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MAGNETIC PROPERTIES OF Nb/Ni SUPERCONDUCTING / FERROMAGNETIC MULTILAYERS

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Dr. Tim Gorringe, Director of Graduate Studies
MAGNETIC PROPERTIES OF Nb/Ni
SUPERCONDUCTING / FERROMAGNETIC
MULTILAYERS

DISSERTATION

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the College of Art and Science at the University of Kentucky

By
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Lexington, Kentucky
Director: Dr. Lance E. De Long, Professor of Physics and Astronomy

Lexington, Kentucky
2013

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ABSTRACT OF DISSERTATION

MAGNETIC PROPERTIES OF Nb/Ni SUPERCONDUCTING / FERROMAGNETIC MULTILAYERS

Magnetic properties of Nb/Ni superconducting (SC) / ferromagnetic (FM) multilayers exhibit interesting properties near and below SC transition. A complex Field (H) – Temperature (T) phase boundary is observed in perpendicular and parallel orientation of ML with respect to DC field. We address the critical need to develop methods to make reliable magnetic measurements on SC thin films and ML, in spite of their extreme shape anisotropy and the strong diamagnetic response of the SC state.

Abrupt, highly reproducible “switching” of the SC state magnetization near the normal-state FM coercive fields has been observed in Nb/Ni ML. The SC penetration depth \( \lambda(\text{Nb}) > \) the SC coherence length \( \xi(\text{Nb}) \approx 40 \) nm >> the FM layer thickness \( \gamma(\text{Ni}) = 5 \) nm, abrupt magnetic reversals might be driven by strong supercurrent densities (\( J \times M \) torques) that have the potential to flow into the Ni layers. Alternatively, sharp magnetization anomalies also can result from strong flux pinning by the periodic layered structure of ML, including “lock-in” of quantized flux lines (FL) parallel to the ML plane. Strong confinement of the supercurrents within ML planes might also lead to various phase transitions of the FL lattice (FLL) composed of one-dimensional chains and other unusual structures.

Possible mechanisms for the switching anomalies must be evaluated while considering other experimental properties of Nb(x)/Ni(y) ML:

1) The upper critical magnetic field \( H_{c2}(T) \) exhibits a highly unusual anisotropy where the SC transition temperature \( T_c (H \rightarrow 0) \) for DC field \( H \perp \) ML plane exceeds the value for \( H \parallel \) ML by \( \sim 0.5 \) K.

2) Nb/Ni ML samples do not consistently exhibit magnetic signatures for the onset of superconductivity, depending on the details of the sample mounting procedure and the AC or DC method used in SQUID magnetometry experiments.

3) Unusual “wiggles” or oscillations of order 10-30 mK were observed in \( H_{c2}(T) \) in AC SQUID experiments with \( H \parallel \) ML and can be even larger (~0.16 K), depending upon the AC drive amplitude \( h_o \) and frequency \( f \).
KEYWORDS: Superconductivity, Multilayers, Magnetic Pair Braking, Superconducting Proximity Effect, Triplet Superconductivity

Sergiy Alexandrovich Kryukov
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January, 2013
Date
MAGNETIC PROPERTIES OF Nb/Ni SUPERCONDUCTING / FERROMAGNETIC MULTILAYERS

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Chapter One - Introduction

1.1. Background for Superconductivity

1.1.1. Discovery

Superconductivity was discovered by the Dutch physicists Heike Kamerlingh Onnes and his student Giles Holst in 1911 [1], three years after Onnes was able to liquefy helium. Holst found that the electrical resistance of mercury dropped dramatically below a temperature of 4.2 K. Therefore, the phenomenon of superconductivity was discovered long before the theoretical means for understanding its microscopic mechanism – i.e., the quantum theory of normal metals or superfluids -- appeared. Hence, a fundamental understanding of this phenomenon remained a mystery until 1950-1960 [2-5].

A first significant step into understanding superconductivity was taken by Fritz London in 1935 [6], when he summarized superconducting (SC) phenomena. Over the next decade, the basic properties of conventional superconductors were discovered, which led to the BCS theory [3]. On the other hand, the more recent phenomenon of unconventional superconductivity is still not completely understood, and continues to attract interest and generate intense debates [7].

In next Section we will review key events in this story and introduce concepts and a theoretical framework necessary to understand the experimental work presented in following Chapters. A special emphasis is placed on the interaction between magnetic fields, ferromagnetic materials and superconductors.


Besides the discovery of superconductivity, Onnes [1] also observed that the superconducting state disappears under application of an external magnetic field.
exceeding a critical value $H_c$ that depends upon the material. Moreover, he noticed that a current larger than a critical value $I_c$ also led to the destruction of the SC state. In subsequent years, a number of materials were shown to undergo a superconductive transition, albeit at very low temperatures - e.g., Th ($T_c \approx 1.4$ K), Ta ($T_c \approx 4.4$ K), Pb ($T_c \approx 7.2$ K) or Nb ($T_c \approx 9.2$ K). Keesom and Van den Ende [8] made the next significant discovery in 1932, when they observed a bump in the electronic specific heat at the SC transition temperature, below which the temperature dependence of the specific heat hinted at the existence of a gap in the excitation spectrum of the SC state. A number of fundamental properties of the SC state were discovered over the next year, when Meissner and Ochsenfeld [9] established that superconductors are not only perfect conductors, but are also nearly ideal diamagnets. Thus, in the presence of an external magnetic field lower than a critical value $H_c$, magnetic flux is completely expelled from the interior of a “Type I” superconductor with the exception of a thin surface layer. If the external field is removed, no flux or induced dipole moment is trapped inside. A constant, zero magnetic flux is maintained by stable (or metastable) currents flowing near the surface of the material in a penetration layer of thickness $\lambda \approx 50$ nm (a phenomenon now known as the Meissner effect). The fundamental difference between a Type I superconductor and a perfect conductor is that regardless of the way magnetic field is introduced, flux will always be reversibly expelled from the interior of a Type I SC material, whereas in case of perfect conductor, the original normal-state flux is maintained inside of it when it undergoes transition to the SC state. Denoting $F_s$ and $F_n$ as the free energy density in the SC and normal phases respectively, the Meissner effect implies that the stability of the SC state can be related to a thermodynamic critical magnetic field $H_c$ defined by the relation:

$$F_s(T) - F_n(T) = -\frac{H_c^2(T)}{8\pi}$$

(1.1)

Based on the detailed behavior of the Meissner effect, superconductors can be categorized as either Type I (presenting perfect diamagnetism anywhere below the critical magnetic field $H_c(T)$, or Type II (presenting a “mixed state” with reduced
diamagnetism relatively close to $T_c$ or at high fields). Type II superconductors (like Nb) have two critical magnetic fields $H_{c1}$ and $H_{c2}$: magnetic flux is completely expelled from the bulk of the material for applied fields below the “lower critical magnetic field” $H_{c1}$, but above this value, it gradually penetrates the sample interior until $bulk$ superconductivity is completely destroyed at the “upper critical magnetic field” $H_{c2}$ (Fig.1.1b).

The application of thermodynamics to the superconductive state has immediate consequences. The first serious theoretical attempts to understand superconductivity were the “two-fluid model” developed by Gorter and Casimir [10] (which proved useful in describing the thermal properties of the equilibrium state), followed by the semi-empirical theory developed by F. and H. London in 1935 [11]. The two-fluid model is an ansatz for the free energy of the $SC$ state and suggests that this state can be described by the interaction between two coexisting phases of the conducting electrons: a $normal$ one, represented by a density $n_n$ of electrons that scatter and dissipate energy as in a normal metal, and a $superfluid$ phase, corresponding to a density $n_s$ of electrons having negligible scattering, but still affected by external electromagnetic fields. Therefore, the total density of electrons is $n = n_n + n_s$. 
Figure 1.1a, left. The field-temperature phase boundary for superconducting Hg, as first observed by Onnes.

Figure 1.1b, right. The magnetic phase diagram for Type II superconductors. Between $H_{c1}$ and $H_{c2}$ (Shubnikov phase or mixed state), the uniform superconductive state is replaced with a complex vortex phase. A "surface superconducting" phase exists between $H_{c2}$ and $H_{c3}$. Adapted from [12]

The London theory was motivated by the diamagnetic characteristics, and actually proved to be a special case of the modern microscopic BCS theory. Thermodynamically speaking, London theory is also based on the minimization of the free energy of the superfluid component in the two-fluid model, which is the component that is dominant over the normal one in the superconducting phase.

London theory models the Meissner effect by replacing Maxwell’s equations with a set of augmented equations under the assumption that the superfluid component supports a supercurrent $\mathbf{J}$ with density of carriers $n_s$ which encounter no resistance:

$$\frac{\partial \mathbf{J}}{\partial t} = \frac{n_s e^2}{m^*} \mathbf{E}$$  \hspace{1cm} (1.2)

$$\nabla \times \mathbf{J} = \frac{n_s e^2}{m c} \mathbf{B}$$  \hspace{1cm} (1.3)
Here, $m^*$ is the effective mass of the carriers. At low temperatures, and assuming a slowly varying current (i.e. neglecting the displacement current), the supercurrent is

$$\mathbf{J} = \frac{e}{4\pi \lambda_L^2} \mathbf{A} \quad (1.4)$$

The supercurrent dominates the normal current so as to limit the penetration of a steady external magnetic field into a superconductor. The equation above is valid with particular gauge choice, known as London Gauge, which requires $\text{div}(\mathbf{A}) = 0$ near the surface and $\mathbf{A} \to 0$ in the interior of bulk superconductor. Using the Maxwell equation $\nabla \times \mathbf{B} = 4\pi \mathbf{J}$ in expression (1.3), we obtain:

$$\Delta^2 \mathbf{B} = \frac{1}{\lambda_L^2} \mathbf{B} \quad (1.5)$$

where $\lambda_L$ is the London penetration depth, a characteristic length scale defining how far field penetrates into the superconductor. London’s theory gives at $T = 0$:

$$\lambda_L = \sqrt{mc^2 / 4\pi e^2 n_s} \quad (1.6)$$

In practice, most measured penetration depths are larger than this value due to a limitation in the original London theory, as we will discuss later. The solution of equation (1.5) gives us a good qualitative explanation of the Meissner effect; for example, a constant external magnetic field $\mathbf{B} = (0,0,B_0)$ applied perpendicular to a planar $xy$ surface of a superconductor decays exponentially inside the material on a scale given by $\lambda_L$:

$$B(z) = B_0 e^{-z/\lambda_L} \quad (1.7)$$

which is a result qualitatively consistent with the Meissner effect. Note that $\lambda_L \to \infty$ when $T \to T_c$, since $n_s \to 0$. Also, when $T \to 0$, $n_s \to n$, and $\lambda(T = 0) = \lambda_L(0) = \sqrt{mc^2 / 4\pi e^2 n}$. But, according to an empirical formula of Gorter and Casimir, the dependence on temperature (below $T_c$) of the superfluid density takes the form:
\[ n_s = n \sqrt{1 - \frac{T^4}{T_c^4}} \]  

(1.8)

Consequently, the temperature dependence of the penetration depth should be

\[ \lambda(T) = \frac{\lambda(0)}{\sqrt{1 - \frac{T^4}{T_c^4}}} \]  

(1.9)

This is an empirical result that works fairly well for most conventional superconductors.

1.1.3. Type I/II Superconductors, Quantized Vortices

The next important development came with the discovery of quantized magnetic vortices. In 1937, Shubnikov et al. [14] found a “mixed phase” near the critical magnetic field of a Type II superconductor. While under the effect of a sufficiently strong external magnetic field, a Type I superconductor exhibits a sharp transition from a diamagnetic Meissner state to a uniform normal state, whereas a Type II superconductor evolves from the Meissner phase to another superconducting “mixed phase” between \( H_{c1} \) and \( H_{c2} \). The mixed phase is characterized by the presence of quantized magnetic vortices, which are whirlpools of electric current swirling around normal cores. If the external magnetic field increases within the mixed state, the vortices increase in number (they nucleate at the edge of a sample) and eventually, the normal cores begin to overlap near the upper magnetic field \( H_{c2} \), at which point the entire material becomes normal. Since the vortices are oriented parallel to the applied field, they have a common helicity of current circulation that causes the vortices to repel each other, thus they arrange themselves in a triangular pattern, called the Abrikosov flux lattice, which was first theoretically treated by Abrikosov [15].
Another landmark in the study of conventional superconductivity was the discovery of the \textit{isotope effect} \cite{16, 17} in 1950, when two independent groups demonstrated that the critical field at zero temperature and the transition temperature $T_c$ both vary with isotopic mass $M$:

$$H_c \propto T_c \propto M^{-\alpha}$$

(1.10)

with $\alpha \approx 0.45$-0.50 for most superconductors. This was a direct hint at a microscopic mechanism for superconductivity based on the interaction between electrons and quantized lattice vibrations – \textit{phonons}. Almost at the same time, H. Fröhlich \cite{18} applied a perturbative approach to a Hamiltonian that included interactions between electrons and phonons, and found instability of the Fermi surface, provided the interaction is strong.

