconducting wires also serve as a mechanical support for the hanging substrates. Care was taken to make sure that none of the wires touched the outer can.

We will estimate the various time constants and the heat capacity of the calorimeter, in order to evaluate its performance. Since the heat capacity addenda will include contributions from the Au beads, the heater and the sapphire substrate, we will make an estimate for each in the following table.

Greene⁵⁷ et al. have calculated the contribution to the addendum due to the finite heat of the wires that constitute the thermal link to the Helium pot. According to them, 1/3 of the heat capacity of the wires should be included in the addendum. Since, in our measured heat capacity, we see only the electronic (γ) and lattice (β) contribution from 1K to 4K and no other higher order contributions, we have estimated γ and β in the following table.

Table II

Material	Estimated mass (gram)	γ ($\mu\text{J}/\text{K}^2$)	β ($\mu\text{J}/\text{K}^4$)	Reference
Sapphire	0.08	--	0.0067	54
Au beads	0.003	0.011	0.0066	58
Au(Fe) wires	0.005	0.019	0.011	58
Cu wires	0.006	0.066	0.0045	58
Wakefield Compound	0.0002	--	≤ 0.002	
Total background	0.094	0.096	0.0308	

For a typical run, the values of γ and β that we obtain are on the order of $0.12 \mu\text{J}/\text{K}^2$ and $0.024 \mu\text{J}/\text{K}^4$ respectively. Therefore the observed values are within 25% of the above estimate.

The sample-to-bath (hereafter the Helium pot, thermal reservoir will be referred to as bath) relaxation time τ_s can be estimated by calculating the total thermal conductance of the wires between the sample and the bath. The largest contribution comes from the copper wires. If we take the value of $6 \text{ Watt}/\text{cm-K}$ at 4K , for the thermal conductivity of Cu from reference 63, the thermal conductance of the 65 cm. long and 0.0075 cm. diameter Cu wire turns out to be $4.08 \times 10^{-6} \text{ Watt/K}$. A value of $6.4 \times 10^{-6} \text{ Watt/K}$ is obtained if we measure the residual electrical resistance of the same length of wire at 4.2K and then use the Weidemann-Franz law to calculate the thermal conductance at 4.2K . Berman et al.⁶⁴ have measured the thermal conductivity of Au(Fe) thermocouple wire. It is given by $K = 0.097T + 0.0045 T^2 \text{ Watt}/\text{cm-K}$. Using these numbers we can estimate the thermal conductance of 0.0038 cm. diameter and 35 cm. long wire at 4K to be $0.6 \times 10^{-6} \text{ Watt/K}$. Estimates based on residual resistivity measurement and the Weidemann-Franz law give $0.17 \times 10^{-6} \text{ Watt/K}$. The thermal conductance of Nb wires in the superconducting state is very small, on the order of $1 \times 10^{-9} \text{ Watt/K}$, and therefore it can be safely neglected. Since all these wires are in parallel,

the total thermal conductance is the sum of all the individual thermal conductances. As a worst case design, if we take the maximum values of various estimates, the total thermal conductance K_b between the sample and the bath turns out taken 7×10^{-6} Watt/K. The estimate of the heat capacity C at 4.2 K is on the order of $2.3 \mu\text{J/K}$. Therefore, the sample to bath relaxation time $\tau_s = C/K_b$ at 4.2K is about 0.33 sec.

The internal time constant τ_{int} can be calculated from the expression $\tau_{int} = \frac{L^2}{(90)^{0.5} n}$ where L is the thickness of the sample and n is thermal diffusivity⁵⁰. N can be calculated from the thermal conductivity of sapphire. Assuming as a worst case, with the thermal conductivity of sapphire taken as $\sim$ watt/cmK at 4.2K, the longest relaxation time we get is on the order of 10^{-6} sec. It is very likely that the largest contribution to the lumped total internal time constant comes from poor contact on the spot-weld of the thermocouple junction to the gold bead and the pressed grease contact between the sapphire strip to which the thermocouple is bonded and the substrate. It is not possible to make any realistic estimates for this time constant. However, as will be explained in the next section, we can make a diagnostic analysis of the thermal data to make sure that these time constants are indeed small. Nevertheless, from the above estimates it is clear that for

any operating frequency between 10HZ and 100HZ we will have $(\omega\tau_2)^2 \ll 1 \ll (\omega\tau_s)^2$. Therefore, according to equation (35), the heat capacity will be inversely proportional to the amplitude of the temperature oscillations ΔT_{ac} at frequency ω where $\omega/2$ is the frequency of the heating current.

There are three temperature measurements involved in the experiment. The reference bath (Helium pot) temperature T_b is determined from the resistance of a calibrated Germanium resistance thermometer⁶⁵ in good thermal contact with the bath. In the heat capacity experiment, there is a dc temperature difference, ΔT_{dc} , between the substrate and the bath, given by equation (34b).

Since one junction of the thermocouple is at the bath temperature T_b and the other at the substrate temperature, the dc thermocouple voltage is a measure of ΔT_{dc} . To determine the amplitude of oscillations ΔT_{ac} we need to know the thermocouple sensitivity $\frac{dE}{dT}$ where $E(T)$ is the thermocouple e.m.f. Au -0.07% Fe vs. Cu thermocouples have been widely used. The National Bureau of Standards has published calibration tables for it. The thermocouple sensitivity is temperature dependent. It is approximately 10 μ V/K near 3K. ΔT_{dc} is usually about 0.15K which corresponds to about 0.15 μ V/K of dc thermocouple voltage. ΔT_{ac} is typically 3 mk which corresponds to about 30 nV of ac thermocouple voltage. Measurement of such small voltage dictates the use of lock-in amplifiers.

In the next section, we will consider the electronics and the experimental procedure in detail.

VI. ac HEAT CAPACITY MEASUREMENT

(i). Electronics

All the data was taken on-line using analog-to-digital converters interfaced to a Data General Corporation NOVA 1200 minicomputer.

The temperature of the bath T_b was determined using a Ge resistance thermometer⁶⁵. A constant voltage output from a digital-to-analog converter was applied across a current limiting resistor and the thermometer in series. The voltage drop across the Ge resistance thermometer was measured using a Data Technology digital voltmeter which was interfaced to the minicomputer. The resistance was determined from the current and the voltage readings. The sign of the current was changed for each resistance measurements in order to cancel out thermal emf's. The heat capacity was measured in a continuous fashion as the temperature drifted through the superconducting transition of the film. Therefore, the above mentioned method for measuring the thermometer resistance was more useful than a conventional bridge technique. The thermometer used in these measurements was calibrated by the manufacturer from 1.5K to 20K. We extended the calibration range down to 1 by comparison with a second Ge resistance thermometer supplied by Scientific Instruments, Inc.⁶⁶

All the calibration data between 1 and 5 were fitted to a polynomial of the form,

$$\log R = \sum_{n=1}^N A_n (\log T)^n$$

The best least squares fit was obtained with $N=9$. The fit was then used to interpolate between the calibrated data points.

The thermocouple pair, used to measure the substrate temperature, was also calibrated in a separate run. One function was heat sunk to the bath (Helium pot). A small Cu block was attached to the bath with a weak thermal link. The second function was heat-sunk to the Cu block. Two separate calibrated Ge resistance thermometers were used to determine the temperature of the bath and the Cu block⁶⁶. The resistance of these thermometers were determined using two separate ac bridges designed by J.C. Solinsky⁶⁷. Two Lock-in amplifiers, a PAR-129 and an HR-8, were used to measure the null and off null signals of the bridge. The off null signal was used, to drive the heater current and electronically regulate the temperature using a feedback loop. This was done separately for the bath and the Cu block. Using the optimum conditions and maximum sensitivities of the lock-in amplifiers we could regulate temperatures to within $\pm 50\mu\text{K}$.

The bath was pumped to 1K. It was stabilized and held at this temperature. The thermocouple emf was measured using a

Keithley 148 nanovoltmeter. The analog output from this meter was interfaced to the computer. The data was taken point by point by signal averaging the thermocouple emf on the computer. The temperature of the block was increased from 1K to 5K in steps of 50 mK. The measured emf $E(T)$ from 1K to 5K is fitted to a polynomial of the form

$$E(T) = \sum_{i=1}^N A_i T^i \quad (36)$$

Figure 6 shows the measured thermocouple emf as a function of T and the best least square fit to the data for $N=7$. The thermocouple sensitivity $S(T) = \frac{dE}{dT}$ was determined using the parameters A_i determined above. Calibration tables for resistance $R(T)$ of the Ge thermometer, the thermocouple emf $E(T)$ and thermocouple sensitivity $S(T)$ were stored on a disk for future data reduction. The tables were in the form of Basic data statements which could be used in a Basic Program to calculate the heat capacity from the raw data.

Figure 7 is a block diagram of the electronics used for the heat capacity experiment. A Kronhite model 4100 oscillator was used as an ac current source for the heater. It can generate sine wave signals that are stable to 1 part in 10^4 . This ac current at a frequency f was applied to a 1M-Ohm current limiting resistor and the substrate heater (Au thin film strip) in series. The ac voltage drop across the heater V_0 , was synchronously detected on an HR-8 lock-in amplifier at the frequency f . This lock-in was

Figure 6. Plot of experimentally measured Au-.07%Fe vs. Cu thermocouple voltage as a function of temperature. One junction was held at a constant temperature $T = 1K$. The solid line is the result of a 7th order polynomial in T , fit to the data.

Figure 7. Block diagram for the electronic measurement of the heat capacity using the ac technique.

operated in the select external reference mode and the reference signal was supplied from the square-wave output of the Kronhite oscillator.

The thermocouple voltage has two components, a dc voltage ΔT_{dc} and an ac voltage ΔT_{ac} at frequency $2f$. The simplest procedure was to measure both signals simultaneously with a lock-in amplifier and dc nanovoltmeter in parallel. The dc component which is typically on the order of $1\text{-}2\mu\text{V}$ was measured using Keithley 148 nanovoltmeter. The input impedance of Keithley on the $3\mu\text{V}$ full scale is 300 kilo-ohms and on the 0.01 mV full scale it is 1 Mega-ohm therefore measurements were taken on the 0.01 mV scale.

The amplifier of temperature oscillations, ΔT_{ac} , at the frequency $2f$ were measured using a PAR lock-in model HR-8 with a PAR-190 transformer followed by type A preamplifier. The impedance of the thermocouple was the lead resistance which is on the order of $30\ \Omega$. The PAR-190 provides turns ratios of 1:100 and 1:1000. The use of a PAR-190 helps to match the low impedance source to the high input impedance of the lock-in type A preamplifier. As a result of this, the noise figure was improved to about .5dB. A $2200\ \mu\text{F}$ electrolytic capacitor was used to block the dc component of the thermocouple voltage from reaching the primary of PAR-190. The HR-8 was operated in the select external mode. For the reference signal, the same Kronhite sine wave output was used but was half-wave rectified using a diode. The half-wave rectified

signal contains the frequency $2f$ in its spectrum of harmonics. The lock-in was tuned to $2f$, and ΔT_{ac} was synchronously detected at $2f$.

The dc analog signals from the lock-in and the Keithley 148, proportional to ΔT_{ac} and ΔT_{dc} respectively, were digitized and read by the minicomputer using separate analog-to-digital converter channels. About 1000 readings were taken in twenty seconds at a given temperature and averaged.

Another HR-8 lock-in with a type A preamplifier was used to measure the resistive transition of the film. This lock-in was used in its internal mode. The reference output of the lock-in supplied a constant ac current to the film through a current limiting resistor. The resultant voltage drop across the sample film strip was synchronously detected. Measuring currents were on the order of $5\mu A$ and the frequency was about 250 HZ. The dc analog output of the lock-in was digitized and read by the minicomputer using a separate analog channel. The sensitivity of the lock-in was chosen so as to have maximum possible sensitivity in the measurement of the normal state resistance at a fixed current. The resistance of the film was measured accurately at 4.2K using an ac bridge or a self-balancing conductance bridge (SHE Corporation Model PCB). The measured film voltage on the lock-in was scaled to this value of the resistance.

(ii). Measurement Procedures

There are number of precautions that were taken before cooling a sample down to Helium temperatures. After the substrate was prepared and all the film evaporations were completed, the spot welded wires on the substrate are soldered to the superconducting wires. The small piece of sapphire substrate with the thermocouple junction is also attached to the large substrate using Wakefield thermal compound. The substrate hangs from these wires about eight centimeters below the Helium pot. A Cu can is then slipped around the substrate and the Helium pot and is sealed against a Cu plate at the top of the Helium pot using an In wire seal. The space inside the can is evacuated at room temperature and is leak tested using a Helium leak detector. This is important because erroneous heat capacity results may be obtained if any small amount of He gas is left inside the can providing an extra path for thermal conduction from the substrate to the Helium pot. Also adsorbed gas can make a large contribution to the measured heat capacity. No exchange gas is used to cool the contents of the can. This makes the cooldown procedure lengthy, but is essential to the success of the experiment.

After the He pot is filled with liquid Helium and is near 4.2 K, the absolute values of the heater and the sample resistances are determined using an ac bridge. The heater resistance R_0 is constant to about 1 part in 10^4 over the range from 1K to 4K.

Typically it takes about 1×10^{-6} Watt power to produce a dc temperature difference ΔT_{ac} on the order of 0.1K. The average power Q_0 is determined by measuring the peak value of the voltage drop V_0 across the heater due to the heater current at a frequency f , and then calculating $0.5 \frac{V_0^2}{R_0}$, from equation (34b),

ΔT_{dc} is proportional to Q_0 and the constant of proportionality is the inverse of the bath-to-substrate thermal conductance K_b . Therefore K_b can be estimated by measuring ΔT_{dc} as a function of Q_0 with the bath held at constant temperature. At 4.2K, we get a value of 4.3×10^{-6} Watt/K for K_b which is within 50% of the value we estimated in the previous section.

For a constant power Q_0 , the frequency dependence of ΔT_{ac} is determined at 4.2K and 1.1K. The frequency f was varied from 3 Hz to 140 Hz. The lock-in amplifier that measures ΔT_{ac} was tuned to the frequency $2f$ each time and the in-phase amplitude ΔT_{ac} was measured. From equation (35) we see that the product $\Delta T_{ac} (2\pi 2f)$ is constant if $(\omega \tau_2)^2 \ll 1 \ll (\omega \tau_s)^2$. A plot of $\Delta T_{ac} (2\pi 2f)$ as a function of f for our calorimeter shows a flat region between 10 Hz and 120 Hz. Therefore for any operating frequency in this range, the frequency dependent terms in the thermal response involving τ_s and τ_2 are small in comparison with unity, and the heat capacity is inversely proportional to ΔT_{ac} . In this range, ΔT_{ac} is inversely proportional to f . Therefore a smaller frequency,

typically between 20 Hz and 40 Hz was chosen, so that the voltage corresponding to ΔT_{ac} can be measured with as large a signal-to-noise ratio as possible. It was necessary to make certain that the phase of the signal did not change as the heat capacity varied with temperature in the range from 1K to 4K.