Another significant theoretical advance was made by V. Ginzburg and L. Landau \cite{6} who used Landau’s theory of second-order phase transitions to extend the London theory to include spatial variations of the superfluid condensate near the critical temperature. The Ginzburg-Landau (GL) model is a macroscopic theory, independent of the microscopic mechanism of superconductivity, and is limited to the thermodynamic parameter space near to the normal-superconductor phase boundary. It employs Landau’s implementation of a complex \textit{order parameter} that characterizes the superconductive state as a function of temperature (vanishing above $T_c$), magnetic field and position: $\phi = \phi(T, B, r) = |\phi| e^{i\phi}$.

The difference between the free-energy densities of the superconductive and normal phases can be expanded in terms of this order parameter $\phi$:

$$F_s - F_n = \alpha |\phi|^2 + \frac{1}{2} \beta |\phi|^4 + \frac{1}{2m} (-i\hbar \nabla - aA) \phi |^2 + \frac{1}{8\pi} |B|^2$$

(1.11)
where $\alpha$ and $\beta$ are phenomenological parameters dependent on temperature with $\alpha(T_c) = 0$. Since $\phi$ is given by the extrema of the energy functional, one can minimize this expression with respect to variations in $\phi$ and $\mathbf{A}$, leading to the time-independent GL equations:

$$\frac{1}{2m}(-i\hbar \nabla - aA)^2 \phi + \alpha \phi + \beta |\phi|^2 \phi = 0 \quad (1.12)$$

$$\mathbf{J} = -\frac{i\hbar q}{2m} (\phi^* \nabla \phi - \phi \nabla \phi^*) - \frac{q^2}{m_c} \phi^* \phi \mathbf{A} \quad (1.13)$$

Here, $q$ is twice the charge of an electron, $q = 2e$. The first equation describes the behavior of the order parameter $\phi$ in magnetic field. The second equation determines the supercurrent $\mathbf{J}$, and is similar to London’s expression (1.4), except that it is position-dependent through $\phi$. One of the most important consequences of this model was the prediction of two length scales characterizing the superconductive state.

First, the penetration depth of a magnetic field into the surface of a superconductor (which is a measure of the superfluid density) is given by

$$\lambda = \sqrt{\frac{m^* c^2}{4\pi q^2 \phi_0^2}} \quad (1.14)$$

where

$$\phi_0^2 = |\phi_0^2(T)|^2 = \frac{\alpha(T)}{\beta(T)} \quad (1.15)$$

is the zero-field equilibrium value of the order parameter that can be substituted into (1.13) to obtain – provided the sample is much larger than $\lambda$ – an expression similar to London’s for the supercurrent (1.4):
\[ J = -\frac{q^2}{mc} |\phi_0|^2 A \]  

(1.16)

If we consider the order parameter as a measure of the coherence inside the superfluid condensate and set \( \phi_0 = \sqrt{\frac{n}{2}} \), eq. (1.14) becomes identical to London’s penetration depth in eq. (1.6).

Second, the coherence length provides a spatial scale for the superconductive phase fluctuations at the phase boundary with the normal state:

\[ \xi = \frac{h^2}{\sqrt{2m^* |\alpha|}} \]  

(1.17)

This quantity can be derived at zero magnetic field by defining a position-dependent solution for eq. (1.12) of the form \( \phi(r) = \phi_0 + f(r) \). In this case, \( f(r) \) satisfies a partial differential equation:

\[ \frac{h^2}{4m^* |\alpha|} \nabla^2 f - f = 0 \]  

(1.18)

The last relation implies that at a superconducting-normal interface there is a finite transition layer, a proximity region, where the order parameter decays into the normal zone on a length scale given by \( \xi \). Note that \( \lambda \) depends on the energy necessary to generate current to screen the magnetic field, while \( \xi \) measures the energy cost to modify the phase of the order parameter. The characteristic lengths \( \lambda \) and \( \xi \) depend on temperature, and the relation (1.8) suggests a dependence of the form \( \left(1 - \frac{T^4}{T_c^4}\right) \) (making \( \lambda \) and \( \xi \) divergent at \( T_c \)), which agrees with most experiments. Nevertheless, the ratio \( \kappa = \lambda/\xi \), dubbed the Ginzburg-Landau parameter, is approximately independent
of temperature. It was shown that $\kappa$ can distinguish between the two types of field exclusion effects mentioned above: Thus, $\kappa < 1/\sqrt{2}$ defines “Type I” superconductors and $\kappa > 1/\sqrt{2}$ defines “Type II”, which will be discussed in more detail, below.

GL theory and an extension of the London equations by A. B. Pippard [20] furthered the practical understanding of superconductivity and inspired a number of theoretical developments and predictions. In particular, an improved notion of coherence length was useful in explaining the interaction between superconductivity and magnetic fields. Since experimental data usually yielded a penetration depth larger than London’s $\lambda_c$, Pippard proposed a non-local expression for the supercurrent density $\mathbf{J}(\mathbf{r})$ which, for nearly constant magnetic fields, takes a form similar to London’s:

$$\mathbf{J}(\mathbf{r}) = -\frac{m^*}{c\varepsilon_n} \frac{\xi}{\varepsilon_0} \mathbf{A}(\mathbf{r}) \quad (1.19)$$

Pippard’s expression assumes that $\mathbf{J}(\mathbf{r})$ at some position $\mathbf{r}$ inside the superconductor feels perturbations in the superfluid extending to a distance $\xi_0$ around that point, due to some sort of coherence manifested by the electrons in the volume of the “wave packet formed by the electronic states”. In other words, the wave function associated with the electrons in the superconducting state has finite spatial extent. Therefore, at the transition temperature, only the electrons within an interval $\approx k_b T_c$ of the Fermi energy can participate in the transition. This energy width corresponds, by the uncertainty principle, to an interval of wavevector, and a corresponding spatial smearing of the supercurrent response to a perturbation. In addition, any external influence – like the application of an external magnetic field – is spatially scaled by an effective coherence length $\xi$ that depends upon the electron mean free path $l$: 

10
\[
\frac{1}{\xi} = \frac{1}{\xi_0} + \frac{1}{l} \quad (1.20)
\]

Therefore, the electron correlation in the superfluid has a maximal spatial span \( \xi \approx \xi_0 \) in the case of low impurity density \( l \to \infty \) in the superconductive material. For pure metals at temperatures \( T \ll T_c \), Pippard used the uncertainty principle [21] to relate \( \xi \) to the normal-superconducting transition temperature, \( T_c \)

\[
\xi_0 \approx \frac{\hbar v_F}{k_B T_c}
\quad (1.21)
\]

where \( v_F \) is the Fermi velocity and \( a \approx 0.18 \), as obtained later from the microscopic BCS theory [2].

Pippard’s supercurrent leads to a more complete description of the behavior of the magnetic field in the penetration layer. Knowing that the effect of a magnetic field on a superconductor is measured by the induced supercurrent density [22-24], one can define the Fourier transform of the generalized supercurrent \( J(k) \) in terms of a “tensorial electromagnetic response kernel”, which is a tensor in general case, and the vector potential \( A(k) \):

\[
J(k) \propto K(k) \cdot A(k)
\quad (1.22)
\]

This kernel is connected to the applied magnetic field \( B_0 \) [11, 23] by

\[
B(r) = \frac{B(0)}{\pi} \int k \sin(kr) k^2 K(k) + k^2 dk
\quad (1.23)
\]

Assuming an infinite planar interface, we can rewrite the equation for penetration depth as:
\[ \lambda = \frac{1}{B(0)} \int_{0}^{\infty} B(r) \, dr \]  
(1.24)

Combining (1.23) and (1.24) yields

\[ \lambda = \frac{2}{\pi} \int_{0}^{\infty} \int_{0}^{\infty} \frac{r \sin(kr)}{K(k) + k^2} \, dk \, dr \]  
(1.25)

We can now deduce kernel \( K(k) \) for the London penetration depth, in Eq. (1.4). The \( k \)th Fourier component of \( J \) can be written as

\[ J(k) = \frac{-c}{4\pi \lambda^2} A(k) \]  
(1.26)

Comparison of Eq. (1.22) to Eq. (1.26) determines the kernel for London theory to be

\[ K = \frac{1}{\lambda^2} \]  
(1.27)

Since the kernel corresponding to Pippard’s expression for supercurrent is always smaller than the London kernel, we deduce that the penetration depth is larger than the value predicted by (1.6), which is approached only in certain conditions. Specifically, when \( \xi \ll \lambda \),

\[ \lambda \approx \lambda_{s} \sqrt{\frac{\xi_{o}}{\lambda_{s}}} \]  
(1.28)

which implies \( \lambda \approx \lambda_{s} \) in pure Type II superconductors. Thus, Pippard’s conjecture contains London’s theory as a limiting case. Note that a simple Meissner decay of the magnetic field does not take into account the variation of \( A \) in a “negligible” volume of extent \( \xi \), so this description is still local and exponential. Alternatively, if \( \xi \gg \lambda \), appropriate for Type I superconductors,

\[ \lambda \approx 0.65 \left( \frac{\xi_{s} \lambda_{s}}{\xi} \right)^{1/3} \]  
(1.29)
so that $\lambda$ does not depend on $I$, the impurity content of the material. In this case, the non-local decay (1.23) applies, which predicts a field reversal at a depth less than that at which the field tends to zero (Fig. 1.2) [25].

**Figure 1.2a.** Local magnetic field penetration as predicted by London theory (dashed line) and the nonlocal BCS-Pippard version (solid line). As visible in the inset, the nonlocal profile is not exponential and has a reversed field region before decaying to zero.

**Figure 1.2b.** Spatial distribution of magnetic field $B$ and order parameter $|\phi|$ of flux lines in a Type II superconductor, calculated from Ginzburg-Landau equations for three $\kappa = N\xi^2$ values.

**Insets.** The $B$ (red line) and $|\phi|$ (blue line) profiles at the boundary of a Type II superconductor with a normal metal. In the absence of $B$, the order parameter decays smoothly in a proximity region of the normal metal. Otherwise, it grows inside the $S$ region as $B$ decays. Adapted from [19].

### 1.1.4. Mixed Phase or Abrikosov Vortex State

The above theoretical considerations show that the destruction of superconductivity by magnetic field in a Type II superconductor is characterized by penetration of magnetic field into a superconductor in applied fields between a lower critical field $H_{c1}$ and an
upper critical field $H_{c2}$. Abrikosov [15] used Ginzburg-Landau (GL) theory to describe this mixed phase. He calculated a two-dimensional periodic solution of the GL equations, which he interpreted in terms of a lattice of flux lines or vortices, each vortex of circulating supercurrent carrying one quantum of magnetic flux

$$\Phi_0 = \frac{h}{2e} = 2.07 \times 10^{-15} \text{m}^2.$$  

In fact [15] (see Fig. 1.3), the vortex is a current cylinder of radius $\approx \lambda$ enclosing a normal core of radius $\approx \xi$ with maximum magnetic field $\approx H_{c2}$ and order parameter $|\phi(r)| = 0$ near the center, as shown in Fig. (1.3).

![Image](image_url)

**Figure 1.3, left.** $5 \times 5 \ \mu m^2$ area MFM image of Nb, acquired at 5 K, in a field of 0.5 mT, at 50-nm scan height. $\Delta f$ of 1 Hz $\approx 5.5 \times 10^{-6} N \text{ m}^{-1}$. In this system attractive interactions correspond to an increase in MFM tip resonance frequency $\Delta f$ (i.e. lighter colors).

**Figure 1.3, right.** Corresponding variation of $\Delta f$ along a cross section through the middle vortex in the x-direction, the location of which is indicated by the white line in the image, adapted from [26].

If the applied magnetic field $H_0 < H_{c1}$, the superconductor is in the Meissner state, with the field entering the material only near the surface. As $H_0$ ranges between

$$H_{c1} \approx \Phi_0 \frac{\ln(\kappa \sqrt{2})}{4\pi\mu_0 \lambda^2} \quad \text{and} \quad H_{c2} = \frac{\Phi_0}{\mu_0 2\pi \xi^2},$$

the vortex lattice gradually forms and densifies.
Eventually, the flux lines overlap and the order parameter becomes zero throughout the material, which corresponds to the suppression of the superconductive state.

1.1.5. Microscopic BCS Theory

A much awaited microscopic approach came in the mid-1950’s, based upon intuitions regarding the possibility of an attractive interaction between super-electrons via an exchange of virtual acoustic phonons. This attractive term was already present in Fröhlich’s Hamiltonian [18] and was a primary focus of the work of J. Bardeen [27]. Equally important was the suspicion (enforced by some experimental data) about the existence of an energy gap near to the Fermi surface [28]. Experimental evidence for such a gap could be inferred as early as 1932 from rather inaccurate specific heat measurements – however, such data were correctly interpreted only much later. In the 1940’s, a quantized electronic excitation (possibly due to a gap) was observed in a set of experiments addressing microwave absorption by superconductors [29]. Bardeen realized the importance of these experiments and suggested [30] that Pippard’s electrodynamics most likely follows from an energy gap. Together with L.N. Cooper and J.R. Schrieffer, he initiated an effort to understand the mechanism of electron condensation within an energy width $k_B T_c$ about the Fermi level. Conveniently, Landau’s theory of Fermi liquids was available as the standard model for the metallic state. The starting point was to identify a ground state wave function as a superposition of normal-state quasiparticles excited above the Fermi level over a range of energy $k_B T_c \approx \Delta \nu_f$ ($\nu_f$ is the Fermi velocity), and “dressed” by the medium in which they are immersed. Thus, $\Delta x \geq \hbar / \Delta p \approx \hbar \nu_f / k_B T_c$, leading to a definition of characteristic length consistent with Pippard’s coherence length Eq. (1.21)
Their effort resulted in microscopic theory of Type I superconductivity called BCS theory [3]. Its main idea is that phonons mediate pairing of electrons into boson quasiparticles termed Cooper pairs. BCS treated the interaction between pairs similar to a previous model developed for polarons by D. Pines [31]. Only a fraction $k_B T_c/E_F \approx 10^{-4}$ of the total number of electrons near the Fermi surface bind into these pairs, which act like giant, overlapping bosons condensed into a zero-momentum state within an energy width about the Fermi level roughly equal to the binding energy of a pair. Coherent superpositions of paired quasiparticles can form macroscopic wave packets that are able to transport charge and spin without scattering (resistance).