Once the operating frequency was chosen, the heater power was adjusted so that the ac signal proportional to ΔT_{ac} was approximately 15 nV at 4.2K. The peak voltage V_0 , across the heater was measured to determine the power. This power, Q_0 was not measured again during a run because in several trial runs it was found that once it was fixed, it remains constant to better than 1 part in 10^4 . The film resistance was also measured using a lock-in-amplifier as described earlier in this section. The analog signals, ΔT_{dc} and ΔT_{ac} and the lock-in output proportional to the film resistance were digitized using separate analog-to-digital converter channels and then read by the minicomputer.

A Basic program controls the on-line data acquisition by the minicomputer. One-thousand calibration data points in the form T , $R(T)$, $E(T)$, $S(T)$ are stored in the memory. T is the temperature, $R(T)$ is the resistance of the Ge thermometer, $E(T)$ is the thermocouple e.m.f. determined from a fit to equation (36), and $S(T)$ is the thermocouple sensitivity. Two-thousand readings of the analog signal are taken and averaged for each set of raw data. The raw data consists of the Ge

thermometer resistance, ΔT_{dc} , ΔT_{ac} and the film resistance, from this raw data the substrate temperature and the heat capacity were calculated in the following way: for the measured resistance of the Ge thermometer, the temperature of the bath T_b was determined by a computer search through the stored calibration tables. Once T_b was known, $E(T_b)$ was also determined from the Tables. Then the measured value of ΔT_{dc} was added to $E(T_b)$ and a computer search through the calibration tables was made to determine the temperature T at which $E(T)$ is equal to $E(T_b + \Delta T_{dc})$. This T is the temperature of the substrate. The thermocouple sensitivity $S(T) = \frac{dE(T)}{dT}$ is also obtained readily from the tables. This value of $S(T)$ can then be used to convert the ac signal at the frequency $2f$ into the oscillation temperature ΔT_{ac} in mk at the temperature T . The heat capacity is determined from $C(T) = \frac{Q_0 \cdot \Delta T_{ac}(T)}{(2\pi 2f)}$ where Q_0 is the heater power in J/sec., f is the frequency of ac heating current in HZ and $\Delta T_{ac}(T)$ is the amplitude of temperature oscillation at a frequency $2f$ in Kelvin.

The on-line acquisition of 2000 readings and the reduction of the raw data as described above were all carried out in about 40 seconds. The bath is allowed to drift up or down in temperature and data is taken at regular time intervals. Therefore the temperature interval at which the data is taken is controlled by the drift rate of the bath (He pot) temperature. This in turn is controlled by the pumping speed and the electrical heating of the

Figure 8. Block diagram showing on line data acquisition by the minicomputer. Various display and recording units that are interfaced to the computer, are also shown.

He pot. Near the transition temperature T_c the drift rate is kept low so that data can be taken at 1mK intervals.

For each run, a set of 250 data points is taken. At the end of the run, the heat capacity and the resistance data are plotted on the Tektronix 4010-1 CRT display terminal interfaced to the computer. If the data is good, then all the raw data and the reduced data are recorded and stored on floppy disks for future analysis. Five or six runs are made, sweeping the temperature in the neighborhood of T_c in order to get a high density of data points which are averaged later.

VII. DATA AND ANALYSIS

(i) Heat Capacity of Aluminium Films

Heat capacity measurements on six Aluminium films are summarized in Table III. The transition temperature T_c has been arbitrarily defined as the temperature where 90% of the BCS heat capacity jump has taken place. The width of the heat capacity transitions are typically the order of 0.05K. Simultaneous measurements of the resistive transition were not carried out except for SPAL-6 and SPAL-9.

Extensive data was taken on the sample SPAL-9. This data will be presented and analyzed here. Figure 9 is a plot of C/T as a function of T^2 for this sample, where C is the total heat capacity including the addenda. The data for $T \gg T_c$ fall on a straight line which implies that the total heat capacity for T above T_c can be represented as

$$C(T) = \gamma_T T + \beta_T T^3 \quad T \gg T_c \quad (36)$$

where $\gamma_T T$ is the total electronic heat capacity from the addenda and the film $\beta_T T^3$ is the total lattice heat capacity from the addenda and the film. The coefficients γ_T and β_T can be determined from the intercept and the slope of the straight line drawn through the data. The plotting of the data and the fitting to a straight line were carried out using the CRT display interfaced to the minicomputer. The values of γ_T and β_T are given in the figure caption. The small rise in the heat capacity near 1.55K is due to the

Table III: Physical parameters for Al Films

Sample	Thickness d (Å)	T_c^a (K)	T^b (K)	ΔC ($\mu J/K$)
SPAL-1	700	1.55	.06	.011
SPAL-2	1250	1.56	.055	.017
SPAL-4	1850	1.56	.06	.02
SPAL-6	1850	1.41	.04	.016
SPAL-8	1950	1.67	.04	.025
SPAL-9	1900	1.535	.065	.015

a T_c is the temperature where 90% of the heat capacity jump ΔC has taken place, when approaching T_c from $T > T_c$.

b ΔT is the width of the transition, defined as the temperature difference between 10% and 90% of the heat capacity jump ΔC .

Figure 9. Total heat capacity of 1900 Å thick Al film sample SPAL-9, plotted as C/T vs. T^2 . The solid line is a fit to Eq. (36), with $\gamma_T = .129 \mu\text{J}/\text{K}^2$ and $\beta_T = .0303 \mu\text{J}/\text{K}^4$.

superconductivity transition of the Al film. The resistive transition is also shown on the same figure. Because the lowest temperature that could be achieved was on the order of 1K and because of the small value of T_c for Al films, it was not possible to obtain heat capacity data for $T \ll T_c$ and thus to carry out a consistent low temperature fit to the BCS theory which is necessary in order to determine any excess heat capacity due to fluctuations near but below T_c .

Therefore only the fluctuation contribution to the heat capacity C_{ex} above T_c could be determined. C_{ex} was obtained by subtracting the measured heat capacity near T_c , the extrapolated background heat capacity as follows.

$$C_{ex} = C(T) - [\gamma_T T + \beta_T T^3]$$

Figure 10 shows a plot of C_{ex} (determined from the subtraction described above) as a function of temperature. C_{ex} represents the deviation of the heat capacity from the mean field behavior that predicts a finite discontinuity ΔC at the BCS or thermodynamic transition temperature and normal state behavior consisting of a sum of terms cubic and linear in T above this temperature. As the precise value of the BCS transition temperature of the film is not known, the above subtraction might actually have been carried out to temperatures somewhat lower than the BCS transition temperature.

The solid line in Fig. 10 is the two dimensional Hartree approximation (see Eqs. 14a and 16), with two fitting parameters τ_0 and T_0 . The BCS coherence length ξ_0 for Al is $16,000\text{\AA}$. The mean free path l estimated from the normal state resistivity ρ_n using $\frac{l}{\rho_n} = 4 \times 10^{-12} \Omega \text{cm}^2$, turns out to be $45\text{\AA}$ ⁶⁸. In the dirty limit ($l \ll \xi_0$), the zero temperature coherence length $\xi(0)$ can be calculated from ξ_0 as follows³⁹.

$$\xi(0) = 0.85 (l \xi_0)^{1/2} \approx 720\text{\AA} \text{ for Al films.}$$

As our films have a thickness $d \approx 2000\text{\AA}$ they satisfy the condition $d < \xi(T)$ for $\xi < 0.13$ and it is reasonable to treat the films as being two dimensional. In the two dimensional Hartree approximation the width parameter is $\tau_0 \approx (k_F^2 l d)^{-1}$ ¹⁸. Using free electron model to express the normal state resistivity in terms of K_F and l , we arrive at a simple result for τ_0 ,

$$\tau_0 = 0.82 \times 10^{-5} R_{\square}^N \quad (37)$$

where $R_{\square}$ is the sheet resistance of the film.

We fit the excess heat capacity data to the Hartree approximation as follows. Equations (14a), (14b) and (16) of section II are combined and written as,

$$f(\bar{C}) = \left(\frac{1}{\bar{C}} - 1\right) + \ln\left(\frac{1}{\bar{C}} - 1\right) = AT + B \quad (38)$$

where $\bar{C}$ is the excess heat capacity scaled by ΔC , the BCS

Figure 10. The excess heat capacity C_{ex} , for the Al film, SPAL-9, plotted as a function of temperature. Two parameters, γ_T and β_T used for background subtraction are determined and given in Fig. 9. The solid line is s_3 Hartree approximation, Eq. (16) with $\tau_0 = 2 \times 10^{-3}$ and $T_0 = 1.56K$. $\Delta C \approx 0.15 \mu J/K$.

Figure 10.

jump at T_c . The value of ΔC estimated from the data.

$$A = \frac{1}{\tau_0 T_0} ; \quad B = \tau_0^{-1} - \ln[(q_c \xi(0))^2 / \tau_0] \quad (39)$$

If we plot both $f(\bar{C})$, defined by Eq. (38), and $\bar{C}$ obtained from excess heat capacity data as functions of T , we should get a straight line with an intercept B and a slope A . Since $q_c \approx \lambda^{-1}$ and τ_0 is the order of 10^{-3} , $\ln[(q_c \xi(0))^2 / \tau_0] \ll 1$. Therefore τ_0 and T_0 can be determined from A and B . According to the theory, T_0 will be higher than the BCS transition temperature. Since there are only two parameters, the fit is unique. The value of τ_0 determined from the fit is 2×10^{-3} . The sheet resistance $R_{\square}^N$ of the film is 1Ω . According to Eq. (37), theory predicts that τ_0 should be 0.82×10^{-5} . Therefore the width parameter required to fit the data to a Hartree form is 250 times greater than that predicted by the theory.

A possible reason for the observed anomalous broadening of the heat capacity transition is that the Al films are inhomogeneous, characterized by a certain distribution of T_c 's in the film. We have considered the theory of fluctuations in such a material in section II. Fig. 2, is a plot of the results from such a theory. As the inhomogeneity increases, we see a broadening of the transition. We should bear in mind that this broadening is not simply due to a distribution of T_c 's. It also takes into account the

fluctuations and their interactions. Because of the complex nature of the resulting equations of the theory and the inaccessibility of the parameters of the theory to independent determination, no attempt was made to make a quantitative comparison of experiment and theory.

(ii) Heat Capacity of Amorphous Nb₃Ge Films

Heat capacity data was obtained on six amorphous Nb₃Ge films. The transition temperatures were between 2.5K and 2.7K. Heat capacities were measured between 1.0K and 4.2K. In addition to an analysis in the regions above T_c , an analysis was also carried out below T_c . By a consistent analysis of the data, both above and below T_c , the BCS transition temperature could be uniquely determined.

For each sample, several different runs of data were obtained in the neighborhood of T_c . The heat capacities for different runs, sometimes varied by a few percent. The data for different runs could be brought into agreement over a wide temperature range, by simply multiplying various runs by a scale factor. The total accumulated data from different runs was then averaged.

The total heat capacity data for Nb₃Ge-4 and Nb₃Ge-6 films is shown in Fig. 11 and 12 respectively. We have shown the results for only two films in order to avoid repetition of similar background heat capacity data. Data for other films was of equally good quality. C/T is plotted as a function of T^2 . For $T > T_{BCS}$ an excellent straight line

Figure 11. Total heat capacity of Nb₃Ge-4 sample, plotted as C/T vs. T^2 . The small jump in the heat capacity at $T_{BCS} = 2.71\text{K}$ is the superconducting transition of the film. The solid lines are obtained by fitting the data to Eqs. (40) and (41) with $\gamma_T = .1375 \mu\text{J/K}^2$, $\beta_T = .0241 \mu\text{J/K}^4$, $\gamma_f = 9.48 \times 10^{-3} \mu\text{J/K}^2$.

Figure 12. Total heat capacity of $\text{Nb}_3\text{Ge-6}$ sample, plotted as C/T vs. T^2 . The small jump in the heat capacity at $T_{\text{BCS}} = 2.6\text{ K}$ is the superconducting transition of the film. The solid lines are obtained by fitting the data to Eqs. (40 and (41) with $\gamma_T = .134 \mu\text{J}/\text{K}^2$, $\beta_T = .0262 \mu\text{J}/\text{K}^4$ and $\gamma_f = 9.58 \times 10^{-3} \mu\text{J}/\text{K}^2$.

fit could be made. As explained in the previous section, the intercept of this straight line at $T = 0$, gives the value of γ_T , the coefficient of the total electronic heat capacity and the slope gives the value of β_T , the coefficient of the total lattice heat capacity. Therefore,

$$C(T) = \gamma_T T + \beta_T T^3 \quad T > 1.2 T_{BCS} \quad (40)$$

The transition temperature T_{BCS} has not been defined at this point. It is a parameter that will be determined from consistent fits of the theory to the heat capacity data for $T > 1.2 T_{BCS}$ and for $T < 0.8 T_{BCS}$.

The fit for $T < T_{BCS}$ needs special comment. Heat capacities of bulk amorphous Nb_3Ge have been measured by Tsuei et al. with 10% accuracy. They have determined the ratio $(\Delta C / \gamma T_c)$ to be 1.5, where ΔC is jump or the discontinuity in the heat capacity at T_c and γ is the coefficient of the electronic heat capacity of the film. According to the weak-coupling BCS theory, this ratio should be 1.43. For these films T_c was about 4K. For $T < T_c$, the variation in the heat capacity was found to be consistent with the BCS prediction, that is, $C \sim a \exp(-b/T)$ with $a = 8.5 \gamma T_c$ and $b = 1.44 T_c$. The tunnelling measurements on amorphous Nb_3Ge ($T_c \approx 3.6$) also indicate that it is a weak-coupled superconductor and closely follows the BCS theory. Our films exhibited even lower transition temperatures, therefore it is very likely that they are even better described by weak-coupling BCS theory for $T < T_{BCS}$.

Since we cannot determine the electronic heat capacity of the film by itself, we are not able to determine the ratio $(\Delta C/\gamma T_c)$ directly. However, from the above, it is reasonable to assume that the heat capacity of our film will follow weak-coupling BCS theory for $T < T_{BCS}$.

Therefore we chose to fit the data for $T < T_{BCS}$ to the following expression,

$$C(T) = (\gamma_T - \gamma_f)T + \beta_T T^3 + C_{BCS}(\gamma_f, T_{BCS}),$$

$$T < 0.8 T_{BCS} \quad (41)$$

where γ_f is the coefficient of the electronic heat capacity of the film and C_{BCS} the BCS heat capacity for $T < T_{BCS}$. The term $(\gamma_T - \gamma_f)T$ represents the total background addendum electronic heat capacity. The parameters γ_T and β_T of the low temperature fit are determined from the fit to the data for $T > T_{BCS}$. Numerical values of C_{BCS} are given in the tables of Ref. 70, tabulated for different values of the ratio T/T_{BCS} at intervals of 0.2. For the present analysis a linear interpolation of the tabulated data was used.

There are two possible ways to fit to the data. The first is to fit the data to Eq. (41), over the full temperature range between the lowest temperature and T_{BCS} . The second possibility is to fit the data to Eq. (41) over a restricted temperature range from the lowest temperature up to about $0.8 T_{BCS}$ (typically 2K). This range of temperature

is far from T_{BCS} and thus the effect of fluctuations on the heat capacity should be negligible. The parameters γ_f and T_{BCS} determined from this fit can then be used to compute the background heat capacity close to T_{BCS} . In this way any excess heat capacity in excess of the BCS heat capacity near T_{BCS} can be systematically determined by subtracting the computed background from the total measured heat capacity. For each fit, T_{BCS} was held constant and was allowed to vary until a best fit to the data was achieved. This procedure was repeated with different values of T_{BCS} . In this way the values of T_{BCS} and γ_f which gave the minimum standard error could be found.

The results of such fits are given in Table-IV. Column A corresponds to the case where only data between the lowest temperature ($\approx 1.1\text{K}$) and $0.8 T_{\text{BCS}}$ ($\approx 2.1\text{K}$) were used for the non-linear fit to Eq. (41). Column B corresponds to the case where all the data from lowest temperature up to $0.98 T_{\text{BCS}}$ were used for the non-linear fit to the same Eq. (41). In both cases, the goodness of the fit was determined by calculating the standard error between 1.1K and $0.8 T_{\text{BCS}}$ only. It is clear from the tables, that if the data is forced to fit the BCS theory all the way up to T_{BCS} , then the result is a worsening of the quality of fit at low temperatures, by a factor of 3, compared to the case where the fit is restricted to the range between 1.1K and $0.8 T_{\text{BCS}}$. This result is consistent with the possibility of there

Table IV: Results of least square fit to equation (41)
of the $T < T_{\text{BCS}}$ heat capacity data of $\text{Nb}_3\text{Ge-4}$

Temperature	Column A		Column B	
	$\sqrt{f}$	Square of standard error of estimate	$\sqrt{f}$	Square of standard error of estimate
2.67	0.9250×10^{-2}	0.7810×10^{-6}	0.1090×10^{-1}	0.2768×10^{-5}
2.68	0.9390×10^{-2}	0.7916×10^{-6}	0.1098×10^{-1}	0.2862×10^{-5}
2.69	0.9514×10^{-2}	0.7382×10^{-6}	0.1107×10^{-1}	0.2494×10^{-5}
2.7	0.9623×10^{-2}	0.7274×10^{-6}	0.1116×10^{-1}	0.2394×10^{-5}
2.705	0.9687×10^{-2}	0.6954×10^{-6}	-	-
2.71	0.9748×10^{-2}	0.6729×10^{-6}	0.1124×10^{-1}	0.2270×10^{-5}
2.715	0.9800×10^{-2}	0.6476×10^{-6}	-	-
2.72	0.9843×10^{-2}	0.6781×10^{-6}	0.1130×10^{-1}	0.2167×10^{-5}
2.73	0.9949×10^{-2}	0.7604×10^{-6}	0.1130×10^{-1}	0.2167×10^{-5}
2.74	1.006×10^{-2}	0.8126×10^{-6}	0.1146×10^{-1}	0.2574×10^{-5}

being a fluctuation contribution to the heat capacity below T_{BCS} . Therefore it seems appropriate to carry out an analysis below T_{BCS} in the same spirit as has been done above T_{BCS} . That is, we carry out a least square, fit of the data for $T < 0.8 T_{BCS}$, to Eq. (41) and then extrapolate the results into the range between $0.8 T_{BCS}$ and T_{BCS} to determine the excess heat capacity. The solid line in Figs. 11 and 12, below T_{BCS} is a result of such a fit to the data. The discontinuity in the solid line at T_{BCS} is the jump in the heat capacity. The excess heat capacity below T_{BCS} is not seen clearly on this graph because of its small value, but it will become obvious when we extract it from the total heat capacity using the procedure described above.

This kind of analysis has been carried out for three films, Nb_3Ge-3 , Nb_3Ge-4 and Nb_3Ge-6 . In displaying the data for BCS jump in the heat capacity $\Delta C = 1.43\gamma_f T_{BCS}$ has been added to the excess heat capacity for $T < T_{BCS}$. This has been done so that the deviations from mean field behavior, both above and below T_{BCS} can be displayed in a continuous fashion. Figures 13 through 15 show such plots for the three films. The resistive transitions are also shown on the same graphs for purposes of comparison. The relevant fitting parameters for these samples are listed in Table- V. The differences between T_{BCS} and temperatures at which the resistance vanished is an interesting feature that becomes evident from the comparisons of these three figures. This

Table V

Sample	Thickness d (Å)	γ_T ($\mu\text{J}/\text{K}^2$)	β_T ($\mu\text{J}/\text{K}^4$)	ΔC (μJ)	γ_f ($\mu\text{J}/\text{K}^2$)	T_{BCS} (K)	T_0 (K)	τ_0	$R_{\square}$ (Ω)
Nb ₃ Ge-2	4500 ±600	.1342	.0242	.124	-	2.7	2.84	4×10^{-4}	54
Nb ₃ Ge-3	1000 ±100	.1477	.0237	.029	7.84×10^{-3}	2.59	2.66	1.66×10^{-3}	330
Nb ₃ Ge-4	1500 ±150	.1375	.0241	.0366	9.48×10^{-3}	2.71	2.77	7.4×10^{-4}	130
Nb ₃ Ge-5	600 ±100	.111	.0193	.014	-	2.3	-	-	500
Nb ₃ Ge-6	1200 ±120	.134	.0262	.0355	9.58×10^{-3}	2.6	2.68	1.43×10^{-3}	250

Figure 13. Excess heat capacity of Nb_3Ge -3 film. The background for subtraction was determined by a consistent fit to the total heat capacity data well above and below T_{BCS} . The solid line is the mean field theory prediction. The relevant fitting parameters are listed in Table IV. The resistive transition is also shown for comparison.

Figure 13

Figure 14. Excess heat capacity of Nb_3Ge -4 film. The background for subtraction was determined by a consistent fit to the total heat capacity data well above and below T_{BCS} . The solid line is the mean field theory prediction. The relevant fitting parameters are given in Table IV. The resistive transition is also shown for the comparison.

Figure 14

Figure 15. Excess heat capacity of Nb_3Ge -6 film. The background for subtraction was determined by a consistent fit to the total heat capacity data well above and below T_{BCS} . The solid line is the mean field theory prediction. The relevant fitting parameters are given in Table IV. The resistive transition is also shown for comparison.

Figure 15

will be the subject of discussion in the next section. For the films Nb₃Ge-2 and Nb₃Ge-5 only an analysis for $T > T_{BCS}$ was carried out. The thinnest film ($d \approx 600\text{\AA}$), Nb₃Ge-5, had a broad peak in the heat capacity below T_{BCS} , which made a low temperature analysis difficult. From Figs. 13 through 15, it can be seen that T_{BCS} is approximately the temperature where 90% of the heat capacity jump has occurred, when T_{BCS} is approached from above. Therefore, this criterion was used in determining the values of T_{BCS} listed in Table-IV for two films, Nb₃Ge-2 and Nb₃Ge-5.

First let us discuss the excess heat capacity from the point of view of fluctuations above T_{BCS} . The zero-temperature coherence length was determined by measuring T_c , the shift in the mid-points of the resistive transition in applied magnetic fields H up to 400 G. From this data $\frac{dH_c}{dT}$ was found to be $\approx 10.8 \times 10^4$ G/K. $\xi(0)$ was then estimated to be 31 Å from the relation

$$\xi(0) = \sqrt{[\Phi_0 / 2\pi T_c (\frac{dH_c}{dT})]} .$$

Johnson et al.⁴⁴ have reported a similar value for amorphous Nb₃Ge. Since the films of the present work are between 1000 Å and 4500 Å thick, they do not satisfy the condition $d < \xi(T)$, except in the immediate vicinity of T_c . The films thus cross over from 3D behavior to 2D behavior near T_c . We will, therefore, use a two dimensional Hartree model, modified in the analysis of data to take into account the cross-over from three dimensional to two-dimensional behavior as

described in chapter II, section (iii).

The zero-temperature coherence length $\xi(0)$ and the measured film thickness of the film were fixed parameters of the analysis. The width parameter τ_0 and the renormalized transition temperature T_0 were the only two fitting parameters. For amorphous Nb_3Ge the "Debye cutoff" $q_c \sim 1 \sim 1 \text{ \AA}$. Therefore $[q_c \xi(0)]^2 / \tau_0 \approx 10^6 > 1$, since τ_0 is on the order of 10^{-3} . Equation (17) is solved for each temperature. $\xi(T)$ which is used to determine $G(T)$ is the coherence length in Hartree approximation, given by Eq. (17). This solution is then used in Eq. (16) to calculate the theoretical excess heat capacity C_{ex} . For ΔC , we use the BCS jump determined from the fit to the background heat capacity, since $\Delta C = 1.43 \gamma_f T_{\text{BCS}}$. Alternatively, we can solve for $\xi(T)$ for each temperature using Eq. (14a), calculate $G(T)$ from this and then use Eq. (18) to determine C_{ex} . The difference in the results of the two procedures is very small. The minicomputer was used for these calculations. As the computer was interfaced to a CRT display terminal, the theoretical curve could be plotted on the screen right on top of the excess heat capacity data. In this way, by varying τ_0 and T_0 a visual fit could be carried out.

The results of such a fit for four Nb_3Ge films are shown in Figs. 16 through 19. The solid line is the fit using Hartree theory. The parameters T_0 , τ_0 , ΔC and d are

Figure 15. The excess heat capacity C_{ex} of Nb_3Ge-2 film, for $T > T_{BCS}$. The solid line is Hartree theory with following parameters: $\tau_0 = 4 \times 10^{-4}$, $T_0 = 2.84K$, $\xi(0) = 30\text{\AA}$, $d = 4500\text{\AA}$, $\Delta C = 0.124 \mu J/K$.

Figure 17. The excess heat capacity C_{ex} of Nb_3Ge -3 film, for $T > T_{BCS}$. The solid line is Hartree theory with following parameters: $\tau_0 = 1.66 \times 10^{-3}$, $T_0 = 2.66K$, $\xi(0) = 30\text{\AA}$, $d = 1000\text{\AA}$, $\Delta C = 0.029 \mu J/K$.

Figure 18. The excess heat capacity C_{ex} of $\text{Nb}_3\text{Ge-4}$ film, for $T > T_{BCS}$. The solid line is Hartree theory with following parameters: $-3\tau_0 = 7.4 \times 10^{-4}$, $T_0 = 2.77\text{K}$, $\xi(0) = 30\text{\AA}$, $d = 1500\text{\AA}$, $\Delta C = 9.48 \times 10^{-3} \mu\text{J/K}$.

Figure 19. The excess heat capacity C_{ex} of Nb_3Ge-6 film, for $T > T_{BCS}$. The solid line is Hartree theory with following parameters: $-3\tau_0 = 1.43 \times 10^{-3}$, $T_0 = 2.68K$, $\xi(0) = 30\text{\AA}$, $d = 1200\text{\AA}$, $\Delta C = 9.58 \times 10^{-3} \mu J/K$.

listed in Table- V and are also given in the figure captions. The agreement between the fit using the Hartree theory and the data is good for all our four films up to about 50% of the jump ΔC , beyond this the data rises much more slowly than the Hartree prediction. The temperature T_0 is about 70mK greater than T_{BCS} .

Figure 20 is a plot of the width parameter τ_0 , determined from the Hartree fit, as a function of the normal state sheet resistance R^N for the four films. τ_0 shows a linear dependence on R as expected from Eq. (37). The slope of the plot of τ_0 vs. R^N determined from the plot is about 0.5×10^{-5} , whereas the theoretical value is 0.82×10^{-5} . The agreement is not bad given that the theoretical result in Eq. (37) is uncertain by a multiplicative factor of the order of unity. Also the error in the determination of τ_0 may be as great as 30%, due to errors in d and $\xi(0)$.

Let us now turn our attention to Figs. 13, 14, and 15. The three films Nb₃Ge-3,4 and 6, show deviations from BCS behavior in the form of a broad bump in the heat capacity near and below T_{BCS} . This bump is qualitatively similar to the peak predicted in the screening approximation calculations (see Fig. 2). We may rule out the following possibilities as explanations of the bump:

(1) The amount of material in the edges of the film is less than 1% of the total film material. The bump in the heat capacity rises to about 20-30% of the BCS jump in the

Figure 20. Width parameter τ_0 , determined from a fit to Hartree theory, as a function of $R_{\square}^n$ for Nb_3Ge films. The solid line is Eq. (37).

heat capacity, ΔC . Therefore the edges with lower transition temperatures than the bulk of the film are too small to account for the bump.

(2) The possibilities of inhomogeneity in the sample can be raised. However, by looking at the Figs. 13 and 14, a consistent explanation can not be given in terms of inhomogeneity. For example, Nb₃Ge-4 has a sharp resistive transition, yet the heat capacity shows a bump in the region where the resistance has gone to zero. On the other hand, Nb₃Ge-3 exhibits a broad resistive transition, the bump in its heat capacity has all but disappeared. The heat capacity being a bulk property, will always show the effects of large scale inhomogeneities. If a broad resistive transition is a sign of inhomogeneity broadening, then one would expect to see an even bigger bump in the heat capacity in the Nb₃Ge-3 film. Furthermore, if the transition were broadened by inhomogeneities, this should have resulted in unreasonably large values for the parameter τ_0 , as we have seen in the case of Al films. Therefore we must conclude that it is very unlikely that the observed bumps in the heat capacity below T_{BCS} are due to inhomogeneities of the samples.

It is not clear at the present time as to the cause of the above features. If they are due to the fluctuations, we need a theory that accounts for the fluctuation heat capacity below T_{BCS} , in the regime intermediate between two and three

dimensions. Qualitatively the features appear to be spread over a wide range below T_{BCS} than the excess heat capacity due to fluctuations is above.

It is interesting to note that the bump seems to move away from T_{BCS} , as the resistive transition broadens. This is clear from the Fig. 21 where all three plots are shown together. The bump seems to be near the tail of the resistive transition. This seems to suggest that it may have some connection with the Kosterlitz-Thouless transition which we will consider in the next section.

(iii) Kosterlitz-Thouless transition

In this section, we will consider the Kosterlitz-Thouless transition as a possible explanation for some of the features of the Nb_3Ge films.

Figure 21 is a plot of the excess heat capacity and the resistive transitions of the three Nb_3Ge films, shown together for purposes of comparison. From top to bottom they are displayed in order of increasing sheet resistance $R_{\square}^N$. One feature that clearly becomes evident is, that the difference between the temperature where the resistance vanishes and the temperature T_{BCS} determined from heat capacity measurements, increases with increasing $R_{\square}^N$.

Let us first consider some elementary explanations.

(1) The first question that one might raise is, whether the temperature scales for the heat capacity and resistance measurements are the same or not. As explained

Figure 21. Figure 13, 14 and 15 are plotted together. (a) shows excess heat capacity and resistance for $\text{Nb}_3\text{Ge-4}$ with $R_N = 130\Omega/\text{sq.}$ (b) same for $\text{Nb}_3\text{Ge-6}$ with $R_N = 250\Omega/\text{sq.}$ (c) for $\text{Nb}_3\text{Ge-3}$ with $R_N = 330\Omega/\text{sq.}$

Figure 21.

earlier, both the heat capacity and resistance were obtained simultaneously using the same thermometer to determine the temperature of the sapphire substrate. Of course the heat capacity measurements require that the substrate be heated resulting in a dc temperature difference between the Helium pot and the substrate. This temperature difference, which was the order of 200mK, was measured using a thermocouple. Two separate runs were carried out, with the heater power on and off. The resistive transitions in each case were found to be within a few mK. This rules out the possibility that the observed shift is a consequence of the temperature gradients set up by steady-state heating and also shows that the thermocouple calibrations were correct.