Cooper [32] proved a fundamental theorem that showed at low temperature, the electron-electron repulsion could be decreased by other residual quasiparticle interactions. In particular, the electron-phonon interaction becomes attractive over a finite range of electron frequencies, which causes the Fermi surface to become unstable with respect to the formation of bound states (in momentum space) of paired electrons with zero total momentum and opposite spin $(k_+^+, k_-^-)$. Thus, we consider a properly antisymmetrized two-body wave function for a pair with center of mass at $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, including the up- and down-spin functions $\alpha_i, \beta_i$, respectively,

$$
|\Psi_0(r)\rangle = (\alpha_1\beta_2 - \alpha_2\beta_1) \sum_\mathbf{k} g_\mathbf{k} \cos(kr)
$$

(1.30)

We insert this function into the Schrödinger equation [4], and obtain the self-consistency condition:

$$
(E - 2\varepsilon_\mathbf{k}) g_\mathbf{k} = \sum_{\mathbf{k} \neq \mathbf{k}_F} g_\mathbf{k} V_{\mathbf{k}, \mathbf{k}_F}
$$

(1.31)
Here, $\varepsilon_k$ are unperturbed plane wave energies, $V_{k,k'}=V_{k',k}$ is the electron-phonon interaction potential [33] in momentum space, and $g_k$ are weighting coefficients. Since most of the states involved in the superconducting transition are presumably within a typical phonon energy (or Debye energy) $\hbar\omega_D$ from the Fermi energy $\varepsilon_F$, Cooper made a simplifying assumption about the potential:

$$V_{k,k'} = \begin{dcases} -V & |\delta_k| < \hbar\omega_D \\ 0 & \text{otherwise} \end{dcases}, \quad \delta_k = \varepsilon_k - \varepsilon_F$$

(1.32)

The right side of (1.31) is then a constant, and we have $g_k = V \frac{\sum g_k}{2\varepsilon_k - E}$. Summing both sides of (1.31) and canceling the $\sum g_k$, we obtain the “gap equation”:

$$\frac{1}{V} = \sum_{k>k_F} \frac{1}{2\varepsilon_k - E}$$

(1.33)

Transforming the sum into an integral and introducing the pair density of states at the spherical Fermi surface $N_0 = \frac{k_F}{\pi^2 \nu_F}$, it follows that

$$\frac{1}{V} = \frac{1}{2} N_0 \int_{\varepsilon_F}^{\varepsilon_F + \hbar\omega_D} d\varepsilon \frac{2 \varepsilon}{2\varepsilon - E} = \frac{1}{4} N_0 \ln \frac{2(\varepsilon_F + \hbar\omega_D) - E}{2\varepsilon_F - E}$$

(1.34)

Therefore, in the weak coupling approximation $N_0 V \ll 1$, the energy is

$$E = 2\varepsilon_F - 2\hbar\omega_D \frac{1}{e^{4/N_0\nu_F} - 1} \approx 2\varepsilon_F - 2\hbar\omega_D e^{-4/N_0\nu_F}$$

(1.35)

That is to say, a bound state is formed with negative binding energy with respect to the filled Fermi sea less two electrons excited into states with $k > k_F$ (i.e., with kinetic energies near to, but in excess of $E_F$). Moreover, defining $N = \sum g_k$, the wave function becomes:

17
\[ |\Psi_0(r)\rangle = N \sum_{k \gg ky} \frac{\cos(k \cdot r)}{2\delta_k + \varepsilon_B} \]

so that the represented state decays rapidly with increasing \( \delta_k \).

Returning to Cooper’s assumption (1.32), which is tantamount to assigning an \textit{s-wave} (isotropic) pairing symmetry to the order parameter, one can calculate the \textit{BCS gap parameter} and the energy eigenvalue for \( |\delta_k| < \hbar \omega_p \) in the weak coupling limit \( N(0)V \ll 1 \):

\[ E \approx N(0)\Delta^2 / 2 \]

\[ \Delta = \hbar \omega_D / \sinh \left[ \frac{1}{N(0)V} \right] \]

Now, using this new energy scale, which is much smaller than \( V \), the classical superconductive parameters can be expressed in terms of a temperature dependent gap \( \Delta = \Delta(T) \) that represents the microscopic mechanism for pairing. For example, returning to Eq. (1.1), the BCS theory predicts a critical magnetic field given by:

\[ H_c = 2\sqrt{\pi N(0)\Delta(0)} \]  

The theory can be easily extended to finite temperatures and it predicts an isotope effect (1.10) with \( \alpha = 1/2 \). The critical temperature can be explicitly related to the gap:

\[ 2\Delta(0) = 3.52k_BT_c \]

with a coherence length given by

\[ \xi = \hbar v_F / 2\Delta. \]

Note that \( \xi \) decreases with increasing \( \Delta \) and \( T_c \). From a physical point of view, a large \( \xi \) means a weak pairing strength, and \( \xi(T) \to \infty \) as \( T \to T_c \).
In spite of the result (1.40), a finite gap is not necessary for the existence of the superconductive state. Even though the amplitude of the GL order parameter is proportional to $\Delta$ [35], the two concepts are different. Being proportional to the superfluid density of states, the GL order parameter is in fact a manifestation of the long range phase coherence between Cooper pairs (in the BCS case, governed by the overlap of wave functions), one of the fundamental characteristics of the superconducting state. Thus, a vanishing order parameter indicates the disappearance of superconductivity, whereas a zero gap is primarily a sign of an energetically unstable condensate state (gapless superconductivity [36]). Moreover, in some Type II superconductors, pairs may bind at temperatures above the superfluid condensation, the excitation spectrum presenting a so-called pseudogap [7] at temperatures exceeding $T_c$, which is defined as the onset of long-range order or phase coherence. In the simplified BCS theory the notions of order parameter and excitation gap can be interchanged.

Another fundamental property of the BCS ground state is that it is not disturbed by nonmagnetic disorder. This phenomenon follows from Anderson’s theorem [37], which shows that the order parameter and the transition temperature result from a general solution of a mean-field theory for binding of two single-particle states related by a time-reversal operation. Electron scattering by magnetic impurities, by breaking the time-reverse symmetry of the BCS state, can depress superconductivity and lead to the aforementioned gapless superconductivity, whereas the phase coherence of the condensate can be barely preserved with nonzero order parameter.
1.2. **Ferromagnetism.**

Despite the relatively long history since its discovery, magnetic order in metals still defies a detailed, consistent description and is the subject of intense research. More recently, there has been a high interest in materials exhibiting inhomogeneous magnetic phase dynamics, which led to the discovery of the unusual magnetotransport properties of manganites [38]. These perovskites exhibit so-called “colossal magnetoresistance” (CMR), which is characterized by a resistivity that strongly depends upon applied magnetic field. They have attracted great interest, not only due to the possible technological applications, but also due to the physics behind their behavior, which involves spin and orbital order and a close connection to the electronic behaviors of the high-$T_c$ cuprate superconductors.

The fundamental driver of ferromagnetism is the *exchange interaction* [39], which can be treated via the Weiss *molecular field*, which is basically a mean-field theory of strongly exchange-coupled spins (not to be confused with the relatively weak electromagnetic coupling between their dipole moments). This is a “self-consistent” theory in which the average magnetization is assumed to be proportional to an effective magnetic (“molecular” or “exchange”) field that is proportional to the average magnetization. Below the Curie temperature, the model yields a collective alignment of spins along a common direction.

The exchange field is most simply viewed as originating from the overlap of wave functions centered on neighboring atomic sites and the Pauli exclusion principle, which requires that the wave function for the interacting electrons be antisymmetric under exchange of their spatial and spin coordinates. Therefore, the spatial part of the
wavefunction must have the opposite exchange symmetry from that of two interacting spins (corresponding to parallel or antiparallel spin alignment). A nonzero electron spin density is driven by minimizing the Coulomb repulsion between electrons that have overlapping wavefunctions. This effect leads to an energy shift between the majority and minority spin bands given by:

\[ h = \varepsilon_{k\downarrow} - \varepsilon_{k\uparrow} \]  

(1.42)

where

\[ h = -2J \sum_{i,j} \mathbf{S}_i \cdot \mathbf{S}_j \]  

(1.43)

is the exchange energy between two electrons in overlapping orbitals, and \( J \) is a coupling constant that depends on the strength of the Coulomb repulsion between the electrons, and is positive for ferromagnetic coupling.

The overlap of wave functions depends on the interatomic distance and radii of the overlapping electronic states. If the magnetic moments are close enough for the wave functions to overlap, there is a so-called “direct exchange” that involves a balance between Coulomb forces, the kinetic energy of electron transfer, and the Hund’s rule coupling strength for intra-atomic Coulomb interactions among electrons.

In the case of moments that are well separated (e.g., beyond nearest neighbors), the interaction may proceed via an “indirect exchange”, mediated by itinerant electrons in metals. In oxides and materials with complex crystal structures, this phenomenon is known as the superexchange interaction, where oxygen ions often serve as a mediator of exchange. The nature of the magnetic ordering (ferromagnetic or antiferromagnetic) depends on a spatially damped, oscillatory coupling between localized and itinerant electrons. Typical example of such is a partially filled 3d electronic shell that is
interacting with a more extended 4s state. This situation can result in a substantial contribution to the electronic density of states at Fermi level as a result of overlap. The overlap leads to an energy band that is exchange-split into two spin bands, $\varepsilon_{k\uparrow}$ and $\varepsilon_{k\downarrow}$, according to (1.42). We denote $N_{\downarrow}$ and $N_{\uparrow}$ to be the number of electrons in the respective spin sub-bands:

$$N_{\uparrow\downarrow} = \int_{0}^{\varepsilon_{F}} G_{\uparrow\downarrow}(\varepsilon) d\varepsilon$$

(1.44)

where $G_{\uparrow\downarrow}(\varepsilon)$ is the density of states. Then, the spin polarization is defined by

$$P = \frac{N_{\uparrow} - N_{\downarrow}}{N} = N_{\uparrow} + N_{\downarrow}$$

(1.45)

Phenomenological assumptions can be made in order to relate microscopic properties, such as the energy dependence of the exchange energy, on the magnetic susceptibility or magnetization -- usually by imposing mean-field approximations meant to reduce the complexity of the problem. E.C. Stoner [40] proposed a simplification in the summation in (1.43) by taking into account only a time averaged $\langle S_{j} \rangle$ generated by all other spins interacting with each spin $S_{i}$. In this case, the coupling term in the one-band Hubbard Hamiltonian [41,42]

$$H = -\sum_{i,j,\sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

(1.46)

takes the following form in the strong Coulomb repulsion limit:

$$Jn_{\uparrow} n_{\downarrow} = \frac{1}{4} \left( n_{\uparrow} + n_{\downarrow} \right)^{2} - \frac{1}{4} \left( n_{\uparrow} - n_{\downarrow} \right)^{2}$$

(1.47)

where only the second term depends on spin, and gives the exchange energy:
\[ h = -\frac{1}{4} J \left( N_\uparrow - N_\downarrow \right)^2. \]  

(1.48)

Assuming a small band splitting so that \( G_{\uparrow\downarrow}(\varepsilon) \approx G(\varepsilon_F) \) is independent of spin in first approximation, the total energy of the band can be written as:

\[ E = \sum_{\sigma=\uparrow,\downarrow} \int_0^{\varepsilon_F} \varepsilon G(\varepsilon) d\varepsilon \approx \frac{N^2 P^2}{4G(\varepsilon_F)} - \mu_0 \mu_B NPH \]  

(1.49)

Adding the exchange energy, the total energy becomes:

\[ E = \frac{N^2 p^2}{4} \left( \frac{1}{G(\varepsilon_F)} - J \right) - \mu_0 \mu_B NPH \]  

(1.50)

Where \( P \) is defined by Eq. (1.45). This yields the so-called “Stoner criterion” for the onset of spontaneous magnetization:

\[ JG(\varepsilon_F) \geq 1 \]  

(1.51)

This criterion is satisfied by ferromagnetic metals like iron and explains why an external magnetic field is not necessary to spin-split the band; i.e., the spontaneous exchange field assumes the role of a local magnetic field that drives the magnetic ordering.