(2) From Fig. 5 we see that only a small strip portion of the total film was used for the resistive measurements. The strip is on one side of the substrate therefore one can raise questions about possible temperature gradients across the length of the substrate. However it must be remembered that even the worst case thermal conductance of the sapphire substrate is too high to account for any temperature gradients. The substrate is definitely an isothermal platform.

(3) There might be a thickness gradient in the film from one end to the other. If this were true, then in the strip we would measure a resistive transition with a different T_c than the rest of the film. Again this possibility can be ruled out by a simple argument; that it will give

rise to a very strong source of broadening in the heat capacity. Therefore we would expect to see a heat capacity transition broadened by several hundred mK in the film where the resistive transition is broadened. But scrutiny of the three figures reveals that the 10% to 90% heat capacity transition occurs over a 100mK temperature interval and is about the same for all the three films. True four-terminal measurements across the whole film are in progress and have revealed that the resistive transition is the same when measured over the rest of the film.

(4) We have seen that as the films get thinner their transition temperatures drop. Therefore film edges will have lower T_c 's and will be shorted out by the rest of the material in the resistive measurements. Therefore it is unlikely that the edges can be responsible for the long tails in the resistive transitions.

The heat capacity measurements on our samples help us to make strong arguments in support of Kosterlitz-Thouless transition as a possible explanation. The analysis of the heat capacity data uniquely determines T_{BCS} . At T_{BCS} there is a thermodynamic signature of the transition which implies that the bulk of the material in the films is undergoing a superconducting transition. As we have seen in the theory section, Kosterlitz-Thouless theory when applied to superconductors, predicts that below the temperature T_{BCS} there will be a finite resistance due to flux flow of free

unbound vortices. Below Kosterlitz-Thouless transition temperature T_{2D} , these vortices will form bound pairs and the resistance should disappear.

In our films we see that with increasing sheet resistance $R_{\square}^N$ the resistance disappears at temperatures lower than T_{BCS} . As shown by Beasley et al.¹¹, T_{2D}/T_{BCS} is a function of $R_{\square}^N$ given by Eq. (26). We have used arbitrary criterion that T_{2D} is the temperature where $R/R_N = 10^{-4}$. Figure 22 shows a plot of T_{2D}/T_{BCS} as a function of $R_{\square}^N$ for five of our films. The solid line is a plot of Eq. (26). One can see that the behavior is qualitatively similar.

We have also studied the effect of a perpendicular magnetic field H on the resistivity of one of the films, Nb_3Ge-6 . The substrate was kept perpendicular to the field to within five degrees. The thermometers were observed to be shifted by 40mK to lower temperatures during this second run using this sample. The reason for this shift which manifested itself in both resistance and heat capacity measurements is not known. All the data on resistivity as a function of field H , will be discussed in the remaining part of this section, are 40mK lower than previous data. A PAR-190, 1:100 transfer and a lock-in offset unit PAR-123 were used to measure resistances to better than 1 part in 10^6 of $R(4.2)$. A superconducting magnet wound on the copper can was used to generate perpendicular magnetic fields up to 400 G. Intermagnetics model 75-M or Harrison 6112A was used

Figure 22. Plot of T_{2D}/T_{BCS} as a function of R_N for fine Nb_3Ge films. T_{BCS} was determined from the heat capacity data. T_{2D} is arbitrarily determined as the temperature where $\frac{R}{R_N} = 10^{-4}$.

for the magnet power supply. Due to a malfunction of the persistent current switch the magnet was not used in the persistent current mode. It was determined that the magnet current was constant to better than 1 part in 10^4 . Two different sets of data were obtained. In one set of measurements temperature was varied through the tail region of the resistive transition with the magnetic field H held fixed. Only the lower 10% of the R vs. T curve was found to be sensitive to H . In the other set of measurements the bath and the substrate temperatures were held constant and the resistance of the film was determined as a function of H . The magnetic field was swept up to 85 G slowly at a rate of 1 G/min., to avoid any eddy current heating effects.

Figure 23 is a plot of the film resistance scaled by $R(4.2K)$, plotted as a function of temperature in the tail region in different fields. The resistance is seen to be very sensitive to small magnetic fields in the range between 2K and 2.2K. There is a small tail in the resistance in zero field between 2K and 2.16K (the residual field in the dewar is less than 5×10^{-4} G). The natural logarithm of the resistance ratio is plotted in Fig. 24 as a function of T between 2K and 2.2K for different fields. Even though there is noise in the data it is clear that there is an exponential dependence of $R(T,H)$ on T . Figure 25 shows a similar semilogarithm plot over a much wider temperature range in zero field and in three different fields. We can note the

Figure 23. Resistance in the tail region of the transition of $\text{Nb}_3\text{Ge-6}$ film, in different magnetic fields a - $< 5 \times 10^{-4}$ G, b - 0.43 G, c - 2.45 G, d - 9.68 G, e - 19.26 G, f - 34.36 G, g - 86.0 G.

Figure 24. Natural log. of the resistance (scaled by $R(4.2)$) in the tail region of the transition, in different magnetic fields. a - $< 5 \times 10^{-4}$ G, b - 0.43 G, c - 2.45 G, d - 9.68 G, e - 19.26 G, f - 34.36 G, g - 86 G for sample $\text{Nb}_3\text{Ge-6}$.

Figure 25. Natural Log. of the resistance (scaled by $R(4.2)$) of $\text{Nb}_3\text{Ge-6}$ as a function of temperature in different fields. X is in a field $H < 5 \times 10^{-4} \text{ G}$.

similarity between this plot and the inset of Fig. 3 in which the results of a model calculation of $R(T,H)/R_N$ as a function of T for different fields is shown. Even though we have not made a quantitative comparison, it is reasonable to say that qualitatively the effects of magnetic fields in the tail region of the resistive transition (that is close to where we expect the transition temperature T_{2D}) are similar to the predictions of the theory.

In order to analyze the field dependence of R , we had to subtract the zero field value of the resistance. Therefore $\Delta R(T,H) = R(T,H) - R(T,0)$, scaled by $R(4.2)$ is plotted on a log-log plot in Fig. 26 for different fixed temperatures. There is no uniform power law dependence on H over the whole range of field. Due to the complex nature of the theoretical results no quantitative analysis could be carried out¹⁰. The data for $H > 10G$ could be fitted to a straight line in the plot of Fig. 26. Such an analysis was done for the set of data at each temperature. The slope of the straight line gives the exponent of H . It is interesting to note that, whereas the value of the exponent is 0.5 below 2K, it gradually rises to a maximum value of 0.95 at 2.12K and then begins to drop again at higher temperatures. At 2.35K it is 0.675 and above 2.45K, the field dependence of R (up to 85G) has all but disappeared.

It should be mentioned here that these resistance measurements were pseudo four-terminal measurements. The

Figure 26. Plot of $\Delta R(T, H) = R(T, H) - R(T, 0)$, scaled by $R(4.2)$ as a function of H on a log-log scale, for different temperatures in the tail region of the resistive transition of $\text{Nb}_3\text{Ge-6}$ film.

total measured resistance includes the resistance of the Au beads and that of small lengths of manganin wire. However the temperature dependence of the resistance of the beads and the manganin wires is very small and does not interfere with the measurements except perhaps in the very tail end of the transition ($R/R(4.2) < 1 \times 10^{-5}$). The temperature dependence of the resistance of the Au beads and the manganin wires was determined from measurements made for $T < 1.5\text{K}$ and was subtracted off from the data near 2K. The effect of the magnetic field was also studied at temperatures below 1.5K in order to make sure that the effects we see near 2K are not due to the magnetoresistance of the manganin wires. At the present time true four-terminal measurements are being carried out on the same samples in order to get more accurate data.

It is also important to mention that all the resistance measurements were carried out at current densities as low as 0.05 A/cm^2 . We did not see any effects of higher current densities on the resistance in the tail region. Special attempts were made to determine the magnitude of any pinning currents. Because of the pseudo four-terminal characters of the resistance we used an ac bridge to cancel out the wire resistances and determined dI/dV . If there was any pinning critical current, it must have been lower than 0.05 A/cm^2 . This is very surprising, since most Type-II materials have typically, very high pinning currents, on the order of tens

of A/cm^2 ⁷¹. On the other hand it is also encouraging, because if we can show by true four-terminal measurements that pinning currents are indeed low, it implies that we have some sort of fluid of vortices. The existence of such a vortex fluid might be an important factor in proving that there is a Kosterlitz-Thouless phase transition in superconductors.

The heat capacity was also measured in a magnetic field of 5 G, and an analysis involving subtraction of the background for $T > T_{\text{BCS}}$ was done. The noise in the data went up by a factor of three relative to the zero-field data mainly due to pick-up in the thermocouple wire coils moving in the field as a result of vibrations. As far as we could tell, the bump in the heat capacity was still present.

(iv) Fluctuation conductivity:

Fluctuation conductivity was observed in the Nb_3Ge films even up to $1.7 T_c$. At the time the data was analyzed, we were not aware of the corrections to the fluctuation conductivity of dirty superconductors⁴⁶. Therefore the data was forced to fit to a three dimensional Aslamazov and Larkin¹⁶ expression given by the Eq. (31b), which can be rewritten as,

$$\frac{\sigma_{\text{ex}}}{\sigma_N} = (R_N - R(T))/R(T) = \frac{g_{\text{AL}} \cdot \rho_n}{2 \cdot \xi(0) \cdot \sqrt{\epsilon}} = C/\sqrt{\epsilon}$$

where R_N and σ_N are the normal state resistance and resistivity respectively. R_N was not independently

determined but it was adjusted so that the data would vary as $\sqrt{\epsilon}$ far away from T_c . This resulted in a value of R_N that was about 2% higher than R at 4.2K. Then the constants C and T_c were adjusted to force agreement between the theoretical curve and the experimental data. The reduced temperature was replaced by $\ln(T/T_c)$ which is appropriate for $T \gg T_c$ ⁷². The result of such a fit to the Nb_3Ge -6 data is shown in Figs. 27 and 28. The parameters C and T_c , for other Nb_3Ge films, determined in this way are listed in Table VI. There is no systematic dependence of C on ρ_n . The theoretical estimate for C is the order of 7×10^{-2} which is about a factor of five larger than what we obtain using above analysis.

However we now understand that the fluctuation conductivity is not supposed to vary as predicted by AL theory. Departures from such a behavior have already been observed in dirty amorphous superconductors^{44,45}. It has been observed that fluctuation conductivity is smaller than that predicted by AL theory. Our analysis also leads to a similar conclusion. The reason for this has been discussed in the theory section. Ami and Maki⁴⁶ have calculated the corrections but their results are too complicated to calculate and compare with the data. A simple approximate form for the conductivity near T_c in their theory is given by Eq. (32). Using this equation, a better numerical agreement with the parameter C obtained from the fit could be achieved.

Figure 27. Plot of (σ/σ_{ex}) as a function of T for Nb_3Ge -6 film. A plot of this kind emphasizes the region, $T \gg T_c$. The solid line is obtained by fitting the data to Eq. (31b) with parameters $R_N = 2879\Omega$, $T_c = 2.458K$, $C = 1.55 \times 10^{-2}$.

Figure 27.

Figure 28. R vs. T for $\text{Nb}_3\text{Ge-6}$ film. The solid line is obtained by fitting the data to Eq. (31b). The parameters used in the fit are given in Fig. 27.

Table VI

Sample	$R_{\square}^N$ ($\Omega/\square$)	T_c (K)	C	ρ_n ($\mu\Omega\text{-cm}$)
Nb ₃ Ge-1	113	2.57	2.22×10^{-2}	-
Nb ₃ Ge-2	54	2.74	2.28×10^{-2}	2500
Nb ₃ Ge-3	330	2.556	1.095×10^{-2}	3300
Nb ₃ Ge-4	130	2.74	1.59×10^{-2}	1950
Nb ₃ Ge-5	500	2.53	1.5×10^{-2}	3000
Nb ₃ Ge-6	250	2.458	1.55×10^{-2}	2500

A more quantitative analysis and an independent determination of R_N is necessary to get a better understanding of the fluctuation conductivity in amorphous Nb_3Ge .

VIII. CONCLUSION

We have measured the heat capacity of amorphous and disordered Nb_3Ge thin films by an ac technique in the temperature range between 1K and 4.3K. The transition temperatures were found to be about 2.6K. Therefore a temperature region as wide as 1.5K was accessible both above and below the transition temperature T_c , where the data could be fit to the expected behavior of heat capacity, away from T_c . Extrapolating results of these fits close to T_c allowed us to extract any departures from the mean field behavior both above and below the BCS transition temperature T_{BCS} .

These departures which we call, the excess heat capacity C_{ex} , can be attributed to thermal fluctuations of the order parameter. Reasonably good agreement was found for C_{ex} , with the Hartree model¹⁸ modified for a semi-infinite three dimensional system for $\epsilon < 0.03$. As T approaches T_{BCS} , C_{ex} rises much more slowly than predicted by the Hartree approximation. Since the Hartree model is based on using the $|\psi|^4$ term in the simplest possible approximation, it will not adequately describe a real system close to T_{BCS} . The interaction between the fluctuations is taken into

account in a perturbative fashion in the screening approximation solution to the problem^{22,28}. These calculations predict a peak in the heat capacity, rising up to about 30% of the BCS jump, ΔC . This peak disappears from the results of the theory as the system becomes inhomogeneous.

We have also seen a broad bump in the excess heat capacity near and below T_{BCS} , that rises to 20% to 30% of the BCS jump. The bump appears to be qualitatively similar to the predictions of the theory. Relative to the resistive transition, the bump in the heat capacity occurs near the end of the transition where resistance is going zero. The theory is strictly valid for a two dimensional system. It is not clear how the results would be modified in the case of our films. Therefore no quantitative comparison of experiment and theory was possible.

Because of the lack of understanding at the present time, no other analysis was done to determine the nature of the excess heat capacity below T_{BCS} . We have seen evidence for Kosterlitz-Thouless transition in our films. But the theoretical predictions indicate that the signature of this transition on the thermodynamic properties is almost nil. For higher sheet resistance films, the bump in the heat capacity gets smaller. If there is a Kosterlitz-Thouless transition in our system, then there should be a large number of free vortices in the tail region of the resistive transition (also the region where we see a bump in the heat

capacity). It is possible that an interaction between the vortices and the order parameter may suppress the fluctuations below T_{BCS} (fluctuation in superconductors below T_{BCS} are known to exist²).

Our work on Nb_3Ge films has also raised the interesting possibility that we are seeing Kosterlitz-Thouless transition involving binding and unbinding of vortices in our high sheet resistance films. The heat capacity measurements, coupled with unique high and low temperature fitting scheme, allows us to determine the thermodynamic transition temperature T_{BCS} relative to the resistive transition. A naive determination of $T_{2\text{D}}$ from the resistive transition gives qualitative agreement for the ratio $T_{2\text{D}}/T_{\text{BCS}}$ predicted by the simple Kosterlitz-Thouless theory. Quantitatively our ratios are smaller for high sheet resistance films. However, we must point out that the present theoretical calculations do not take into account the interaction of other vortex pairs. This will renormalize the interaction between two vortices yielding a distance dependent dielectric constant. This could lower the value of $T_{2\text{D}}$ from the present theoretical estimates, giving better agreement with our results.

The magnetic field and temperature dependence of the resistance in the tail region has also served as a means for probing this type of transition. Our results are in qualitative agreement with recent calculation by Doniach et al.¹⁰.

Turkevich⁷³ has pointed out that the calculations, of Doniach et al. and Halperin et al.⁷⁴ are actually a low vortex-density calculation. In the superconducting case it is possible to have a high density of vortex pairs near the transition. It is not clear what features of the treatment of Doniach et al. and Halperin et al. would survive in a fully renormalized high density calculation.

The interpretation of our work was carried out in the middle of a very recent and rapidly growing theoretical interest in the possibility of a topological phase transition in superconductors. The evidence for such a phase transition in our system is not conclusive at this point. More theoretical work is necessary, based on realistic models. Experimentally one will have to find more quantitative evidence. It might be important to establish the presence of a vortex fluid in the system. The easiest way might be to quantitatively determine the small size of the pinning currents and to investigate the limiting behavior of $R(T)$. Direct evidence showing the motion of the vortices would be a conclusive way of studying the proposed vortex fluid.

REFERENCES

1. L.D. Landau and E.M. Lifshitz, Statistical Physics, Pergamon (London) 1958.
2. R.V. Carlson and A.M. Goldman, Phys. Rev. Lett. 31, 880 (1973) and 34, 11 (1973).
3. V.L. Ginzburg, Sov. Phys. S. S. 2, 1824 (1960).
4. P.C. Hohenberg, Proceedings of the Conference on Fluctuations in Superconductors; A. Silomar, California, W.S. Goree and F. Chilton, Editors, 1968, Stanford Research Institute.
5. J.M. Kosterlitz and D.J. Thouless, J. Phys. 6, 1811 (1973) and 7, 1046 (1974).
6. D.R. Nelson and J.M. Kosterlitz, Phys. Rev. Lett. 39, 1201 (1977).
7. I. Rudnick, Phys. Rev. Lett. 40, 1454 (1978).
8. D.J. Bishop and J.D. Reppy, Phys. Rev. Lett. 40, 1727 (1978).
9. J. Pearl, Appl. Phys. Lett. 5, 65 (1964), LT-9, 566 (1969).
10. S. Doniach and B.A. Huberman, submitted to Phys. Rev. Lett.
11. M.R. Beasley, J.E. Mooij and J.P. Orlando, submitted to Phys. Rev. Lett.
12. V.L. Ginzburg and L.D. Landau, Zh. Eksp. Toer. Fiz. 20, 1064 (1950).
13. L.P. Gorkor, Sov. Phys. JETP 9, 1364 (1959).

14. R.A. Ferrell, J. Low Temp. Phys. 1, 241 (1969).
15. H. Schmidt, Z. Physik. 216, 336 (1968).
16. L.G. Aslamazov and A.I. Larkin, Sov. Phys. S. S. 10, 875 (1968).
17. R.A. Ferrell, Int. Symp. on Contemp. Phys. Trieste (1968).
18. L. Gunther and L.W. Gruenberg, S.S. Comm. 10, 567 (1972).
19. S. Grossman, P.H. Richter and C. Wissel, S. S. Comm. 11, 433 (1972).
20. S.K. Ma, J. Math. Phys. 15, 1866 (1974).
21. R.A. Ferrell and D.J. Scalapino, Phys. Lett. 41, 371 (1972).
22. D.J. Scalapino and R.A. Ferrell, Phys. Rev. Lett. 31, 292 (1973).
23. R.A. Ferrell and J.J. Quinn, Phys. Rev. 108, 570 (1957).
24. R.A. Ferrell and J.J. Quinn, Phys. Rev. 112, 812 (1958).
25. A.J. Bray and G. Rickayzon, J. Phys. F. 2, 409 (1972).
26. E. Simanek and J.C. Hayward, J. Phys. F. 5, 2330 (1975).
27. E. Simanek, J. Phys. F. 6, 1661 (1976).
28. A.J. Bray, Phys. Rev. 13, 3807 (1976).
29. J.F. Cochran, Annals. of Phys. 19, 186 (1962).
30. L.T. Barnes and R.R. Hake, Phys. Rev. 153, 153 (1967).
31. P.A. Lee and S.R. Shenoy, Phys. Rev. Lett. 28, 1025 (1972).
32. R.F. Hasing and R.R. Hake, Phys. Rev. Lett. 30, 6 (1973).

33. A.J. Bray, Phys. Rev. 9, 4752 (1974).
34. D.J. Thouless, Phys. Rev. Lett. 34, 946 (1975).
35. S.P. Farrant and C.E. Gough, Phys. Rev. Lett. 34, 943 (1975).
36. G.D. Zally and J.M. Mochel, Phys. Rev. 6, 4142 (1972).
37. G.D. Zally and J.M. Mochel, Phys. Rev. Lett. 27, 1710 (1971).
38. A.M. Goldman, J.C. Solinsky and T.J. Magee, J. Low Temp. Phys. 20, 339 (1975).
39. M. Tinkham, Introduction to Superconductivity, McGraw Hill, 113 (1975).
40. K. Maki, Progr. Theoret. Phys. (Kyoto) 39, 897 (1968) and 40, 193 (1968).
41. R.S. Thompson, Phys. Rev. B1, 327 (1970).
42. B.R. Patton, Phys. Rev. Lett. 27, 1273 (1971).
43. B. Keck and A. Schmid, S. S. Comm. 17, 799 (1975).
44. W.L. Johnson and C.C. Tsuei, Phys. Rev. B13, 4827 (1976).
45. W.L. Johnson, C.C. Tsuei and P. Chaudhari, Phys. Rev. B17, 2884 (1978).
46. S. Ami and K. Maki, Phys. Rev. B18, 4714 (1978).
47. R.H. Buitrago, Doctoral Dissertation, University of Minnesota (1973), unpublished.
48. R.W. Cohen and B. Abeles, Phys. Rev. 168, 444 (1968).
49. J.J. Hauser, Phys. Rev. 3, 1611 (1971).
50. P.F. Sullivan and G. Seidel, Phys. Rev. 173, 679 (1968).
51. R. Viswanathan and C. Varmazis, private communications.

52. G.D. Zally, Doctoral Dissertation, University of Illinois (1970), unpublished.
53. NBS Monograph 131, U.S. Department of Commerce (1973).
54. R. Viswanathan, J. Appl. Phys. 46, 4086 (1975).
55. P. Manuel and J.J. Veyssie, Phys. Rev. Lett. 41A, 235 (1972).
56. Alterovitz, Deutsher and Gershenson, J. Appl. Phys. 46, 3637 (1975).
57. R.L. Greene, C.N. King and R.B. Zubeck, Phys. Rev. 6, 3297 (1972).
58. R. Viswanathan, Analytical Calorimetry 3, 81 (1974).
59. Insaco Inc., P.O. Box 422, Quaker Town, PA 18951.
60. R.V. Carlson, Doctoral Dissertation, University of Minnesota (1975).
61. C. Varmazis, R. Viswanathan and R. Caton, Rev. Sci. Instrum. 49, 549 (1978).
62. R. Rosenbaum, Rev. Sci. Instrum. 39, 890 (1968).
63. R.L. Powell, H.M. Roder and W.M. Roger, J. Appl. Phys. 28, 1283 (1957).
64. R. Berman, J.C.F. Brock and D.J. Huntley, Cryogenics 4, 233 (1964).
65. Cryocal Inc., Rivera Bearu, Florida 33404.
66. Scientific Instruments Inc., 632 South F. Street, Lake Worth, Florida 33460.
67. J.C. Solinsky, Doctoral Dissertation, University of Minnesota (1973), unpublished.

68. W. Masker and R. Parks, Phys. Rev. B1, 2164 (1970).
69. C.C. Tsuei, W.L. Johnson, R.B. Laibowitz and J.M. Viggiano, S. S. Comm. 24, 615 (1977).
70. B. Mühlischlegel, Z. Physik 155, 313 (1959).
71. P.M. Horn and R.D. Parks, Phys. Rev. B4, 2178 (1971)
and the references therein.
72. E. Abrahams and J.W.F. Woo, Phys. Lett. 27A, 117 (1968).
73. L.A. Turkevich, J. Phys. C, to be published.
74. B.I. Halperin and D.R. Nelson, submitted to J. Low Temp. Phys.

PART II

Low Temperature Electrical Resistivity
Measurements on Dilute Pd(Fe)
Alloy Thin Films.

I. INTRODUCTION

In the past decade there has been intensive experimental and theoretical effort directed at understanding the critical behavior of systems undergoing higher-order phase transitions. A wide variety of types of ordering have been studied including magnetic, liquid-gas, order-disorder and ferro-electric. Although a good deal of progress has been made towards understanding of equilibrium properties at these transitions, the non-equilibrium properties are less well understood. There has been an increasing interest in the non-equilibrium properties, even though the exact nature of the singularities have not been determined theoretically for real systems. It is quite clear that for a variety of model systems mean field calculations are not adequate.

Most recently attention has begun to shift towards understanding the behavior of transport process in the neighborhood of the critical point. Transport properties near critical points appear to be more system dependent than equilibrium properties. It appears that a detailed understanding will require a knowledge of the specific interactions involved in each system. Oftentimes, transport properties provide a sensitive and rather simple means of studying the details of the microscopic interaction.

In order to probe the behavior of dilute Pd(Fe) alloy films, in the neighborhood of the ferromagnetic phase transition,

we have attempted to study one of the transport properties, namely, resistivity. In the past 10 years a substantial amount of data has accumulated concerning resistivity anomalies in materials exhibiting magnetic phase transitions. These anomalies are usually characterized by the temperature derivative of the resistivity $\frac{d\rho}{dT}$ near the transition temperature T_c .

The theory and the experimental results will now be presented in the following order. Section II contains a brief account on the Fisher and Langer theory¹, and a review of spin fluctuation enhancement effects and properties of giant moments in Pd and Pd(Fe) alloys. This section will also contain a brief review of the previous resistivity measurements on bulk Pd(Fe) alloys. In Section III we describe, in detail, the sample preparation and the evaporation techniques. Section IV describes our results on some Pd(Fe) alloy films. The differences between our experimental results on Pd(Fe) alloy films, and the previous measurements on the bulk Pd(Fe) alloys of similar composition are discussed in Section V.

II. THEORY

This section contains a review of the theories and previous experimental work pertinent to the discussion of our results.

(i) Fisher and Langer Theory

Resistive anomalies of ferromagnetic metals were first explained by Fisher and Langer¹. Their model is the same as the one used by deGennes and Friedel², namely, a lattice of magnetic ions with spins $\bar{S}_i$ at site $\bar{R}_i$ and a band of free conduction electrons with spin density $\bar{S}_e$. The exchange interaction between the conduction electrons and magnetic ions is described by ,

$$H_{ei} = G \sum_i S(\bar{r} - \bar{R}_i) \bar{S}_i \cdot \bar{S}_e(\bar{r}).$$

Qualitatively, any disorder in the alignment of the magnetic ions will scatter the conduction electrons giving rise to high-temperature disorder scattering. As the temperature approaches T_c , the ordering of the magnetic ions decreases this scattering and hence the resistivity $\rho(T)$. The resistivity due to spin scattering is $\rho = \frac{m}{ne^2} \tau_m$, where n , m and τ_m are, respectively, the density of the conduction electrons, effective mass and the relaxation time,

associated with scattering from spin fluctuations. The relaxation time is given by,

$$\frac{\tau_0}{\tau_m} = \frac{2\pi}{\sigma_0} \int_0^\pi \sigma(\theta) (1 - \cos\theta) \sin\theta d\theta \quad (1)$$

τ_0 and σ_0 are the relaxation time and total cross section in high temperature limit, respectively. The differential scattering cross-section $\sigma(\theta)$ can be calculated in the Born approximation. After summing over final states and performing a thermal average over initial states, it is of the form.

$$\sigma(\theta) = \frac{\sigma_0}{4\pi} \sum_{\vec{R}_i} \Gamma(\vec{R}_i, T) \exp(i\vec{R} \cdot \vec{R}_i) \quad (2)$$

where,

$$\sigma_0 = \frac{1}{4\pi} \left(\frac{MG}{h^2} \right)^2 S(S+1), \text{ and}$$

$$\Gamma(\vec{R}_i, T) = \frac{\langle \vec{S}_0 \cdot \vec{S}_i \rangle - \langle \vec{S}_0 \rangle \cdot \langle \vec{S}_i \rangle}{S(S+1)} \quad (3)$$

is the static spin-spin correlation for two spins separated by $\vec{R}_i$. If correlations between the ionic moments on different sites are neglected, then,

$$\sigma(\theta) = \frac{\sigma_0}{4\pi} \left[1 - \frac{\langle \vec{S} \rangle^2}{S(S+1)} \right]$$

and

$$\frac{\rho_m}{\rho_0} = \frac{\tau_0}{\tau_m} = 1 - \frac{\langle S \rangle^2}{S(S+1)} \quad (4)$$

Equation (4) describes the dominant source of decrease in resistivity below T_c , that decreasing as $\langle \bar{S} \rangle^2$, the square of the magnetization.

In order to describe the temperature dependence of the resistivity above T_c , the correlations of spin fluctuations have to be taken into account. deGennes and Friedel² calculated τ_m , with $\Gamma(\bar{R}, T)$ given in the Ornstein-Zernike approximation,

$$\Gamma(R, T) \sim \frac{1}{R} \exp(R/\xi) \quad (R \neq 0) \text{ with } \xi \sim \left(\frac{T - T_c}{T_c} \right)^{-\frac{1}{2}} \quad (5)$$

Here ξ is the coherence length over which fluctuations are correlated. Equation (5) predicts that $\rho(T)$ has an upward-pointing cusp at T_c , and that $\frac{d\rho_m}{dT}$ has a logarithmic divergence which is positive as $T \rightarrow T_c$ and negative as $T \rightarrow T_c^-$.

Most experiments disagree with the above theory. The resistivity $\rho(T)$ decreases monotonically with temperature through T_c and $\frac{d\rho}{dT}$ shows a positive divergence for $T \rightarrow T_c^\pm$.