1.2.1. Finite Size Effects on Ferromagnetic Ordering

The physics of ferromagnetic state presents other surprises when strong anisotropy has to be taken into account. The main subject of our study - thin film multilayers - is a case of extreme shape anisotropy. Thin films of ferromagnetic material sometimes can be practically viewed as two-dimensional systems of moments characterized by a dominance of short-range order and uniaxial, “Ising” behavior induced by anisotropy. The \( T_c \) of the ferromagnetic transition, coercive field and other important parameters have been intensively studied as functions of thin film thickness [43, 44]. In ultrathin films, there's a
significant probability that the orientation of the spontaneous magnetization (easy-axis) will switch from a perpendicular to an in-plane direction at low temperatures [45]. Thick films usually exhibit magnetic properties close to those of the bulk material, whereas reducing film thickness leads to increased magnetic fluctuations; even a complete destruction of ferromagnetic order is possible if a film is made sufficiently thin [46, 47].
1.3. The Proximity Effect

Much attention has been devoted to high-temperature copper oxide superconductors; therefore, interest in highly metallic (low-$T_c$) superconductors has lessened over the last two decades. Nevertheless, low-$T_c$ materials have also undergone tremendous development. Low-$T_c$ superconductors are typically easier to work with than high-$T_c$ cuprates, due to their larger coherence length and simpler synthetic routes that can facilitate economical manufacturing processes. The last decade has seen many improvements, including the ability to produce high-quality interfaces and junctions between superconductors and insulators ($S/I$), superconductors and normal metals ($S/N$), and superconductors and ferromagnets ($S/F$). Researchers also were able to manufacture *mesoscopic* thin film features with characteristic sizes in the sub-micron range, which has opened new fields of research.

1.3.1. Superconductor–Normal-Metal Structures

When a superconductor is in close contact with another normal material, the physical properties of the combination might be very different from either pure material, with both the normal and SC metal being affected. Scientists have studied this phenomenon, known as the “proximity effect”, for many years and have developed several theories that are in good agreement with experimental data. It was shown that the properties of SC thin-film layers that are in close proximity with insulating ($I$) materials do not change much from the isolated thin-film behavior. A typical example is a SC thin film deposited on an insulator substrate like glass or sapphire, and whose $T_c$ remains very close to the bulk value. In contrast, the physical
properties of both materials can change significantly in the case of a clean $N/SC$ (see Fig. 1.4) junction.

![Figure 1.4. Superconducting-normal bilayer interface](image)

The close proximity of clean layers of different types allows for coherent superconducting correlations to exist within $N$, $F$, or $I$ layers located very near to an interface with a $SC$ material. The $SC$ condensate penetration length into the $N$ region $\xi_N$ can be modified by various pair breaking processes, including inelastic and spin-flip scattering. The characteristic mean-free paths for these processes (destructive for $SC$ pairing) may be quite long at low temperatures, reaching a few microns. Various $SC$ coherence effects, and properties such as critical current and $T_c$ oscillations in an external magnetic field, have been intensively studied [48, 49]. Most research was concentrated on studies of $SC/N$ bi-layer and $SC/N/SC$ tri-layer structures that were easier to fabricate and investigate [50, 51]. It quickly became apparent that the superconductor may alter the properties of the normal metal and vice-versa. It was noticed that superconductivity is depressed near the $N$ material on the scale of the correlation length $\xi_S$. This means that the order parameter $\phi$ is much smaller near the
interface when compared to values in S/I structures at positions much further away from the interface boundaries, and in the bulk.

The penetration of the SC wavefunction into the interior of a normal material makes possible the so-called Josephson effects [52] in S/N/S junctions that were studied extensively and are well reviewed [53-55]. Replacement of the normal metal layer with an insulating layer between two superconductors leads to a significantly different situation. In order to allow Cooper pairs to penetrate through the insulator in S/I/S structures, the I-layer thickness has to be much smaller, since the pair wave functions will decay in the insulator within a few dozen atomic layers. This also results in orders-of-magnitude reductions of the critical currents of S/I/S structures with thick insulating layers.

It was also found that in an S/N structures the SC transition temperature was decreasing with increasing thickness of the normal layers [50, 51]. This effect was interpreted as due to the destruction of Cooper pairs that penetrated into the normal metal, where Cooper pairing is not favored. A number of scanning tunneling microscopy (STM) experiments were performed in the 1980’s [56, 57], to study S/N interfaces, trying to detect existence of a SC condensate in the normal metal at the S/N interface. Only recently was the presence of SC carriers directly measured in a N-layer at the S/N interface in a spatially resolved local density of states measurement [58, 59]. Fig. 1.5 shows dI/dV at different bias voltages, which is proportional to the local density of states [58], which can be used to calculate the SC gap. One can see how an increase in the thickness of normal metal layers in S/N multilayer films reduces concentration of SC condensate in the N-layers.
Figure 1.5. DOS measured at 60 mK with STM at the Au surface for Nb/Au bilayers with varying Au thickness $d_N$. One can see how the SC gap is decreasing as $d_N$ is increasing. Adapted from [59].

A simple description of the proximity effect is obtained from the Ginzburg-Landau (GL) equation for the order parameter $\phi$ [4]. If the temperature is close to $T_c$, one can simplify the GL expressions for the free energy by assuming a small order parameter and a slow spatial variation of $\phi$ (the coherence length and penetration depth are large close to $T_c$). The Ginzburg-Landau equation near $T_c$ [89] for a S/N interface can be written as:

$$\xi_{GL}^2 \frac{\partial^2 \phi^2(r)}{\partial r^2} + \phi(r)[\text{sgn}(T_{c,N} - T) - \frac{\phi^2(r)}{\phi_0^2}] = 0$$

(1.52)
\[ \xi^2 \frac{\partial \phi^2(r)}{\partial r^2} + \phi(r)[\text{sgn}(T_{cS} - T) - \phi^2(r) / \phi_b^2] = 0 \]  \hspace{1cm} (1.53)

Here, \( \xi_{GL} \) is the coherence length in the \( N \) and \( S \) regions at temperatures close to their respective critical temperatures, \( T_{cN}, T_{cS} \). In the diffusive limit this length is equal to

\[ \xi_{GL} = \sqrt{\frac{\hbar D_{N,S}}{8 k_b |T - T_{cN,S}|}} \]  \hspace{1cm} (1.54)

where \( D_{N,S} \) is the diffusion coefficient in either the \( N \) or \( S \) regions. The Ginzburg-Landau equation describes the order parameters correctly only if they vary slowly on a spatial scale \( v_F / T_c \) for the clean case, or \( \sqrt{\hbar D_{N,S} / 2 \pi k_b T_c} \) in the diffusive, “dirty” case.

One can use Eq. 1.54 to describe the spatial distribution of the order parameter in any \( N/S \) structure if we assume that normal metal in Eq. (1.52) is actually a superconductor with transition temperature \( T_{cN} < T \), and the superconductor has a transition temperature \( T_{cS} > T \). The quantity \( \phi_b \) is the value of the order parameter in a bulk superconductor \( S \); it goes to zero as the temperature approaches the transition temperature \( T_c \). We can see from the form of Eq. (1.53) that in the \( S \) region, sufficiently far from the \( N/S \) interface, the order parameter \( \phi(r) \) equals the bulk value \( \phi_b \). In the \( N \) region, \( \phi(r) \) decays exponentially to zero on a length scale \( \xi_N \). Eqs. (1.52) and (1.53) can only be used to describe \( S/N \) contacts when temperature \( T \) is close to the transition temperatures \( T_{cN} \) and \( T_{cS} \), respectively. If \( T_{cN} = 0 \) (e.g., in a normal metal in a \( S/N \) junction), the \( N \) region does not have a
superconducting transition at finite temperatures; then more complicated equations should be used.

1.3.2. Superconductor-Ferromagnet Structures

Much of the work in the present study is related to $S/F/S$ structures, where $F$ is a ferromagnetic metal and $S$ is superconductor. The pair wave function could, in principle, extend far into the normal $F$ region with little decay, as occurs in $SC/I$ structures. However, in the presence of a high magnetic field (or exchange field), electrons with different spins will have different energies, and will be forced into different energy bands. The $SC$ condensate may be strongly influenced by the high exchange field typical of ferromagnets, and this effect may be strong enough to significantly reduce superconducting correlations in the $SC$ material near a $S/F$ interface. The suppression of the superconducting correlations by magnetic interactions is a fundamental consequence of the Pauli principle. In most superconductors electrons of opposite spin pair together and form Cooper pairs with zero total spin. In other words, the two-body wavefunction must be antisymmetric under the exchange of quantum numbers for spin and orbital degrees of freedom, which would not happen if they occupied an orbital singlet and had the same spin. If the exchange field of the ferromagnet is sufficiently strong, it can re-align the spins of the electrons of a Cooper pair parallel to each other, thus breaking Cooper pairs and suppressing superconductivity.

In the case of $S/F$ interfaces, the penetration of the $SC$ condensate into the $FM$ material is reduced. The ratio of condensate penetration distance into a given
ferromagnet relative to one into a nonmagnetic normal material is estimated to be proportional to $\sqrt{k_B T_c / h}$, where $h$ is the exchange energy (see Eq. (1.43)) and $T_c$ is the critical temperature of the isolated $S$ material. The exchange energy in conventional ferromagnets such as Fe, Ni or Co is several orders of magnitude higher than $k_B T_c$ and therefore the penetration depth in ferromagnets is much smaller than that in normal metals. Proximity effect studies of $S/F$ heterostructures began several decades ago and have developed into a very active field of research at present [60-63]. The suppression of superconductivity in $S/F$ heterostructures has been observed experimentally [64-66] and corresponds in the first approximation to the picture of the destruction of singlet superconductivity by the $FM$ exchange field.

The fact that SC is suppressed much more strongly in $S/F$ rather than in $S/N$ heterostructures seems to make the study of $S/F$ heterostructures less interesting. On the contrary, $S/F$ heterostructures exhibit new and very interesting physics that is not found in non-magnetic $S/N$ structures. For example, under some circumstances superconductivity is not necessarily suppressed by ferromagnetism because the presence of the latter may be accommodated by triplet superconducting pairing, which is resistant to spin splitting by magnetic fields [67, 68]. Generally, ferromagnetic order will dominate over the superconducting state, but in some cases we will see the opposite effect, where superconductivity will reduce and even suppress ferromagnetism [69, 70]. This can even affect strong ferromagnets with a Curie temperature much larger than the $T_c$ of the superconductor (relevant to the Nb/Ni interfaces of our study).
Recent experimental and theoretical studies revealed a variety of nontrivial effects in $S/F$ structures, many more than one would have expected before. We will focus on new, “exotic” phenomena observed in $S/F$ multilayers. We consider phenomena to be “exotic” when observations go beyond what would have been expected from the simple picture of a superconductor in contact with a homogeneous ferromagnet. We expect to see the most interesting effects when the exchange field is strongly varying—e.g., at the $S/F$ interface or near intrinsic nonhomogeneities in a ferromagnet, such as domain walls.

In some cases the exponential decay of the $SC$ condensate function in a $FM$ material may also oscillate as a function of FM layer thickness, which may lead to oscillations of the critical superconducting temperature $T_c$. Another possible effect is an oscillation of the critical Josephson current $I_c$ in $S/F$ structures, which is correlated with the thickness $d_F$ of the ferromagnetic layers, as predicted by Buzdin, Kupriyanov and Radovic in 1990-1991 [71, 72]. The first observation of such behavior was reported by Jiang [72] on Gd/Nb structures. Indications of the non-monotonic behavior of $T_c$ as a function of $d_F$ was also reported by Wong [73], Strunk [74], Mercaldo [75], Ketterson [76] and others [77-79].

However, oscillatory behavior is not always present in $S/F$ junctions; for example, $T_c$ monotonically decreases in Pb/Ni heterostructures [64] as the thickness of the Ni layer increases. Both monotonic and oscillating behaviors of the critical temperature were observed in Fe/Nb/Fe trilayer [65] and V/Fe [66] multilayer films. Different behavior as a function of $d_F$ can be explained by possible variations of the $S/F$
interface transparency. Chien and Reich [80] have made a great effort to analyze this effect, taking into consideration effects of sample quality and materials variation.

Another very important piece of information was obtained from measurements of the Josephson critical current in $S/F/S$ junctions. Due to the oscillatory behavior of the superconducting condensate in the $F$ region the critical Josephson current could change its sign in a $S/F/S$ junction (so-called “$\pi$-junction”). This phenomenon, predicted long ago by Bulaevskii et al. in 1977 [81], has been only recently confirmed experimentally [82-87]. Transport properties of $S/F$ structures were intensively studied experimentally during the last decade; for example, measurements of ferromagnetic wire attached to a superconductor underwent an unusual drop in electrical resistance [88,89] when the temperature was lowered below the superconductor’s $T_c$. In both experiments the strong ferromagnets Ni and Co were used as the normal metal in close contact with a superconductor. A simple picture of $S/F$ interactions would predict only a small change in resistance due to the effect of destruction of superconductivity by the magnetic exchange field of the ferromagnet. Contrary to expectations, the resistance reduction was close to 10%, and was attributed to a “long-range proximity effect”.

This raises an interesting question: How can relatively weak-coupled, long-range superconducting effects occur in a ferromagnet with a strong magnetic exchange field? In the case of an inhomogeneous magnetic field inside of $FM$ metal near the $SC/FM$ interface, a triplet $SC$ state may occur and can penetrate the $F$ region over distances comparable to $\xi_N$ of a normal metal. This phenomena, known as “triplet SC pairing”
or “odd frequency triplet SC” or simply “odd triplet” is a very new effect and currently a subject of intensive research [90 - 93].

$S/F$ bilayers, $S/F/S$ trilayers and $[S/F]_n$ multilayers are very interesting and natural objects for studying pairbreaking, proximity and Josephson effects. The thickness of both the $SC$ and $FM$ layers, as well as the transparency of the interface, can be varied experimentally, which makes possible a detailed study of many interesting physical quantities. However, these are not the only interesting effects observed, and several new ones have recently been proposed theoretically. They have not yet been unambiguously confirmed experimentally, but many researchers are attempting to set up such experiments.

Generally, we would expect the proximity of a ferromagnet to a superconductor to lead to a decrease in the amplitude of the critical current. One may consider two cases: First, with $F$ layers of parallel magnetization with an $S$ layer sandwiched in between; and second, a similar structure with antiparallel $F$ layers. The critical current for some samples with the antiparallel configuration was found to be larger than in parallel case, and even larger than the critical current through non-magnetic layers. This work leads to a surprising, nontrivial conclusion: “ferromagnetism can enhance the critical current” [90].

Another way to observe “odd triplet” superconductivity was suggested in [90], where current could flow through the ferromagnetic layers. The simplest expectation would be that critical current would be depressed very rapidly with increasing thickness of the ferromagnetic layer; however, the critical current behavior might be different if odd triplet superconductivity is present. One could try to introduce a triplet
component by changing the relative direction of the $FM$ polarizations of the adjacent ferromagnetic layers in an $F/S/F$ trilayer. This component should not exhibit a strong pair-breaking effect in the presence of a magnetic exchange field, and can penetrate the $FM$ layers at distances similar to those in a normal metal, and makes possible the existence of large critical currents (Figs. 1.6a, 1.6b). This effect can therefore be used to detect and manipulate the triplet component of superconductivity.
Figure 1.6a, top. Dependence of the normalized critical current on $h$ for different temperatures in the case of an antiparallel orientation of FM layers. Here $eV_c = eRI_c$, $h_F$ is the effective exchange energy in FM layer (see eq. 1.43), $R$ is resistance, $t = T / \Delta_0$, and $\Delta_0$ is the superconducting order parameter at $T = 0$ and $h = 0$.

Figure 1.6b, bottom. Same as 1.6a with parallel orientation of the FM layers. Adapted from [90].
The largest and most easily observed effect of a $S/F$ interaction is the suppression of superconductivity by a ferromagnet; however, in some cases the inverse effect is also possible. A weak $FM$ state can be strongly affected by superconductivity, as was observed in bulk magnetic superconductors [94]. Here, by “weak” ferromagnets we mean materials that have a $FM$ transition temperature close to the $T_c$ of the $SC$ material, whereas “strong” ferromagnets have much higher $T_c$. Nevertheless, superconductivity may also influence strong $FM$ materials in $S/F$ systems if the thickness of the $FM$ layers is sufficiently small. If we consider an $S/F$ structure as one macroscopic system, in some cases it is easier to change the spin orientation in the ferromagnet than to destroy the superconductivity. If the thickness of the $FM$ layers is smaller or comparable to the size of the Cooper pairs $\xi_s$, the $SC$ state becomes much less sensitive to the presence of $FM$ order and can even destroy it. It would be less profitable from the point of view of energy cost to destroy ferromagnetism when the $FM$ layers are thick in comparison to the $SC$ layers. Therefore, the destruction of the $SC$ state would be more probable, and this was the conclusion drawn from several experiments [65, 95].

One more unusual phenomenon was discovered in some $S/F$ structures when the SC material was interfaced with a strong ferromagnet: the “inverse proximity effect” [96]. It was already known that supercurrent can penetrate into a $FM$ layer; however, inverse effect is also possible, when a magnetic moment is induced in the superconductor near the interface. It can be explained in a simple model, assuming that one of the electrons that form a Cooper pair has a probability to enter the ferromagnet, while the other electron of the pair remains in the superconductor. Then, the electron
that has entered ferromagnet will be polarized by the exchange field, while the second
electron of the pair must have opposite spin, comprising an opposite magnetic moment
– the inverse of the one in the ferromagnet – near the $S/F$ interface. The depth of this
effect is determined by superconducting coherence length $\xi_s$. In the extreme case
where 100% of electrons in the ferromagnet are polarized, and with transparent $S/F$
interface, the total magnetic moment of the ferromagnet might be completely screened
by the inverse magnetic moment in the superconductor.

Another possible source of magnetization in a superconductor may arise from the
penetration of a triplet component of the condensate that is induced in the ferromagnet.
Theoretical possibility of this effect was first discussed by Bergeret and Volkov [90],
and some experimental evidence was presented by Jing Xia and Shelukhin [97].
Destruction of superconductivity, for instance by heating, will also destroy this
moment, which gives the opportunity to test the presence of this effect experimentally.
In contrast to the Meissner effect, in which the screening is due to the orbital electron
motion, this is a kind of spin screening. Clearly, the experimental study of proximity
effects in $S/F$ structures is still in its early stages and many more theoretical and
experimental studies are needed in order to bring one closer to understanding the
physical conditions under which these and other exotic $S/F$ proximity effects can be
observed.

1.3.2.1. **Superconductor-Ferromagnet Structures with Uniform Magnetization**

In this section we consider the proximity effect between a superconductor $S$ and a
ferromagnet $F$ that is a metal and has a conduction band. The ferromagnet and
superconductor are in contact with each other (Fig. 1.7), allowing electrons and $SC$
pairs to travel though the $S/F$ interfaces. In addition, there is an exchange field due to
spins of localized electrons in other bands.

![Figure 1.7. Drawing showing schematic of superconductor (S) / ferromagnet (F) interface](image)

The effective exchange field acts on spins of the conduction electrons in the ferromagnet, and an additional term $\hat{H}_{\text{ex}}$ describing this action appears in the total Hamiltonian

$$\hat{H}_{\text{tot}} = \hat{H} + \hat{H}_{\text{ex}}$$  \hspace{1cm} (1.55)

$$\hat{H}_{\text{ex}} = -\int d^3r \psi^+_\alpha(r)[\mathbf{h}(\mathbf{r}) \sigma_{\alpha\beta}] \psi_\beta(r) d\mathbf{r}$$  \hspace{1cm} (1.56)

where $\psi^+(\psi)$ are creation and destruction operators, $\mathbf{h}$ is the exchange field, $\sigma_{\alpha\beta}$ are Pauli matrices, and $\alpha, \beta$ are spin indices [98]. The Hamiltonian $\hat{H}$ represents all non-magnetic interactions and kinetic energy, and will describe system properties when the exchange field is not present. The energy of the spin-up electrons differs from the energy of the spin-down electrons by the Zeeman energy $2h \{44\}$. $\hat{H}_{\text{ex}}$ describes all of the exchange interactions, such as the condensate matrix (Green’s function $\hat{f}$) [99]
(see below), and in general, will contain non-zero diagonal and off-diagonal terms in spin space. This situation will simplify if the direction of the exchange field is invariant with respect to translations. We may choose a $z$-axis along the direction of exchange field $\mathbf{h}$ and consider electrons with spin up and spin down as separate subsets. If we also assume that the exchange field $\mathbf{h}$ is homogeneous, then the SC condensate matrix $\hat{f}$ will be diagonal and we can represent it in the form:

$$
\hat{f} = f_3 \hat{\sigma}_3 + f_0 \hat{\sigma}_0
$$

(1.57)

where $f_3$ is the triplet component and $f_0$ is the amplitude of the singlet component with total spin of Cooper pair projection on $z$-axis equal to zero ($S_z = 0$). Both components are always present in a SC condensate; however, in the case of an $S/N$ structure, the singlet component will dominate and the condensate function will be proportional to $\hat{\sigma}_3$. The presence of the exchange field will suppress singlet component increasing the role of the triplet part proportional to $\hat{\sigma}_0$. The amplitudes of $f_3$ and $f_0$ will be proportional to the correlation functions $\langle \psi_+ \psi_+ \rangle$, as shown in [52,100-102]:

$$
f_3(t) \propto \langle \psi_+(t)\psi_+(0) \rangle - \langle \psi_+(t)\psi_+(0) \rangle,
$$

$$
f_0(t) \propto \langle \psi_+(t)\psi_+(0) \rangle + \langle \psi_+(t)\psi_+(0) \rangle
$$

(1.58)

Once one determines the condensate function in Eq. (1.57), one will be able to determine physical quantities such as the DOS, critical temperature $T_c$, or the Josephson critical current through an $S/F/S$ junction. The following discussion is devoted to physical properties in $S/F$ systems with homogeneous magnetization.
1.3.2.2. Density of States

Several limiting cases of the S/F interface problem are schematically shown in Fig. 1.7. Assuming a case of a weak proximity effect, the condensate matrix \( \hat{f} \) will quickly diminish outside the S region. The general equations can be linearized in the diffusive limit, resulting in an equation for the matrix \( \hat{f} \) containing an extra term due to the exchange field \( h \) [98],

\[
D_F \frac{\partial^2 \hat{f}_F}{\partial x^2} + 2i(\varepsilon \hat{\sigma}_0 + h \hat{\sigma}_3) \hat{\sigma}_F = 0
\]

(1.59)

where the subscript \( F \) stands for the ferromagnetic region, and \( \varepsilon \) is the energy. The \( x \)-axis is directed perpendicular to S/F interface. In the absence of the exchange field \( h \), Eq (1.59) reduces to the equation appropriate for a S/N structure:

\[
D_N \frac{\partial^2 \hat{f}_F}{\partial x^2} + 2i \varepsilon \hat{f} = 0
\]

(1.60)

Note that Eq.(1.59) is valid for a homogeneous \( h \) only, and the presence of any inhomogeneous magnetic field makes the equation much more complicated. Eq. (1.59) should be complemented by boundary conditions (described in the work of Buzdin and Bergeret [63, 98]) that take the form

\[
\gamma_F \frac{\partial \hat{f}_F}{\partial x} = -\hat{f}_S
\]

(1.61)

Here, \( \gamma_F = R_b \sigma_F \), \( R_b \) is the boundary resistance per unit area on the S/F interface, \( \sigma_F \) is the conductivity of the \( F \) region, and \( \hat{f}_{F,S} \) are the condensate matrix functions in the \( F \) and \( S \) regions. The assumption of a weak proximity effect implies that the deviation of \( \hat{f}_S \) from its BCS matrix \( \hat{f}_{BCS} = \hat{\sigma}_3 f_{BCS} \) is small, and on the right-hand side of Eq. (1.61) one can write \( \hat{f}_S = \hat{\sigma}_3 f_{BCS} \), where \( f_{BCS} \) is the BCS solution for bulk.
superconductors. The boundary condition at the ferromagnet/vacuum interface is given as \( \partial_x f_F = 0 \), since \( R_b \to \infty \). Using boundary conditions for \( S/F \) and ferromagnet/vacuum interfaces, one can successfully solve Eq. (1.59) for \( \hat{f} \). By setting \( x \equiv 0 \) to be position of the normal metal (or ferromagnet) interface with the superconductor (\( x \) is the coordinate perpendicular to the interface), then the second boundary of the \( FM \) layer will have coordinate \( x = d_F \), and the half-space at \( x > d_F \) is empty. Solving for the diagonal matrix elements \( f_{\pm} \equiv f_{11(22)} \) one can write the solution as

\[
f_{\pm} = \begin{cases} 
\pm f_{BC2} \cosh\left[k_{\pm}(x-d_F)\right], & 0 < x < d_F \\
\frac{k_{\pm}\gamma_F}{\sinh(k_{\pm}d_F)}, & x > d_F
\end{cases}
\]

(1.62)

Here \( k_{\pm} = \sqrt{-2i(\varepsilon \pm \hbar)/D_F} \) is a characteristic wave vector representing the penetration depth of the condensate function \( f_{0,3} \) into the \( F \) region. In strong ferromagnets the exchange energy \( h \) is much larger than \( \varepsilon \) \((\varepsilon \propto \max\{\phi, T\})\), which means that the condensate penetration depth \( \xi_F = \sqrt{D_F/\hbar} \ll \xi_N = \sqrt{D_F/\varepsilon} \) for a normal (nonmagnetic) metal.

The exchange interaction in the \( FM \) metal will align spins and force them to be parallel to the magnetization vector, effectively destroying singlet Cooper pairs that have zero total magnetic moment. In the case of a thick \( F \) layer \((d_F \gg \xi_F)\), the condensate function \( f_{\pm} \) can be simplified and Eq. (1.62) takes the following form:

\[
f_{\pm} = \pm \frac{\phi}{E_s k_{F\pm}\gamma_F} \exp(-x/\xi_F)\left[\cos(x/\xi_F) \pm i \sin(x/\xi_F)\right]
\]

(1.63)
where $E_\varepsilon = \sqrt{\varepsilon^2 - \phi^2}$, and $k_{Fz} = k_{Fz}(\varepsilon)$ at $\varepsilon = 0$. Bergeret et. al. [98] have calculated several examples of $SC$ condensate local density of states ($DOS$) functions that exhibit oscillations in the $F$ layer for different $d_F / \xi_0$ parameter ratios (Fig.1.8). The predicted damped oscillations of $f_z$ may be a source of new, interesting effects. One of those effects that can be experimentally detected is a non-monotonic dependence of the critical temperature on the thickness $d_F$ of $S/F$ structures, such as those studied in this work.