Fisher and Langer¹ pointed out that each term in equation (2) represents the interference in the scattering of electrons from fluctuating spins separated by $\bar{R}_i$. Even if these spins are strongly correlated, electrons will not scatter from them coherently if $\bar{R}_i$ is appreciably greater than the electron mean free path ℓ . They argue that $\Gamma(R, T)$ should be damped by a factor $p(R)$ which decreases monotonically from unity on a scale fixed by ℓ . Since ℓ remains finite near T_c , they concluded that the detailed form of the resistance anomaly will be determined by

the short range part of $\Gamma(R, T)$ for which, the Ornstein-Zernike approximation is not valid. They also note that since the magnetic energy involves only nearest neighbor interactions and the same correlation function, it will also have the same dominant singularity as $\Gamma(R, T)$, $R \neq 0$. This leads to a divergence in $\frac{d\rho}{dT}$ which is the same as that of heat capacity C_p at the critical point.

$$\frac{d\rho}{dT} = C_p \sim \left(\frac{T - T_c}{T_c} \right)^{-\alpha} \quad T > T_c$$

This relationship is verified by using a more sophisticated form of correlation function based on a scaling hypothesis. $\rho(T)$ is continuous at T_c and the dominant contribution to $\frac{d\rho}{dT}$ for $T < T_c$ comes from the incoherent scattering term $\Gamma(0, T)$, thus,

$$\frac{d\rho}{dT} \sim \langle S \rangle^2 \sim |M_0(T)|^2 \sim \left(\frac{T - T_c}{T_c} \right)^{2\beta - 1} \quad \text{for } T < T_c$$

for $T > T_c$, $\rho(T)$ is constant and takes on its high temperature limiting value of spin disorder resistivity. Calculations have also been carried out using an itinerant electron model³, which also shows that short-range correlations lead to a similar kind of divergence.

So far experiments⁴⁻⁷ on Ni, have been in good agreement with the above predictions. However in the case of Pd(Fe), as we shall see in the next section, even though there

is qualitative agreement $\frac{d\rho}{dT} > 0$ for $T \rightarrow T_c^\pm$, the transitions are too broad and T_c is not precise. Therefore one does not have well defined critical exponents for this system.

(ii) Some Properties of Pd and Pd(Fe) Alloys

The element Pd is a very interesting metal. A lot of theoretical and experimental work has been carried out in order to understand the detailed nature of the quantum mechanical many-body effects taking place in this system. It will be helpful to review these developments briefly before we attempt to understand the behavior of our films. The following are the main features of Pd and Pd(Fe) alloys.

(1) Pd with atomic number 46, has 10 electrons outside a Kr like core. The ground state configuration is $(Kr)(4d)^{10}$, but the $(4d)(5s)^1$ configuration lies only $6.56 \times 10^3 \text{ cm}^{-1}$ above this state⁸. In metallic Pd the 5s state is lowered relative to the 4d state, and the broad conduction band, arising from the 5s and 5p states, overlaps the narrow 4d band. Consequently, as states are filled up below Fermi level, there are 0.36 unoccupied d states. Due to the narrowness of the d-band the density of states of itinerant electrons at the fermi energy is much larger than most metals. This is reflected by the large contribution of the itinerant electrons to the electronic specific heat.

(2) The magnetic properties of Pd are most interesting. Because of the high densities of states $N(\epsilon_F)$, one would expect

a high value for Pauli susceptibility. However the measured values of the static spin susceptibility⁹ is an order of magnitude greater than even such an estimate. It is now believed that this is due to a short-range, interatomic (Coulomb) interaction between the d electrons. Simple Hartree-Fock theory¹⁰ indicates that the susceptibility of the metal is higher than the Pauli susceptibility by a factor $[1 - U_0 N(\epsilon_F)]^{-1}$, known as Stoner enhancement factor, where U_0 is a measure of the strength of electron-electron interaction. Hartree-Fock theory indicates that if $U_0 N(\epsilon_F) \geq 1$, then the system is unstable with respect to the ferromagnetic state. For Pd, $U_0 N(0) \approx 0.9$, which implies that interatomic coulomb interactions are so strong in Pd that the d band is near the threshold of instability with respect to a ferromagnetic state.

(3) Giant moments: Low and Holdman¹¹, using neutron scattering, have investigated the distribution of the magnetic moment in Pd around an Fe impurity. The general picture is that at the site of each Fe atom there exists a magnetic moment of $3 - 4\mu_B$. Surrounding this site, Pd atoms are polarized up to a distance of about $10 \text{ \AA}$.

The nearest-neighbor atoms of the Fe impurity carry a moment of about $0.07\mu_B$. This moment falls off exponentially with distance at such a rate that the total moment of the complex is $10\mu_B$. The giant moment thus consists of a rather small spin density spread out over many atoms surrounding the impurity.

Such a long range polarization is too large to be explained by the Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction. Clearly it seems to be related to the very large susceptibility of the Pd host. Details of the theory of the wave-vector dependent susceptibility $\chi_n(k)$ can be found in reference 12. If one approximates the short range electron-electron interaction $v(q)$ by a constant v_0 one gets the following expression for the enhanced susceptibility,

$$\chi_n(k) = \frac{\left(\frac{g\mu_B}{2}\right)^2 F(k)}{[1 - v_0 F(k)]} \quad (6)$$

where

$$F(k) = -\sum_q \frac{n_{k+q} - n_k}{[\epsilon(k+q) - \epsilon(k)]}$$

where the $\epsilon(k)$ is the renormalized energy in the random-phase approximation (to the extent of replacing $\frac{\hbar^2 k^2}{2m}$ by $\epsilon(k)$), g is the splitting factor and μ_B is the Bohr magneton. In the absence of electron-electron interactions, $F(k)$ goes over to the density of states at the Fermi level $N(\epsilon_F)$ times the Lindhard function. When the above equation (6) is used to calculate the conduction electron spin polarization $\sigma(r)$ around the impurity,¹³ one finds that the oscillation in the RKKY interaction are washed out and the range of polarization is extended somewhat. However Clogsten^{14, 15} has argued that one has to assume a unrealistic values of the interaction strength to bring the range function

into agreement with experiment. In addition to the effect of the intra-atomic exchange interaction, he also considers inter-atomic exchange between electrons on the nearest neighbor atoms. Clearly the electron-electron interaction becomes wave-vector dependent. Even though the results are very complicated in detail, under certain approximations $\chi_n(k)$ can again be written in the form of equation (6), except that the v_0 is replaced by another k -dependent term $\lambda(k)$. $F(k)$ also gets modified but for $k \rightarrow 0$ it reduces to $N(\epsilon_F)$. The central point is that in the limit of $k \rightarrow 0$, $\lambda(k)$ reduces to $(J + J^1 Z)$ where J is the intra-atomic exchange energy J^1 is the inter-atomic exchange energy, Z is the number of the nearest neighbors. The spin density around an impurity again shows a washed out RKKY behavior, but the largest contribution to the enhancement factor α (the denominator in the expression for $\chi_n(k)$ in the equation (6)) comes from J^1 term.

(4) Spin fluctuation effects in Pd. Above we have seen that the Stoner enhancement factor is quite large in Pd, which implies that the repulsive inter-atomic coulomb interactions are so strong that the d-band is near the threshold of instability with respect to the ferromagnetic state. In this situation one expects to find the long-wavelength, low frequency fluctuations in the spin-density of the d electrons to have large amplitude. Such fluctuations also known as "paramagnons," can have very

interesting effects on the various transport and thermodynamic properties of strongly interacting fermion systems, such as Pd and also liquid ³He . We will consider here, only the effect of paramagnons on the low temperature resistivity of Pd and Pd alloys. One considers the scattering of S electrons from spin-density fluctuations in the d-band. Such a scattering gives rise to a resistivity proportional to T^2 , which can be observed at low temperatures where phonon contribution is small.

Schindler and Rice¹⁶ have found that resistivity of Pd indeed exhibits a T^2 term below 9K. Adding Ni (< 2 at .%, so that the alloy is nonmagnetic) to Pd, increases the coefficient of the T^2 term. They also give a theoretical analysis which requires the spin-fluctuation spectral density function $A(q, \omega)$, obtained from the imaginary part of the exchange enhanced spin susceptibility discussed above. To apply the theory to alloys, they introduced an average intra-atomic coulomb interaction $\bar{U}$, which increases with increasing impurity concentration. Lederer and Mills¹⁷ argue that the region of space in the vicinity of the magnetic impurity cell would be much more closer to the magnetic instability than the host Pd matrix. Therefore the amplitude of the spin-fluctuations is enhanced in the vicinity of the impurity cell, compared with the amplitude in the host material far from the impurity cell. Hence a local enhancement model is reasonable, with the intra-atomic

potential U_I in the impurity cell, modified from that in pure host U_0 by $\delta U = U_I - U_0$. The results show that the change in the coefficient of the T^2 is approximately proportional to $\left(\frac{\delta U}{U_0}\right)^2 \alpha^2$, where α is the local Stoner enhancement factor.

It should be emphasized that all this work attempts to explain the increase in T^2 term as a consequence of local or uniform enhancement effects. It does not consider the effect of potential scattering.

(iii) Review of Previous Experimental Work

The present work was initiated in order to study the effect of the influence of the proximity effect between magnetic and superconducting films on the superconducting fluctuations above T_c . The idea was to make a superconductor-oxide-superconductor junction with one side replaced by a proximity sandwich of a superconducting and a magnetic film. By measuring the pairfield susceptibility of the proximity sandwich, one can study the temperature dependence of anomalous spin flip scattering time in the magnetic film via its signature in the spectrum of the order-parameter fluctuations in the superconducting films^{18, 19} For this work we wanted thin films which would ferromagnetically order around 2K. Magnetic susceptibility and electrical conductivity measurements have been carried out on bulk AuNi and dilute Pd(Fe) alloys. Attempts to make good AuNi films were not successful, therefore the details of the

work on this system including metallurgical characterization by electron diffraction will not be discussed here. Only the work on thin films of Pd(Fe) alloys will be considered here.

Ferromagnetic ordering in Pd(Fe) alloys has been studied extensively²⁰. The curie temperatures of such alloys can be lowered by decreasing their Fe content. Ferromagnetic ordering has been studied by looking at the behavior of the resistivity near the curic point²¹⁻²⁵. All the experiments show a peak in $\frac{d\rho_m}{dT}$, and are in qualitative agreement with the theory of Fisher and Langer.¹ Dilute Pd(Fe) alloys (≤ 1 at .% Fe) are also interesting. Even a 0.092 at .% Fe alloy shows a phase transition at 0.4K²⁶. Alloys below 0.3 at .% Fe have very sharp transitions and there has been some attempt to extract critical exponents from the temperature dependence of $\frac{d\rho_m}{dT}$.^{22, 27, 28} Heat capacity, as measured in some Pd(Fe) alloys^{29,30}, shows a peak near the curie temperature in agreement with Fisher and Langer theory.¹

Most of our Pd(Fe) alloy films are in the range of 0.2 - 0.35 at .% Fe concentration. It will be helpful to reproduce some of the previous experimental results on bulk Pd(Fe) alloys of comparable Fe concentration. In Fig. - 1, we exhibit a plot of the magnetic part of the resistivity $\rho_m(T)$ and $\frac{d\rho_m}{dT}$ for two alloys with 0.25% and 0.1% Fe concentration, reproduced from reference 22. Note that $\rho_m(T)$ is obtained by subtracting the

FIG. 1. $\Delta\rho_m(T) = \rho_m(T) - \rho_m(T_L)$ and $d\rho_m/dT$ for 0.1 and 0.25 at. % of Fe in Pd. T_L is the lowest temperature of the data and is 0.4°K for 0.1% and 2.0°K for 0.25% sample. The arrows indicate the respective ordinate scales.

$$\rho_m(T, c) = \rho(T, c) - \rho_{pd}(T) - \rho_0(c)$$

Figure 1. (from ref. #22)

FIG. 1. Comparisons of the thermal and electrical resistivities of palladium with Eq. (2) of the text. In these plots the intercepts of the straight lines yield the coefficients in the electron scattering terms, while the slopes yield the coefficients in the phonon scattering terms. Error bars represent, respectively, $\pm 0.5\%$ and $\pm 0.1\%$ of the measured thermal and electrical resistivities. The straight lines were obtained by fitting the data to Eq. (2) with a conventional least-squares technique.

$$\begin{aligned} \rho - \rho_0 &= A1.T^2 + A2.T^5 \\ A1 &= 3.1 \times 10^{-5} \mu\Omega\text{-cm/K}^2 \\ A2 &= 1.1 \times 10^{-8} \mu\Omega\text{-cm/K}^4 \end{aligned}$$

Figure 2. (from ref. #31)

temperature dependent part of the pure Pd resistivity $\rho_{Pd}(T)$ and the residual resistivity ρ_0 . Obviously Mathiessen's rule has been tacitly assumed to hold.

Figure-2 is a plot of the resistivity of pure Pd below 10K, taken from reference 31. There has been lot of work on low temperature resistivity of pure Pd^{16, 23} in an attempt to understand the nature of T^2 dependence down to very low temperatures. It is believed that the T^2 term is due to electron-electron scattering induced by paramagnons¹⁶. The purpose of Fig.-2 is to exhibit the magnitude of $\rho_{Pd}(T)$ in the temperature range of interest. The coefficient of the T^2 term is about $3.1 \times 10^{-5} \mu\Omega \text{ cm/K}^2$. The change in the pure Pd resistivity $\Delta\rho_{Pd}(T)$ from 1K to 10K is on the order of $3 \text{ n}\Omega\text{cm}$. The change in the magnetic part of the resistivity $\Delta\rho_m(T)$, from 1.5K up to the temperature where it becomes temperature independent, varies according to the alloy concentration. For concentrations between 0.1% and 0.3% it is on the order of $20\text{-}50 \text{ n}\Omega\text{cm}$. Therefore in order to study the critical behavior of $\rho(T)$, near T_e , one has to subtract $(\rho_{Pd}(T) + \rho_0)$ from the total resistivity. Figures-3 and 4 taken from references 26 and 24 respectively show the total resistivity vs T . Again the change in the resistivity $\Delta\rho_m$, due to magnetic transition is on the order of $20 \text{ n}\Omega\text{cm}$.

We have reproduced these results to describe qualitatively and quantitatively the behavior in the bulk Pd(Fe) alloys. They

Figure 3. (from ref. 26)

FIG. 1. Resistivity of PdFe alloys as a function of T^2 . The figures on the left-hand ordinate are residual resistivities obtained by extrapolating the straight lines to $T=0$. The right-hand scale applies to the 1450-ppm Fe alloy.

FIG. 1. Temperature dependence of the electrical resistivity for Pd+0.2 at.% Fe with and without hydrogenation. The arrow represents the Curie temperature of the hydrogen-free sample. Note that H/M refers to the hydrogen-to-metal ratio.

Figure 4. (from ref. 24)

will be useful for purposes of comparison with our data on thin films which seem to agree qualitatively with the results on bulk alloys, but which in some films exhibit values of $\Delta\rho_m$ several orders of magnitude higher than in bulk alloys.

III. MATERIALS AND METHODS

The work considered in the previous section was done on bulk Pd(Fe) alloys. This is the first time to our knowledge, anybody has attempted to study magnetic ordering in dilute Pd(Fe) alloy films. This section explains in detail the methods used for film preparation and data acquisition.

(i) Sample Preparation

Thin films of Pd(Fe), (Fe concentration ≤ 0.3 at.%) were prepared by vacuum evaporation. Alloy charges were prepared by melting the desired amounts of Fe and Pd in an alumina crucible. A vacuum system with an oil diffusion pump and a LN_2 cold trap was first evacuated to 10^{-7} torr and then backfilled with about 1 atm. of He gas. The alloy charge was then melted several times by heating the crucible up to 1550°C . The charge was then annealed at 800°C for 3-5 hours in a 10^{-7} torr vacuum. Two different procedures were used to evaporate the alloy charge.