Intensive study of the $DOS$ in $S/F$ structures has been undertaken in theoretical and experimental investigations. The $DOS$ in $S/F$ structures were studied by Halterman and Valls [103], Baladie et al [104], Zareyan et al. [105], and Bergeret et al [99]. Dirty $S/F$ structures were studied by Fazio and Lucheroni [106] and Buzdin [107], and the results of a study of the DOS in dirty $S/F/N$ structures were published recently by Golubov et al. [108].
Figure 1.8. Calculated change of the local density of states $\delta n_F$ for a S/F bilayer at the outer F interface. The solid line corresponds to a F layer thickness $d_F = 0.5 \xi_0$, where $\xi_0 = \sqrt{D_F / \Delta}$, and $\Delta$ is the order parameter in the bulk superconductor. The dashed line corresponds to $d_F = (0.8) \xi_0$. The latter curve is multiplied by a factor of 10. After [98].

1.3.2.3. Transition Temperature – Non-monotonic Variations

The exchange field greatly affects electron pairing in conventional superconductors, and it may significantly reduce the critical temperature of the superconducting transition $T_c$ in S/F structures with a high interface transparency. The critical temperature for S/F bilayer and multilayered structures was calculated in many works, and experimental studies of $T_c$ were also reported in number of publications [65, 66, 72, 109, 110]. Agreement between theory and experiment has been achieved in some cases (see Fig. 1.8).
Figure 1.9. Dependence of superconducting transition temperature $T_c$ on the thickness of the Fe layer $d_{Fe}$ in Nb/Fe multilayered film as determined by resistivity measurements. The dashed line is a fit assuming a perfect interface transparency while the solid line corresponds to an imperfect interface. Adapted from [109].

One should mention that despite many papers published on this subject, the problem of the transition temperature $T_c$ in $S/F$ structures is not completely solved. For example, there are claims [72,111] that the non-monotonic dependence of $T_c$ on the thickness of the ferromagnet observed in Gd/Nb multilayers was due to the oscillatory behavior of the condensate function in the $F$ layers. However, Aarts [66] showed in other experiments on V/Fe/V trilayers that the interface transparency plays a crucial role in the interpretation of data that can exhibit both non-monotonic and monotonic dependences of $T_c$ on $d_F$. In other experiments [64], the critical temperature of Pb/Ni bilayers was observed to decrease with increasing $d_F$ in a monotonic way.
From the theoretical point of view, $T_c$ cannot be predicted exactly. In most papers it is assumed that the transition from the normal to the superconducting state is of second order; however, this is generally not the case. Let us consider, for example, a thin $S/F$ bilayer with thicknesses obeying the condition: $d_F << \xi_F, d_S << \xi_S$, where $d_{F,S}$ are the thicknesses of the $F(S)$ layer. In this case the Usadel equation can be averaged over the thickness [90] and reduced to an equation describing a uniform magnetic superconductor with an effective exchange energy $\tilde{h}$ and order parameter $\tilde{\phi}$. The difference between the $S/F$ bilayer system and a bulk magnetic superconductor is that the effective exchange energy $\tilde{h}$ depends on the thickness of the $F$ layer and may be significantly reduced in comparison with its value in a bulk ferromagnet.

The behavior of these systems and, in particular, $T_c$, was studied long ago by Sarma [112], Larkin and Ovchinnikov [113], Fulde and Ferrell [114], and Maki [115]. It was established that both first- and second-order phase transitions may occur in these systems if $\tilde{h}$ is less than, or on the order of, $\tilde{\phi}$. If the effective exchange field $\tilde{h}$ exceeds the value $\tilde{\phi} / \sqrt{2} \approx 0.707 \tilde{\phi}$, the system remains in the normal state (this is known as the Clogston [116] and Chandrasekhar [117] “paramagnetic limit”). Larkin and Ovchinnikov [113] and Fulde and Ferrell [114] independently found that in a clean system, and in a narrow interval of $\tilde{h}$, the homogeneous SC state is unstable and an inhomogeneous state with a spatially varying order parameter is established in the system. This state, denoted as the Fulde-Ferrel-Larkin-Ovchinnikov (FFLO) state, was not observed in bulk materials until the recent discovery of ferromagnetic
superconductors [118-120]. In S/F bilayers such a state is not expected to be realized because of a short mean-free-path.

In the case of a first-order phase transition from the superconducting to the normal state, the order parameter abruptly drops from a finite value to zero. The study of this transition requires the use of nonlinear equations for $\phi$. It was shown by Tollis [121] that under some assumptions both first- and second-order phase transitions may occur in a $S/F/S$ structure. If we consider a second-order phase transition, we can linearize the corresponding (Eilenberger or Usadel) equations with respect to the order parameter. Then, assuming that $T$ is close to $T_c$, we can use the Ginzburg-Landau expression for the free energy and find the critical temperature of an $S/F$ structure from the self-consistency condition:

$$\phi_{N,S}(t) = \lambda_{N,S} f(t, t)$$

(1.64)

where $\lambda_{N,S}$ is the electron-electron coupling constant that promotes the formation of superconducting condensate, and

$$f(t, t') = \psi^\dagger(t)\psi(t')$$

(1.65)

where $\psi^\dagger(t)$ is the condensate function. In the Matsubara representation, the critical temperature can be calculated via the following equation,

$$\ln \frac{T_{c}}{T_{c}^*} = (\pi T_{c}^*) \sum_{\omega_n} \left( \frac{1}{|\omega_n|} - \frac{if_{\omega_n}}{\phi} \right)$$

(1.66)

where $T_c$ is the critical temperature in the absence of the proximity effect and $T_c^*$ is the critical temperature taking into account the proximity effect. The function $f_{\omega}$ is the condensate (Gor’kov) function in the superconductor; it is related to the function

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\[ f_{ss}(i\omega_n) = i\omega_n \] where \( \omega_n = \pi(2n+1) \) is the Matsubara frequency. Strictly speaking, Eq. (1.66) is valid for a superconducting film with a thickness smaller than the coherence length \( \xi_s \) because in this case \( f_{ss} \) is almost constant in space.

The quasiclassical Green’s function \( f_{ss} \) obeys the Usadel equation (in the diffusive case) or the more general Eilenberger equation. This problem has been solved for several cases where an oscillation of \( T_c \) as a function of the \( F \) layer thickness was expected (see Fig. 1.9). In most of the papers referenced above, magnetization vectors \( M \) in different \( F \) layers are assumed to be collinear. Only Fominov et al. [122] considered the case of an arbitrary angle \( \alpha \) between the \( M \) vectors in each of the two bounding \( F \) layers that are separated by a superconducting layer. In this case, a \( F/S/F \) structure will permit all triplet components with different projections of the spin \( S \) of the Cooper pair. Authors have demonstrated that \( T_c \) depends on the angle \( \alpha \), and the transition temperature has a maximum \( T_{c_{\text{max}}} \) at \( \alpha = 0 \) and decreases to \( T_{c_{\text{min}}} \) when the angle between the two magnetization vectors in the bounding \( F \)-layers approaches \( \pi \). However, as we show in Chapter 3, the \( SC \) film itself also exhibits strong angular anisotropy between in- and out-of-plane applied magnetic fields, independent of the presence of \( F \) layers.

### 1.3.3. The Josephson Effect in S/F/S Junctions

The oscillations of the condensate function in the ferromagnet (see Eq.(1.63)) lead to interesting peculiarities, not only in the dependence of \( T_c(d_F) \), but also in the Josephson effect in \( S/F/S \) junctions. Both the amplitude and phase of the critical
current through the junction may oscillate (0-π transitions [52, 102]). Even though experimental studies of the dependence \( T_c(d_F) \) do not converge to a single conclusion, measurements of Josephson current in \( S/F \) junctions give us more evidence concerning the nature of these oscillations.

The Josephson current through a \( S/F/S \) junction was calculated for the first time by Buzdin et al. [123]. Different aspects of the Josephson effect in \( S/F/S \) structures were studied in many subsequent papers by Buzdin and Kupriyanov [71], Fogelström [124], Heikkilä et al. [125], and others. Some additional confirmations of 0-π transitions in \( S/F/S \) junctions have been presented in recent experimental studies [84-87]. All of those studies showed evidence of an oscillation of the critical current \( I_c \). An example is shown in Fig. 1.10, where the temperature dependence of \( I_c \) as measured by Ryazanov et al. [84] is shown. We can see how the critical current has a maximum at \( T = 5.5 \) K and then decreases to zero at \( T = 2 \) K, even though one would expect an increased critical current as temperature decreases.

The dependence of \( I_c \) on the thickness \( d_F \) measured by Blum et al. [85] is shown in Fig. 1.11. The measured oscillatory dependence is well fitted by the theoretical dependence calculated by Buzdin et al. [123] and Bergeret et al. [90] for a π-state in a Josephson junction.
Figure 1.10. Measurements of the critical current $I_c$ as a function of temperature for a Nb/Cu$_{0.48}$Ni$_{0.5}$/Nb junction. The thickness of the CuNi layer is $d_F = 22$ nm. Adapted from [84].

Figure 1.11. Critical current of a Nb/Cu/Ni/Cu/Nb junction as a function of the Ni layer thickness $d$. The squares are the measured points. The theoretical fits are presented according to Buzdin et al. [123] (dashed line) and Bergeret et al. [126] (solid line). Adapted from Blum et al. [85].
Chapter Two - Experimental Techniques and Research Tools

2.1. SQUID Magnetometer

We have specialized in precise measurements of both the AC and DC magnetic moment $m(H,T)$, which has been much less studied than transport critical current $J_c(H,T)$ due to the small magnetic signal and shape anisotropy typical of SC and FM thin-films. Our Group has developed unique AC susceptibility and frequency relaxation techniques, including their application at variable field and sample angle [127-132]. These techniques were useful in our experiments on SC/FM ML and heterostructures. We routinely use a Quantum Design MPMS5 SQUID Magnetometer to measure the DC and AC magnetic moments of thin-film materials.

2.1.1. AC Measurements

We used the AC option of MPMS5 SQUID magnetometer to measure AC magnetic moment at frequencies $0.1 \leq f \leq 10$ Hz and RMS drive amplitudes $0.01 \leq \mu_0 h_0 \leq 0.35$ mT in a “longitudinal” geometry with both DC and AC fields applied along the ML plane. The real part ($m'$) of the AC moment of superconducting materials measures the supercurrent (circulating perpendicular to the DC field) that screens the AC field and reflects FL pinning strength; and the imaginary part ($m''$) mainly measures AC losses that sensitively probe FL dynamics [133].

The MPMS Transverse Sample Rotator was also employed in measurements of the AC moment as a function of the angle $\theta$ between the normal to the ML plane and the DC magnetic field. However, difficulties arise when dealing with large demagnetization effects (planar shape) and low signal-to-noise (small mass) typical of thin-film samples

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Moreover, AC SQUID data do not necessarily reflect equilibrium phase boundaries between \( N \) and SC states, particularly at high AC field amplitudes [132].

2.1.2. DC Measurements

The MPMS5 implements a quasi-DC (non-inductive) measurement technique involving motion of the sample up and down the DC solenoid axis through three pickup coils connected in series as part of a SC “flux-locked loop” [134]. The 2-cm-diameter pickup coils (Fig. 2.1a) are separated along the field axis by \( A = 1.5 \) cm, and arranged into a highly sensitive “second-order magnetic gradiometer” [135,136] that minimizes noise. The flux changes generated in the gradiometer by the sample movement are coupled into a SQUID sensor and monitored by the “SQUID voltmeter” output \( V(z) \) that is proportional to the total magnetic flux linking the coils when the sample is at position \( z \):

\[
v(z) = a \Phi(z) = \sum_{k=1}^{k_{\text{max}}} \sigma_k G_k(z_k) \tag{2.1}
\]

\( V(z) \) is then mathematically modelled by assuming the sample is a point-dipole, and a best fit of \( V(z) \) is calibrated by measuring a Pd standard having known magnetic properties to yield the measured magnetic moment \( m(H,T) \) [137]. A typical example of the voltage response vs. position is shown in Fig. 2.1b.
Figure 2.1a, left. MPMS SQUID pickup coils that form a second-order gradiometer that links magnetic flux due to sample moment as it moves through the coils. The -1 to 2 to -1 turns ratio of the three coils gives rise to the three-lobed SQUID voltmeter response to a point dipole, as shown on the right. Here, Δz is the sample position (displacement from zero position), R is the radius of magnetic pickup coil, L is the distance between top and bottom pickup coils.

Figure 2.1b, right. Voltage response vs. sample position when Nb layers are in the normal state and Ni layers are in the FM state produces a point-dipole-like response with Regression Fit R > 99%.

2.1.3. SQUID RSO Option

The Quantum Design “Reciprocating Sample Option” (“RSO”) [138] is a sensitive variation of the MPMS DC technique in which the sample is moved back and forth sinusoidally in time through the center pickup coil of the flux-locked loop. The RSO “amplitude” can be varied up to 5 cm. This technique uses a digital signal processor and lock-in techniques to maximize the signal-to-noise of the SQUID voltmeter output and
attain a magnetic moment sensitivity of $5 \times 10^{-8}$ emu. It is known that thin $SC$ thin films oriented perpendicular to the applied field present large demagnetization effects that may induce unwanted magnetic moment reversals in the presence of small $DC$ field gradients [134]. Our early RSO measurements employed a small amplitude (3 cm, corresponding to a $\pm1.5$ cm displacement about the center gradiometer coil) that was commonly recommended for minimizing artifacts generated by small field gradients in the case of weak-flux-pinning superconductors [134].