Method A

Here the charge was evaporated at a slow rate where rates of the species is governed by their vapor pressure. According to Raoult's Law, which applies to dilute solutions, the vapor pressure P_A^* of the solution is lower than that of the pure solvent P_A by

an amount which is proportional to the concentration of the solute³²⁻³⁴. Therefore if X_A and X_B are the mole fractions of the solvent and solute respectively, then Raoult's Law states,

$$P_A \equiv (P_A^* X_A) \cdot f_A$$

$$P_B = (P_B^* X_B) \cdot f_B$$

where f_A and f_B are activity coefficients which for a simple dilute solutions can be taken to be equal to 1. Deviations from Raoult's Law imply $f_A, f_B \neq 1$.

The rate of evaporation of each constituent is proportional to its vapor pressure and is given by³³.

$$R_{\left(\frac{A}{B}\right)} = 5.85 \times 10^2 \cdot P_{\left(\frac{A}{B}\right)}^* \cdot M_{\left(\frac{A}{B}\right)} \cdot \frac{1}{T} \quad (\text{gm cm}^{-2} \text{ sec}^{-1})$$

Assuming that the surface area for evaporation is the same for both A and B one obtains the ratio of the atomic % of A and B in the vapor phase as

$$\frac{d_A}{d_B} = \left(\frac{M_B}{M_A}\right)^{3/2} \left(\frac{P_A^*}{P_B^*}\right) \left(\frac{W_A}{W_B}\right) \dots \quad (7)$$

with $d_A + d_B = 1$

Here $M_{\left(\frac{A}{B}\right)}$ are the gram-atomic masses and $W_{\left(\frac{A}{B}\right)}$ are the actual

weights of the constituents in the alloy charge.

It is clear from the equation (7) that the composition of the alloy in the evaporated film is determined by the ratio of the vapor pressures at the temperature of evaporation and the ratio of

the weights of the constituents. The vapor pressures of Pd and Fe in the temperature range 1300° - 1800°C can be found in reference 34. The melting points for Fe (1539°C) and Pd (1550°C) and their vapor pressures at higher temperatures are quite close, therefore they are good candidates for this method. The ratio of

$\left(\frac{P_{Fe}^*}{P_{Pd}^*}\right)$ at the evaporation temperatures of 1600°C is about 3.1 .

1 gram of alloy charge was prepared with $\left(\frac{W_{Pd}}{W_{Fe}}\right) = 2494$, which

implies an Fe concentration of 0.076 at.%. If equation (7) is obeyed during the evaporation at 1600°C, one would expect to get about 0.33 at % Fe in the evaporated film.

The alloy charge was put in an alumina crucible in the vacuum system. The crucible was heated with a Ta crucible heater ³⁵. The temperature of the crucible was measured using an optical pyrometer. The pressure during the evaporation was about 1.5×10^{-6} torr. The rate of evaporation was about 5 Å/sec. Two films, PdFe-1 and PdFe-2 were prepared using this method.

Method B: Flash Evaporation

A small amount of alloy charge was quickly evaporated to completion. The composition of the evaporated film remains the same as that of the alloy charge unlike method A. Such quick heating cannot be achieved by heating a crucible. Thus one has to use thin (5 or 10 mil) Tongston boats. However a serious problem is

that, Pd and Fe both attack W, Mo and Ta. Therefore the only chance for success is to put small amounts of the alloy charge in a Tungston boat and as soon as it melts, evaporate it quickly before it has a chance to attack the boat. The Fe concentration in the alloy was about 0.25 at.%. The evaporation temperature was about 1800 - 1900°C, and evaporation rates of 80 Å/sec could be achieved. However there was another problem that developed with this method. Films deposited this way on to glazed alumina substrates cracked as soon as they were cooled down below room temperature. Films deposited on sapphire substrates failed in a similar way. We believe that Pd(Fe) films deposited at high rate are under high stress which tends to increase upon subsequent cooling³⁶. In the case of Ni films, it has been found that the internal stress can be reduced by depositing the film at about 1/3 of its crystalization temperature³⁷. We tried to evaporate PdFe films onto alumina substrates held at about 130°C. Films prepared this way did not crack and the phonon resistivity behaved in a normal fashion. PdFe-7 and PdFe-8 were prepared this way. Two other films that we studied, PdFe-3 and PdFe-4, were made by E. Chock at University of California, Los Angeles by sputtering technique from a Pd-0.2 at.% Fe target.

All of our films had well-defined lengths and widths. Thicknesses were monitored during preparation using a quartz crystal oscillator thickness monitor and were later measured

interferrometrically. After the evaporation of a PdFe film, about 1000 Å thick Al pads and leads were evaporated to make electrical contacts for 4-terminal resistance measurements.

(ii) Data Acquisition

All the low temperature resistivity measurements were made in the cryostat designed by R.V. Carlson³⁸. Films evaporated on Al_2O_3 substrates, were held in a copper block. Four terminal contacts were made to the evaporated pads through beryllium-copper spring-loaded rods using a ternary eutectic solder of Bi-Th and Hg. The copper block containing the sample was in loose thermal contact with an inner ^4He -bath which could be pumped down to about 1K.

The temperature of the sample block was measured with a calibrated Ge-resistance thermometer using an A.C. bridge³⁹ employing a PAR 129 to measure the off-null signal. The output of the bridge was fed back to a heater, on the sample block, an arrangement which permitted the temperature to be controlled and held constant to better than 100 μK . The thermometer was calibrated from 1K to 20K with an absolute accuracy of 3 mK.

The sample resistance measurement was carried out using a Data General Nova 1200 minicomputer equipped with analog-to-digital and digital-to-analog converters. A signal from a digital-to-analog converter was used as a current source for the sample through a large current limiting resistor. The D.C. voltage

drop across the sample was measured using one of the A/D channels. The current was determined by measuring the voltage across the current limiting resistor on a second channel. The direction of the current was switched for each reading by the computer and an average of the voltages across the sample for such sign was computed so as to cancel thermal e.m.f.s. The sample block was stabilized at a given temperature and about 1000 readings of the current and voltage signals were recorded using the computer. These readings were then averaged and the final resistance value and the temperature were stored in the computer. In this way point-by-point the data was taken at regular temperature intervals. The data from a given run were finally stored on floppy disks for future analysis. Changes in resistance of about 1 part in 2000 could be resolved using the above procedure.

In some of the samples $\Delta\rho_m$ became too small to be measured by the above method. In those samples (PdFe-7 and PdFe-8) resistance was measured on an A.C. bridge at 400 Hz using a PAR-HR-8 lock-in amplifier as a null detector. Both in-phase and out-of-phase signals were balanced for each reading. Changes in $R(T)$ of better than 1 part in 10^5 could be resolved.

A cryogenic linear temperature sensor was used as the thermometer for the measurement of the temperature dependence of resistivity from room temperature down to 20K. This sensor has accuracy of about 0.5K.

IV. RESULTS AND ANALYSIS

On Figures 5 through 7, we show plots of the total low temperature resistance $R(T)$ of three of our thin films PdFe-1, PdFe-3 and PdFe-7. The resistivity $\rho(T)$ is also indicated by the numbers in large parenthesis. There are four contributions to $\rho(T)$ in the range $1K < T < 20K$:

$$\rho(T) = \rho_0 + \rho_m(T) + A_1 T^2 + \rho_{ph}(T)$$

Here ρ_0 is the temperature independent residual resistivity at the lowest temperature attained in the measurements. $\rho_m(T)$ is the temperature dependent resistivity due to the magnetic phase transition. $A_1 T^2$ is the resistivity due to electron-electron scattering¹⁶ in the Pd host. $A_1 \approx 3 \times 10^{-5} \mu\Omega\text{cm}/K^2$ for pure bulk Pd. $\rho_{ph}(T)$ is the phonon part of the resistivity which varies as $A_2 T^5$ at low temperatures and is quite small below 10K. Typically ρ_0 and $\rho_m(T)$ are quite large in our samples compared to the other two terms, as can be seen from the flat region above T_c which shows a very weak temperature dependence. Therefore no attempt was made to subtract this slowly varying background from the total $\rho(T)$ in the first three samples.

For some reason, $\Delta\rho_m(T)$ is very small in PdFe-8. Therefore a background subtraction had to be made. First $(\rho(T) - \rho_0)/T^2$ was plotted as a function of T^3 . The slope of the

Figure 5. Temperature dependence of the electrical resistivity of sample PdFe-1.
 $d \approx 500 \text{ \AA}$, $\rho_0 = 35.2 \mu\Omega\text{-cm}$, $\Delta\rho_m = 2.395 \mu\Omega\text{-cm}$.

Figure 6. Temperature dependence of resistivity and dR/dT for sample PdFe-3.
 $d \approx 1400 \text{ \AA}$, $\rho_0 = 8.67 \mu\Omega\text{-cm}$, $\Delta\rho_m = 0.87 \mu\Omega\text{-cm}$, $T_c \approx 2.17 \text{ K}$.

Figure 7. Temperature dependence of the resistivity and dR/dT of sample PdFe-7.

$d = 670 \text{ \AA}$, $\rho_0 = 18.9 \text{ } \mu\Omega\text{-cm}$, $\Delta\rho_m = 0.166 \text{ } \mu\Omega\text{-cm}$, $T_c \approx 6.0 \text{ K}$.

Fig. 8(a)

Fig. 8(b)

- (a) The total resistivity after subtracting $\rho_{ph}(T)$ is plotted as a function of T^2 for Pdfe-8. The solid line is a straight line fit to the data with $A_1 = 7.69 \times 10^{-5} \mu\Omega cm/K^2$
- (b) $\rho_m(T) + \rho_0$ obtained after subtracting $A_1.T^2$ and $A_2.T^5$ terms from the total $\rho(T)$, as a function of Temperature for Pdfe-8.

Figure 9. Log-log plot of $(-d^2R/dT^2)$ vs E . + is for PdFe-3 with $T_c = 2.17$. O is for PdFe-7 with $T_c = 6$ K.

data between 10K and 20K then gives $A_2 = 1.54 \times 10^{-8} \mu\Omega\text{cm}/\text{K}^4$.

It is interesting to note that this value is within 30% of the value reported^{31, 40} for pure Pd. The $\rho_{ph}(T) = A_2 T^5$ term was then subtracted from $\rho(T)$, and the resulting $\rho(T)$ was plotted as a function of T^2 which is shown in figure 8(a). Above about 7K one can see that $\rho(T)$ is varying as T^2 , as expected, since $\rho_m(T)$ becomes temperature independent. The parameter A_1 can be easily determined from this plot. A similar analysis was carried out on samples PdFe-3 and PdFe-7. In figure 8(b) we plot $\rho(T)$ after further subtraction of the $A_1 T^2$ term. This remaining resistivity should be equal to $\rho_0 + \rho_m(T)$.

Figure 5 is a plot of total $\rho(T)$ vs T for PdFe-1. This film was made by slow evaporation from an Al_2O_3 crucible. The transition is not very clean, but its resistance begins to drop at about 7K. No further analysis was done on this sample.

Figures 6 and 7 show the total $\rho(T)$ vs T for PdFe-3 and 7 respectively. The film PdFe-3 was made by sputtering from a 0.2 at. % Fe target and therefore might be more homogeneous than the evaporated films. It was about 1400 Å thick. PdFe-7 was made by flash evaporation and was about 670 Å thick with an alloy composition of about 0.25 at. % Fe. Both these films show fairly clear transitions. PdFe-3 with 0.2 at. % Fe has a behavior qualitatively very similar to the 0.2 at. % Fe bulk alloy reported in reference-24. $\frac{dR}{dT}$ was computed for both these

samples by method of sliding averages⁴. A parabola is fitted to a set of adjacent experimental points. Then one calculates the derivative of the fitted curve at the middle point and assigns this value as the derivative at that experimental point. By sliding the parabola along the curve, $\frac{dR}{dT}$ can be generated over the whole transition region. $\frac{dR}{dT}$ generated this way is also shown on the same graph.

To extract the critical exponents, the following standard analysis was carried out: we can write,

$$\frac{d\rho}{dT} \cong \frac{d\rho_m}{dT} = \frac{A}{\lambda} (\epsilon^{-\lambda} - 1) + B$$

where

$$\epsilon = \left(\frac{T - T_c}{T_c} \right)$$

where we have assumed that the AT^2 term is small and slowly varying. It will have even less significance when the second derivative is computed:

$$\frac{d^2R}{dT^2} \cong \frac{d^2\rho_m}{dT^2} = -\frac{A}{T_c} \epsilon^{-(\lambda + 1)}$$

T_c is taken to be at the peak of $\frac{dR}{dT}$ curve. Then a log-log plot of the above equation gives λ directly. Figure 9 is such a plot for the samples PdFe-3 and PdFe-7. It is clear that there is no well-defined exponent, however values of $\lambda = 3$ and 2.35 are similar to values found for bulk samples described in reference 22. The following parameters were defined and calculated for all the films:

- (1) $\Delta\rho_m$ is the change in resistivity due to the magnetic transition. It is equal to the difference between the resistivity in the flat region above T_c and the resistivity ρ_0 at the lowest temperature.
- (2) $\Delta\rho_{ph}$ is the change in phonon part of the resistivity from room temperature down to about 6K.
- (3) T_{knee} was defined as the temperature at which the resistance begins to decrease.
- (4) T_{peak} was defined as the temperature where the peak in $\frac{dR}{dT}$ appears (only in samples where such an analysis could be done).

All these parameters are listed in Tables I and II. We can summarize our result by pointing out following similarities and dissimilarities with results on bulk Pd(Fe) alloys:

- (1) Even though the films were prepared by evaporation the composition achieved in the films was close to what was expected, as judged from their R vs T behavior. The resistivity anomaly occurred approximately at the right temperatures. In particular for PdFe-3, prepared by sputtering, the anomaly is very similar to that seen in a 0.2 at .% bulk alloy²⁴.

Table I

Sample	Thickness	Residual resistivity ρ_0 ($\mu\Omega$ -cm)	$\Delta\rho_{ph}^*$ ($\mu\Omega$ -cm)	T_c (Peak) (K)	T_{knee}^{**} (K)	Method of Preparation
PdFe-1	500	35.2 ± 3.5	12.4 ± 1.2	-	7.0	By slow evaporation from Al_2O_3 crucible (Method-A of text)
PdFe-3	1400	8.67 ± 0.87	10.93 ± 1.1	2.17	2.8	By sputtering (condition not known) from 2000ppm Fe target
PdFe-4	1400	36.05 ± 3.6	11.08 ± 1.1	-	2.8	By sputtering (condition not known) from 2000ppm Fe target
PdFe-7	670	18.89 ± 1.9	11.97 ± 1.2	6.0	7.1	By flash evaporation (Method B of text)
PdFe-8	670	9.48 ± 0.9	13.22 ± 1.3	-	5.5-6	By flash evaporation (Method B of text)

* $\Delta\rho_{ph}$ is the change in phonon part of the resistivity from room temperature down to 7K.