A key issue is that standard MPMS signal processing software requires the largest sample dimension $l$ be much less than the pickup coil diameter (e.g., $l < 0.2 \ D \approx 4$ mm [136]) and separation $A = 1.5$ cm, in order that the detected SQUID voltmeter signal can be accurately fitted to a calculated point-dipole response [139,140]. Clearly, the assumptions of the MPMS algorithm are no longer strictly valid for thin-film samples that generally have both a finite spatial extent (roughly square areas of 4 - 9 mm$^2$ for studies reported here) and large shape anisotropy (demagnetization effect). Any effort to reduce the area of a thin-film sample to better satisfy software requirements introduces a reduced signal that is already diminished due to the small volume fraction of the thin film compared to the substrate material. Moreover, the sample mounting method (e.g., radial displacement from the magnetometer symmetry axis) can induce a non-point-dipole signal [136]. Type-II $SC$ thin films present additional problems since they typically exhibit inhomogeneous magnetization due to vortex pinning and strong edge (Meissner) currents [141,142]. $SC/FM$ ML and heterostructures present even more potential complications due to spatial inhomogeneities generated by $FM$ domain walls.
Unfortunately, orienting a finite-area SC/FM ML parallel to the DC field is not sufficient to guarantee point-dipole response: The effective sample position could vary due to movement of macroscopic FM domains during magnetization reversal, for example. Therefore, we initially selected the MPMS “Iterative Regression” (IR) analysis, since this software option permits the effective sample position to vary in fits of the raw output of the SQUID voltmeter [139].

Such difficulties make it advisable to constantly monitor the quality of the fits of SQUID voltmeter output using the “Regression Fit” parameter $R$ provided by the MPMS software:

$$R = 1 - \frac{1}{V_{\text{peak}}^2 (N-1)} \sum_{i=1}^{N} (V_{M(i)} - V_{F(i)})^2$$  \hspace{1cm} (2.2)

$V_{\text{peak}}$ is the maximum value of the SQUID voltmeter over a scan, $V_{F(i)}$ is the fitted voltage, and $V_{M(i)}$ is the measured voltage, at sample position $z_i$. We have assumed that SQUID voltmeter data fits having $0.90 \leq R < 1.0$ (allowing for finite signal-to-noise) indicate a sample magnetization distribution well approximated by a point-dipole.
2.2. Vibrating Reed Technique

Vibrating reed (VR) magnetometry is an alternative well suited for measurements of thin-film or anisotropic samples [143], and is essentially a “transverse” $AC$ susceptibility technique that employs very low $AC$ fields generated perpendicular to the $DC$ applied field [143,144] by oscillatory motion of the sample off the $DC$ field axis.

The VR is formed by gluing a sample $ML$ onto one end of a thin, rectangular Si reed whose opposite end is mounted onto one side of a piezoelectric transducer to form a cantilever beam arrangement. The transducer is driven at a frequency $f$ that is usually tuned to the fundamental vibrational mode of the Si reed (e.g., $f = 10^2$ to $10^4$ Hz), and the amplitude $A$ of the reed is detected using a sensitive resonant $RF$ cavity technique [143,135]. A transverse $AC$ field is generated perpendicular to the $DC$ applied field in the moving VR frame. It is important to note “transverse susceptibility” usually refers to off-diagonal elements of the susceptibility tensor derived from a moment detected perpendicular to a $DC$ applied field [143], which does not exactly correspond to the VR case. A comparison of the basic measurement geometries of these two techniques is given in Figs. 2.2a and 2.2b. The basic VR setup is shown in Figs 2.3a and 2.3b. The VR frequency $f$ (measured by the transverse $m'$) measures the magnetic restoring torque exerted on supercurrents that screen the $AC$ field, and the inverse VR amplitude $A^{-1}$ measures $AC$ losses (measured by the transverse $m''$) generated by FL motion [133].
**Figure 2.2a.** AC SQUID geometry with AC field $\mathbf{h} \parallel$ DC field $\mathbf{H}$. The left-hand diagram is the “longitudinal” or “parallel” case, and the right-hand diagram is the “transverse” or “perpendicular” case. Note the term “longitudinal susceptibility” denotes diagonal elements of the susceptibility tensor from a moment detected parallel to the AC driving field which, in this case is also parallel to the DC applied field. See [133, 143, 144] for additional technical details.

**Figure 2.2b.** Vibrating reed geometry with effective AC field $\mathbf{h} \perp$ DC field $\mathbf{H}$ for the “longitudinal” case in the left-hand diagram, or the “transverse” case in the right-hand diagram with $\mathbf{h} \perp \mathbf{H}$. The curved arrows illustrate the vibrational displacement of the reed that generates $\mathbf{h}$. Note the term “transverse susceptibility” traditionally denotes off-diagonal elements of the susceptibility tensor from a moment detected perpendicular to the AC driving field; in the present case we use this terminology for detecting an AC moment perpendicular to the DC applied field.
2.3. **Transmission Electron Microscopy**

Transmission electron microscopy (TEM) was performed by Dr. Wentao Xu, using a JEOL 2010F operated at 200 kV with scanning (STEM) functionality for structural and compositional analysis. Due to time and cost considerations only selected samples were analyzed with this instrument. Our STEM images yielded interface roughness and layer thickness estimates that were in good agreement with low-angle X-ray diffraction data provided by Prof. Jose Vicent’s Group [145].

2.4. **Polarized Neutron Reflectometry**

Polarized neutron reflectometry [146,147] measurements of Nb/Ni $ML$ were performed (on samples having areas in the range 0.1 to 1.0 cm$^2$) by Dr. Michael Fitzsimons and Dr. Brian Kirby at the Asterix Beamline [148] at Los Alamos National Laboratory’s Lujan Neutron Scattering Center. A polychromatic neutron beam was incident on the sample, alternately polarized spin-up or spin-down relative to a magnetic field applied parallel to the sample plane. The sample’s non-spin-flip specular reflectivity was measured as a function of wave vector transfer $Q$ at multiple scattering angles. Fits of these data determined the structural and magnetization (component parallel to $ML$) depth profiles of the samples.
Chapter Three - Experimental Results

3.1. Nb/Ni Multilayers

3.1.1 Background

The study of competing cooperative mechanisms for long-range order - in particular, the interaction of superconductivity and magnetism - is one of the most important topics in basic and applied condensed matter research. Metallic “multilayers” (ML) are well suited to study effects related with basic phenomena; for example, one interesting subject is to vary the different length scales that govern the SC and FM phenomena. Coupling and dimensionality problems can be addressed using the appropriate ML systems [127,149]. SC/FM ML are superconducting (SC) / ferromagnetic (FM) heterostructures consisting of interleaved SC and FM layers, and may behave as quasi-two-dimensional systems when they are sufficiently thin to “confine” the SC and FM order parameters along the direction \( \mathbf{n} \) normal to the ML plane [76].

Proximity effects at the SC/FM interfaces and magnetic pairbreaking within the FM layers alter the magnitude and phase of the SC order parameter, which can be non-zero in all layers [60,63]. The interactions across an interface separating a superconductor from a ferromagnet produce exchange polarization and spin flips of Cooper pairs that could lead to changes in the properties of both the superconductor and magnet within the proximity length on either side of the interface [79,82,150]. These effects are crucial to the potential development of nanoscale SC/FM hybrid devices for applications in magneto-electronics or spintronics.

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These magnetic interactions may induce exotic SC pairing states and cause oscillations of the SC transition temperature $T_c$ with FM layer thickness $y$ (as observed in Nb($x$)/Ni($y$) ML [151]). Chapter 1 gave several examples of SC/FM systems that have been intensively studied over the last several years; however, most of these systems involved “weak” FM layers (for example Ni$_3$Cu$_y$ and similar alloys). Recently research has shifted towards studies of ML with “strong” FM materials. For example, V/Ni multilayers [152] exhibit a striking reversal of the critical field anisotropy close to the SC critical temperature $T_{sc}$. The dependence of $T_{sc}$ on either the SC or FM layer thickness are crucial signatures of this kind of system: the literature includes observations of oscillations of $T_{sc}$ with FM layer thickness in Nb/Fe [77] and NbN/GdN [153], and monotonic decreases in V/Fe [68] and Nb/Gd [154].

Although rarely done, AC and DC magnetometer experiments are essential complements to ubiquitous electrical transport studies on ML [60,63,76], since they probe bulk properties, including compositional homogeneity, magnetic vortex dynamics and non-equilibrium effects in the SC state, as well as shape/confinement effects. In this study we concentrate our efforts on systems that have strong FM ordering, that is the FM $T_c$ is much higher than the SC $T_c$. Nb/Ni remains a strong ferromagnet at very low layer thicknesses, which permits a wide range of SC/FM structures to be made, and which possibly will reveal new, “exotic” phenomena at SC/FM interfaces. Details of $T_c(y)$ depend upon SC length scales such as the penetration depth $\lambda$ and the coherence length $\xi$, and the SC layer thickness $x$ [60, 63, 67, 98].
3.1.2 Sample Preparation and Initial Characterization

We concentrate our efforts on three types of ML: one is a stack of 5 Nb/Ni bilayers (\([\text{Nb}(23\text{nm})/\text{Ni}(x)]_3\)), a related ML with an additional Ni capping layer (Ni[Nb(23nm)/Ni(x)]_3), and a set of trilayers (Nb(x)/Ni(y)/Nb(x) or Nb(y)/Ni(x)/Nb(y)). We have used a Quantum Design MPMS5 SQUID Magnetometer to perform most of our DC and AC magnetic measurements of the superconducting onset temperature, superconducting phase boundary (critical magnetic field \(H_{c2}(T)\)) and magnetic moment. Also we used VR magnetometry for additional phase boundary studies with the external DC field directed parallel to the ML plane.

Professor Jose Vicent’s Group at the Universidad Complutense in Madrid provided a first set [46] of ML that were grown on Si(100) substrate at ambient temperature by magnetron sputtering of 99.99% Nb and 99.98% Ni targets in 99.99% pure Ar gas (1 mTorr). The base pressure of the sputtering system was \(6 \times 10^{-8}\) Torr. Typical growth rates were 0.18 nm/s for Nb and 0.2 nm/s for Ni. The substrate-to-target distance was 3 cm. Standard X-ray diffraction with the scattering vector perpendicular to the film surface was performed by the Madrid Group with an X’Pert Diffractometer using Cu \(K_\alpha\) radiation and low- and high-angles of incidence. Low-angle diffraction profiles show good layering quality (Fig. 3.1a). For all samples, clear superlattice peaks are visible, resulting from the spacing of the Nb/Ni bilayer repeat unit. In between the superlattice peaks we find seven oscillations, the so-called “Kiessing fringes” [155], which are related to the total ML thickness. The structural coherence length perpendicular to the layers, determined from full-width at half-maximum of the \(\theta - 2\theta\) scan at the first-order Bragg peak position, is limited by the ML thickness. The relevant structural parameters of the
ML, such as superlattice period, thickness, roughness, and interdiffusion of the layers, were obtained from the low-angle X-ray profile using the Suprex program [156]. In Fig. 3.1a, the simulated profiles are also presented. Typically, Vicent’s Group found roughness of \( \approx 0.2-0.3 \text{nm} \) at the interfaces between Nb and Ni, and negligible interdiffusion between them. The bilayer thicknesses are within 5% of their nominal values. A hint of high-angle superlattice satellite peaks appears between the main Ni and Nb peaks. It is worth noting that the Nb/Ni ML has a structural lattice mismatch of 14.8%, very close to the limit of 15% for which high-angle superlattice peaks are not expected [157].

Our collaborator Dr. Wentao Zu [43] has developed TEM cross-section images in order to obtain information about the roughness of the ML interfaces, and Nb and Ni layers. All films studied at the U. Kentucky were grown in the same conditions as described above. From the study of the line profile of the topographic images it can be deduced that the values of roughness (variation of thickness of Nb or Ni at the Nb/Ni interface) for all the samples checked were below 0.3 nm.
Figure 3.1a, left. Measured and simulated low-angle X-ray diffraction profile of the [Nb(10nm)/Ni(2.2nm)]₈ ML. Inset shows high angle Bragg reflections.

Figure 3.1b, right. Temperature dependence of resistivity for [Nb(10nm)/Ni(x)]₈ with x = 1.0, 1.5, 1.8, 2.2nm. The inset shows Tₛₑ as a function of tₑ and the symbol (▲) denotes Tₛₑ of a 200-nm-thick Nb film. Adapted from [46].