** T_{knee} is the approximate temperature where the resistance begins to decrease due to magnetic phase transition.

Table II

Sample	Approximate F_e concentration* (at. %)	Expected $\Delta\rho_m$ (from data on bulk) ($\mu\Omega$ -cm)	Observed $\Delta\rho_m^*$ in our films ($\mu\Omega$ -cm)	Coefficient of T^2 term ($\mu\Omega$ -cm/K ²)	Coefficient of T^5 term A ² ($\mu\Omega$ -cm/K ⁴)
PdFe-1	$.27 \pm .03$	$(.03-.05)^a$	$2.395 \pm .24$	-	-
PdFe-3	.2	$.012^b$	$.87 \pm .09$	227.8×10^{-5}	-
PdFe-4	.2	$.012^b$	.003	-	-
PdFe-7	$.25 \pm .03$	$(.02-.05)^a$	$.166 \pm .02$	9.4×10^{-5}	-
PdFe-8	$.25 \pm .03$	$(.02-.05)^a$	$.0043 \pm .0005$	7.69×10^{-5}	1.54×10^{-8}

* Estimates for samples PdFe-1, PdFe-7 and PdFe-8 are based on the composition of the target and the method of evaporation used. For PdFe-3 and PdFe-4, which were prepared by sputtering, it is the target composition.

a Estimate from Ref. - 23.

b Estimate from Ref. - 24.

** $\Delta\rho_m$ is the change in the resistivity due to the magnetic transition. It is calculated as follows

$$\Delta\rho_m = \rho(\text{above } T_{\text{knee}}) - \rho(\text{at the lowest temperature})$$

- (2) The change in the phonon resistivity $\Delta\rho_{ph}$ is of the right order. In pure Pd it is about $11\mu\Omega\text{cm}$ ⁴¹.
- (3) The magnetic transition in these Pd(Fe) systems (including bulk) is perhaps not as simple as in the description of alloys by Fisher and Langer¹. Therefore analysis to extract critical exponents does not carry much meaning. Nevertheless, the results of analysis carried out on our samples do resemble similar analysis on bulk alloys, indicating that we are seeing qualitatively the same behavior.
- (4) The most puzzling aspect of our results is the magnitude of $\Delta\rho_m$. For some of our samples it is very large, varying from a few times the value in bulk alloys as in PdFe-7 to about 2 orders of magnitude higher than in bulk as in PdFe-1 and PdFe-3. This is a comparison of films with bulk Pd(Fe) alloys of similar Fe concentration. The absolute error in determining the resistivity can be no more than 10-20%. The fact that the $\Delta\rho_{ph}$ was found to be of the right order, eliminates the possibility that there are large scale structural defects, such as, pits and valleys in the film which are making the calculation of $\rho(T)$ from $R(T)$ incorrect. It is even more surprising that in PdFe-8 and PdFe-4, $\Delta\rho_m$ is even smaller than expected, by a factor of 4. PdFe-4 prepared by sputtering with same composition as PdFe-3 exhibited an anomaly at about the same temperature as seen in

PdFe-3. In this case $\Delta\rho_m$ was 4-5 times smaller than that expected from bulk measurements. Unfortunately the coefficient of the T^2 term A_1 was not determined for this film.

- (5) The films in which $\Delta\rho_m$ was large, also showed equally large enhancements of the parameter A_1 , the coefficient of the T^2 term coming from electron-electron scattering. For PdFe-3 A_1 was enhanced by a factor of 70, as compared to the value expected in pure Pd. For PdFe-7, the enhancement factor was only about 4 (at least) and for PdFe-8 it was close to 1. Therefore there appeared to be some correlation between the enhancements of $\Delta\rho_m$ and of the electron-electron scattering term at low temperature.
- (6) Some of the films were recycled from room temperature several times. The low temperature behavior was very reproducible upon recycling.
- (7) We Auger analyzed some of these films. The depth profile indicated a fairly constant Pd and Fe peak ratio as a function of thickness. Quantitative analysis could not be carried out because the Fe signal was very small and suitable standards for calibration were not available. No other metallurgical analyses were done on these films.

V. DISCUSSION

The most puzzling aspect of these results is the large variation in the $\Delta\rho_m$ observed. The first doubt that comes to one's mind is that, there might be an inhomogeneous distribution of Fe or clustering effect. The result of this would be to smear out the transition. But all the films studied indicate that the transition occurs at about the same temperature as in bulk alloys of the same Fe concentration. The films prepared by sputtering would be expected to have a low probability of compositional inhomogeneity. Two films prepared in this way, PdFe-3 and PdFe-4 were sputtered from the same target. They showed resistance anomalies very similar in nature occurring at about the same temperature, but $\Delta\rho_m$ differed in magnitude by a factor of 200.

A_1 , the coefficient of T^2 term was also determined in some of the films. It seems to increase in proportion with $\Delta\rho_m$. The smallest A_1 observed was still 2 times higher than A_1 for pure Pd. This was in the case of PdFe-8, which had a value of $\Delta\rho_m$ approximately 4 to 5 times smaller than that seen in bulk alloys. In the case of PdFe-3, A_1 and $\Delta\rho_m$ were both about 70 times higher than in bulk. We know that the $A_1.T^2$ term comes from s electron scattering from Paramagnons. This would then tend to indicate that for some reason in some of the films the spin fluctuations are enhanced relative to the bulk Pd.

The reason for such an enhancement is not clear at the present time. The residual resistivities do not give any clue since they depend on various parameters. All the films that were prepared by slow evaporation have higher values of ρ_0 compared to other films because they have perhaps more impurities. The fact that the Pd films prepared by rapid evaporation showed a tendency to crack, might be significant. These films (PdFe-7 and PdFe-8) had to be annealed to relieve the stress in the films. The films that were evaporated fast but not annealed, showed higher room temperature resistivities. This indicates that perhaps stress might be playing some role. Work is in progress to prepare pure Pd films under different conditions of stress and to study any correlation of stress with the $A_1 T^2$ term in the resistivity.

Values of the residual resistivity ρ_0 are typically 10-20 times higher than that in bulk alloys.²³ This indicates that there is a large amount of potential scattering. All the work on $\Delta\rho_m$ in fluctuation resistivity discussed in Section II, assumes no potential scattering. Purwins et al.⁴² have reported that the addition of Rh (up to 7 at .%) to Pd decreases the $A_1 T^2$ term. A_1 for PdRh is smaller than that of pure Pd, but the static susceptibility $\chi(0)$ goes up⁴³. However, the A_1 term is the same for $(\text{PdRh})_{1-x}\text{Ni}_x$ systems as it is for $\text{Pd}_{1-x}\text{Ni}_x$. From reference 17, we know that A_1 , the coefficient of the T^2 term is given by

$$A1(c) = A1(o) [1 + c \left(\frac{\delta u}{u_0}\right)^2 x_{\text{host}}^2 \alpha^2 \gamma_0]$$

Where α is the local enhancement factor, and γ_0 depends on the band structure. The authors of reference 43 claim that even though x_{host} increases for PdRh due to increased potential scattering, α the local enhancement factor, decreases such that $x_{\text{host}} \alpha$ remains constant.

Gillespie⁴⁴ has calculated the effect of potential scattering on the spin fluctuation resistivity, for both uniform and local enhancement models. The major effect is to shift the distribution of spin fluctuations towards the high q regime. The result is an increase in the coefficient of T^2 term as a function of the meanfree path l . The maximum increase is about 100% for $l \sim 5-10\text{\AA}$. However they assume that the entire change in the spectral density function from potential scattering, is the result of the change in $\chi(\omega)$ of the host (neglecting the change in $\chi(\omega)$ local). This assumption will not be valid if the local enhancement factor α is large. ($\delta U \text{Re } \chi(o) \sim 1$). They indicate, therefore that their results should be viewed as a lower bound for the model. Since Fe forms local moments in Pd, we do expect α to be close to 1. Therefore the effect of potential scattering in Pd(Fe) is an open question and would need calculations on a model with large α . Experimentally, it would be interesting to see, what the effect of a systematic variation of

both the strain and of the potential scattering, would be on the coefficient of the T^2 term of the Pd host.

If the enhancement of Spin fluctuations by several orders of magnitude is real, it raises some very interesting questions. Berk and Schreiffer⁴⁵ have shown that when the static magnetic susceptibility is strongly exchange enhanced, a large repulsive contribution to the kernel of the BCS equation results. They suggest that this interaction may be sufficiently strong to completely suppress the superconducting transition in Pd. However this conclusion is for s-wave pairing which gives rise to a repulsive interaction. It is possible that due to the lack of Coulomb repulsion in p-state, formation of Cooper pairs in the p-state might energetically be more favorable.^{46, 47} It has also been shown that paramagnons should enhance p-wave pairing⁴⁸. Fay and Apple⁴⁶ have calculated the p-state T_c due to the spin-fluctuation interaction alone and it is only of order 10^{-5} K. Levin and Valls⁴⁹ have calculated the triplet superconducting transition temperature $T_c(I)$ for paramagnon induced pairing as a function of the interaction parameter I . T_c shows a maximum at $I = 0.995$. Pinski et al.⁵⁰ have calculated p-wave pairing from the electron-phonon interaction in Pd. They get T_c of 10^{-186} K. No superconducting transition has been observed in pure Pd down to 0.002K⁵¹. It might be interesting to look for evidence of a superconducting transition down to the lowest possible temperatures in those Pd films that

show enhanced Spin-fluctuations. If a transition were found in the light of above estimates it would probably be an example of paramagnon induced superconductivity. However, this is only a very optimistic and speculative viewpoint.

In conclusion, we have seen some evidence of an enhancement of Spin fluctuations and of the electron scattering near the magnetic transition in Pd(Fe) alloy films. Both these effects varied from film to film, and the reason for their origin and the variation is not very well understood. However we believe that, it is not due to inhomogeneity or some irregularity in the structure of the films. Therefore it warrants further careful and systematic investigation in these films.

REFERENCES

1. M.E. Fisher and J.S. Langer, Phys. Rev. Lett. 20, 665 (1978).
2. P.G. de Gennes and J. Friedel, J. Phys. Chem. Solids 4, 71 (1958).
3. Der-Ruenn Su, J. Low Temp. Phys. 24, 701 (1976).
4. F.C. Zumsteg and R.D. Parks, Phys. Rev. Lett. 24, 520 (1970).
5. P.P. Craig, W.I. Goldburg, T.A. Kitchens and J.I. Budnick, Phys. Rev. Lett. 19, 1334 (1967).
6. D.G. Howard, B.G. Dunlap and J.G. Dasl, Phys. Rev. Lett. 15, 628 (1965).
7. P. Handler, D.E. Mapother and M. Rayl, Phys. Rev. Lett. 19, 356 (1967).
8. J.C. McLennan and G. Smith, Proc. Roy. Soc. A112, 110 (1976).
9. D.N. Budworth, F.E. Hoare and J. Preston, Proc. Roy. Soc. (London) A257, 250 (196).
10. E.C. Stoner, Proc. Roy. Soc. (London) A165, 372 (1938).
11. G.G. Low and T.M. Holden, Proc. Roy. Soc. (London) 89, 119 (1966).
12. P.A. Wolff, Phys. Rev. 120, 814 (1960), and 129, 84 (1963).
13. B. Giovannini, M. Peter and J.R. Schrieffer, Phys. Rev. Lett. 12, 736 (1964).
14. A.M. Clogston, Phys. Rev. Lett. 19, 583 (1967).

15. J.R. Schrieffer, Phys. Rev. Lett. 19, 644 (1967).
16. A.I. Schindler and M.J. Rice, Phys. Rev. 164, 759 (1967).
17. P. Lederer and D.L. Mills, Phys. Rev. 165, 837 (1968).
18. O.E. Wohlman, G. Deutscher and R. Orbach, Phys. Rev. Lett. B11, 219 (1975).
19. O.E. Wohlman and R. Orbach, LT-14 (Submitted).
20. G.J. Nieuwenhuys, Adv. Phys. 24, 515 (1975).
21. S. Skalski, M.A. Kawatra, J.A. Mydosh, and J.I. Budnick, Phys. Rev. B2, 3613 (1970).
22. M.P. Kawatra, J.I. Budnick and J.A. Mydosh, Phys. Rev. B2, 1587 (1970).
23. G. Williams and J.W. Loran, J. Phys. Chem. Solids 30, 1827 (1971).
24. J.A. Mydosh, Phys. Rev. Lett. 33, 1562 (1974).
25. B.R. Coles, J.H. Waszink, and J. Loram, Proc. Int. Conf. Mag., 166 (1974).
26. P.A. Schroeder and C. Uher, Phys. Rev. B18, 3884 (1978).
27. M.P. Kawatra and J.I. Budnick, Int. J. Mag. 1, 61 (1970).
28. M.P. Kawatra, S. Skalski, J.A. Mydosh and J.I. Budnick, Phys. Rev. 40, 1202 (1969).
29. G.J. Nieuwenhuys, B.M. Boerstoe1, J.J. Zwart, H.D. Dokter and G.J. Van den Berg, Physica 62, 278 (1972).
30. B.W. Veal and R.A. Rayne, Phys. Rev. 135, A443 (1964).
31. J.T. Schriempf, Phys. Rev. Lett. 20, 1034 (1968).

32. Maisse1 and Glong, Hand Book of thin film Technology, Page I-73.
33. L. Holland, Vacuum deposition of thin films, Page 182.
34. J.M. Lafferty and S. Dushman, Scientific foundations of vacuum Techniques, (Wiley Second Edition), Page-710.
35. Supplied by R.D. Mathis Co. Long Beach, California 90806.
36. H.P. Murbach and H. Wilman, Proc. Roy. Soc. (London) B68, 474 (1955).
37. Hoffman, Proc. Roy. Soc. (London) B70, 497 (1954).
38. R.V. Carlson, Doctoral Dissertation, University of Minnesota (1975), unpublished.
39. J. Solinsky, Doctoral Dissertation, University of Minnesota (1973), unpublished.
40. M. Star, Physica 59, 128 (1972).
41. L.F. Bates and P.B. Unstead, Proc. Conf. Mag., 190 (1964).
42. H.G. Purwins, Y. Talmor, J. Sierro and F.T. Hedgcock, S. S. Comm. 11, 361 (1972).
43. R.W. Cochrane, F.T. Hedgcock, J.P. Tidman and M.J. Zuckermann, Can. J. Phys. S3, 145 (1974).
44. D.J. Gillespie, Phys. Rev. B14, 4021 (1976).
45. M.F. Berk and J.R. Schrieffer, Phys. Rev. Lett. 17, 433 (1966).
46. D. Fay and J. Appel, Phys. Rev. B16, 2325 (1977).
47. A. Layzer and D. Fay, Int. J. Mag. 1, 135 (1971).

48. W.F. Brinkman, J.W. Serene and P.W. Anderson, Phys. Rev. A10, 2386 (1974).
49. K. Levin and O. Valls, Phys. Rev. B15, 4256 (1977).
50. F.J. Pinski, P.B. Allen and W.H. Butler, Phys. Rev. Lett. 41, 431 (1978).
51. R.A. Webb, J.B. Ketterson, W.P. Halperin, Vuillemin and N.B. Sandesara (to be published).

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