The superconducting critical temperature Tₛₑ and the temperature dependence of the upper critical field Hₑ₂ are basic SC state parameters that are affected by the SC/FM layered structure. Fig. 3.1b shows the resistivity vs. temperature in Nb/Ni ML, and the effect of Ni layers on the superconductivity of Nb layers is illustrated in the inset of Fig. 3.1b, where the Tₛₑ of the ML (for constant Nb layer thickness, 10nm) is plotted against tₑ. As the thickness of the Ni layers increases, Tₛₑ drops, and finally, is completely
suppressed when \( t_{Ni} > 2.2 \) nm. This sharp decrease is around 50% more dramatic than observed in similar superconducting/paramagnetic superlattices [158]. The upper critical fields were measured using the resistive transition values obtained in field sweeps up to 9 T at constant temperature. Fig. 3.2 shows the temperature dependence of the resistively determined parallel and perpendicular critical fields of \([\text{Nb(10nm)/Ni(x)}]_8\) ML, where \( x = 1.0, 1.5 \) and \( 1.8 \) nm. The shape of the phase boundary near \( T_{sc} \) exhibits an abrupt change in slope for \( x = 1.8 \) nm, which implies a 3D-2D crossover regime. Using the parallel \( H_{c2}(T) \) data, Vincent’s Group determined the superconducting coherence length \( \xi_s(T=0) \) of the “bulk” ML structure perpendicular to the layers to be approximately 2.7 nm [46], using Eq. (3.1) [13]:

\[
H_{c2} = \frac{\Phi_0}{2\pi \xi^2_s(T)}
\]  

(3.1)

This implies that SC wave functions of different layers of Nb could couple through normal metal layers having thickness \( \leq 2.7 \) nm. However, when a FM layer is used instead of normal metal, this simplistic approach does not work as the coherence length gets strongly modified by ferromagnetism in the Ni layers.

ML structures having SC wave functions overlapping in FM layers are a primary subject of our study, and we expect them to exhibit exotic physical properties. The TEM characterization of (Nb/Ni) multilayers by Dr. Wentao Xu [43] shows the Madrid samples are high-quality with negligible interdiffusion and a roughness of \( \approx 0.2 - 0.3 \) nm at the interfaces between Nb and Ni. We chose to study the \([\text{Nb(23nm)/Ni(x)}]_5\) ML series for our magnetic studies since their \( T_{sc} \)’s are generally above 5 K, whereas our vibrating reed apparatus has a lower temperature limit of 4.5 K. The ML series with Nb(10nm)
layers generally have too low $T_{sc}$’s to be conveniently studied with our magnetometry facilities.

![Graph showing $H_{c2}$ vs. T for Nb(10nm)/Ni(x)]

**Figure 3.2.** Critical field phase boundary $H_{c2}(T)$ for $[\text{Nb}(10\text{nm})/\text{Ni}(x)]_8$ films with $d_{\text{Ni}} = 1.0, 1.5, 1.8 \text{ nm}$, with external field applied parallel and perpendicular to ML surface. Unpublished data from J. Vicent’s Group.

The Nb(10nm) and Nb(23nm) series are compared in Fig. 3.3, where low-angle X-ray data show both series have approximately equal interface roughness and interdiffusion characteristics. An SEM image of the $[\text{Nb}(23\text{nm})/\text{Ni}(x)]_5$ ML section is shown in Fig. 3.4a. The interlayer diffusion can be estimated at 2-3 atomic layers from such high resolution TEM images (see Fig. 3.4b).
Figure 3.3. Low-angle X-ray comparison of Nb(23nm) and Nb(10nm) ML
Figure 3.4a. TEM cross-section showing \([\text{Nb}(23\text{nm})/\text{Ni}(5\text{nm})]_5\) ML (III97C) layer structure. The electron beam is perpendicular to the sample plane. The Si substrate is in the lower left-hand corner, and the last Nb/Ni bilayer repeat has been milled off (upper right) in section preparation (image obtained by Dr. Wentao Xu [43]).
Figure 3.4b. TEM cross-section of $[\text{Ni}(5\text{nm})/\text{Nb}(23\text{nm})]_5$ ML perpendicular to growth direction. Note the 5-nm Ni layer is mainly oriented along the (111) direction (see lattice planes). Roughness (of order 2-3 atomic layers) is apparent at Nb/Ni interface. Image obtained by Dr. Wentao Xu [43].
3.1.3 H-T SC Phase Boundary

We have found that the normal-SC phase boundary $H_{c2}(T)$ exhibits complex structure, depending on whether AC or DC SQUID techniques were employed, the AC frequency or drive levels used, or whether a given Nb/Ni ML was oriented parallel or perpendicular to the applied field [131,151]. Measurements were taken in two sample orientations: external magnetic field near-perpendicular, and near-parallel to the ML surface, with an uncertainty in orientation estimated to be less than 5 degrees. Moreover, unusual discrepancies in the superconducting onset temperatures persisted for $H \rightarrow 0$ for [Nb(23nm)/Ni(5nm)]$_5$. For example, $T_C \approx 6.5$ K for $H \perp ML$, and $T_C \approx 5.8$-6.1 K for $H \parallel ML$, as shown in Fig. 3.5, which is the reverse of the anisotropy expected for strong FL pinning by confining Ni layers [130, 131]. Occasionally, a sample did not appear to be superconducting to $T = 1.8$ K, or exhibited an onset as low as 3.0 K, whereas other AC data showed a transition near $5.8 – 6.1$ K. Similar behavior is observed for another sample with a thinner Ni layers ([Nb(23nm)/Ni(3.5nm)]$_5$). There $T_C \approx 6.7$ K for $H \perp ML$, and $T_C \approx 6.0$-6.2 K for $H \parallel ML$, as shown in Fig. 3.6.

Typical field-cooled (FC) data from this set of measurements are shown in Fig. 3.7. In the normal state, above the SC transition temperature, the AC signal is near the noise floor for our SQUID magnetometer (around $5 \times 10^{-8}$ emu). The first point in a temperature scan that is clearly above (below) the base line for m’ (m”) was taken as the SC onset temperature, indicated by arrows in Fig. 3.7b. We attribute this sample behavior to an interplay between SC condensate and the FM domain distribution [60,63], or possible complications due to DC field inhomogeneities [134] or the “paramagnetic
Meissner effect” [159], that are observed in SC films in the perpendicular field orientation.

These considerations suggested that AC measurements in the parallel field orientation should be the most reproducible, which we therefore maintained in the majority of our experiments. However, careful field-cooled (FC) AC experiments always exhibited small oscillations or instabilities \( \Delta T_c(H) \approx 0.03-0.16 \) K of \( H_{C2}(T) \) that were more prominent in the parallel orientation, and persistent “reverse anisotropy” of \( T_c(H=0) \), opposite to that expected from a demagnetization effect [130, 131, 138], as shown in Fig. 3.5. These oscillations are not quantitatively reproducible from one experiment to another, but are qualitatively reproducible. The number of jumps does not change, but their exact position in field is not constant, and when the experiment was repeated with different AC drives, the positions of the peaks would shift in field randomly by approximately 0.03 T. Shifts of \( T_C \) greater than 0.03 K are considered outside experimental error.
Figure 3.5. $H$-$T$ phase boundaries for [Nb(23nm)/Ni(5nm)]$_5$ derived from AC data obtained at frequency $f = 10$ Hz and AC drive $\mu_0 h_0 = 0.1$ mT.
Figure 3.6. H-T phase boundary for [Nb(23nm)/Ni(3.5nm)]₅ derived from AC data obtained at frequency f = 10 Hz and AC drive μ₀h₀ = 0.1 and 0.3 mT.
Figure 3.7a, left. AC magnetic moment vs. temperature for \([\text{Nb(23 nm)/Ni(5 nm)}]_5\) ML; \(m'\) (circles) represents the real part the AC moment, \(m''\) (triangles) – the imaginary part (losses).

Figure 3.7b, right. Expanded view of SC transition for Nb/Ni ML is shown. Arrows indicate SC onset temperatures for the real \((T', \text{circles})\) and imaginary \((T''', \text{triangles})\) parts of the AC magnetic moment.
Figure 3.8. Field (H) – temperature (T) phase boundary for [Nb(23nm)/Ni(5nm)]₅ ML for H ‖ ML from SC onsets in the real (m’) and imaginary (m’’) parts of the FC AC magnetic moment for AC drive $\mu_0 h_o = 0.2 \text{ mT}$ and frequency $f = 10 \text{ Hz}$. Lines are guides to the eye. After [131].

3.1.4 Evidence of Multiple SC transitions

Inspired by the anomalous H-T phase boundary in the $H \parallel ML$ geometry, we have performed detailed, high-resolution (in temperature) measurements of the superconducting onset temperature ($T_c$). Samples were demagnetized at $T = 8.0 \text{ K}$, zero-field-cooled (ZFC), and then AC moment measurements were taken during very slow warming. Parameters of the AC magnetic field were: amplitude $h_0 = 1 \text{ Oe}$, frequency $f = 10 \text{ Hz}$, and applied external DC magnetic field $H = 0$. 
Fig. 3.9 shows the imaginary part $m''$ of the $AC$ moment vs. temperature for the [Nb(23nm)/Ni(5nm)]$_5$ sample. Note that there may be an additional transition observed below $T = 3.6$ K. The real part $m'$ of the $AC$ moment data also has a slope change; however, its manifestation is not so obvious. To make this more visible we extracted a digital derivative $d(m')/dT$ from the $m'(T)$ data which is shown in Fig. 3.10. There are two extra anomalies for the sample with thickest $FM$ layers ($d_{Ni} = 5$ nm), one anomaly for the $ML$ with $d_{Ni} = 3.5$ nm, and none for the sample with thinnest $FM$ layers ($d_{Ni} = 1.5$ and 2.5 nm), as shown in Table 3.1.

In Table 3.1 we summarize data for all measured samples from UCM [160] and for samples from Prof. Jack Bass’ Group at MSU [161] in Table 3.2. These values are to be compared with $T_c = 8.6$, 7.0 and 5.7 K, as observed for single-layer control films of Nb with thicknesses $t = 100$, 20 and 10 nm, respectively. $T_c$’s of control films serve as a reference that reflect the depression of the transition temperature well below the bulk value of 9.3 K by the effects of finite Nb layer thickness $x \leq \xi_0 \leq 43 nm$ [162], and the coherence length of bulk Nb [163].
Figure 3.9. Imaginary part of AC moment ($m''$) vs. temperature ($T$). An additional onset may occur below $T = 3.6$ K, well below the main SC transition at $T = 6.1$ K.
Figure 3.10a, upper. Change of slope at $T = 5.5 \, K$ indicates possible additional transition.

Figure 3.10b, lower. Digital temperature derivative of $m'(T)$ determines $T_C$ more accurately. Anomaly near $T = 4.3 \, K$ may be associated with possible thermal instabilities near the liquid He boiling temperature at 4.2 K, and should be ignored. The sample is [Nb(23 nm)/Ni(3.5)]$_3$ ML from MSU [161].
Table 3.1. Superconducting $T_c$ of $[\text{Nb}(x)/\text{Ni}(y)]_z \text{ML}$ from Madrid

<table>
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<th>X (nm)</th>
<th>y (nm)</th>
<th>Z (capping layer?)</th>
<th>$T_c$ Onset (K)</th>
<th>Second onset</th>
<th>Third onset</th>
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NOTE: “UCM” is U. Complutense, Madrid. SC $T_c$’s are determined by AC or DC SQUID magnetometry. Experiments performed on a given sample may include: FMR, TEM, VR (vibrating reed), NR (neutron reflectivity), XRS (X-ray scattering).

[1] – transition seen as change of slope in $m$’ data,
[2] – transition seen as another onset in $m^\prime$ data

Sample III110 is from the Ni(y)[Nb(23nm)/Ni(y)]$_3$ ML series, which has an additional FM layer, so that every Nb layer has two adjacent Ni layers. This change in structure leads to $T_c$ values that are significantly lower than in the III97 series (without the extra Ni capping layer), as shown in Table 3.1. Similar behavior is observed for the [Nb(10nm)/Ni(y)]$_8$ ML series, as measured by Vicent et. al. [46]. The $T_c$’s determined from resistivity measurements of samples with Ni thicknesses $y = 1.0, 1.5, 1.8 \text{ nm}$ were
above 4 K. However, samples with the additional Ni layer (the III101 series in Table 3.1) didn’t show a SC transition above 1.8 K. Since the SC transitions registered for the III97C ML series in AC magnetic measurements and in resistive measurements are in close agreement (with a difference of order 20-30 mK), it is possible that the uncovered Nb layer in III97 series (Table 3.1) may undergo a SC transition at a different temperature from internal layers, yielding higher $T_c$ values. Another possibility is that not only the external Nb layer, but also all internal layers will have different SC transition temperatures that depend upon the coupling of the SC wave functions across the FM layers.

We have also briefly studied similar ML samples from another source, made by Prof. Jack Bass’s group at Michigan State University (MSU) [161], and a summary is presented in Table 3.2. Samples from MSU without an extra FM layer have similar zero-field $T_c$’s = 6.2 K - 6.4 K (compare to 6.2 K – 6.0 K for samples from UCM); however, the series with an extra capping Ni layer show significantly higher SC transition temperatures as compared to capped samples from UCM. We have not done any detailed structural studies (low-angle X-ray interference or TEM), and there is consequently no data to assess the Nb/Ni interface quality of samples from MSU; therefore, we only can speculate why there is such a significant difference in the SC onset temperature. The fact that both UCM and MSU sample sets without an extra FM capping layer have similar $T_c$’s suggests that the thicknesses of Nb and Ni layers are similar for both sample series, as well as the oxygen content in Nb layers.
Table 3.2. Superconducting $T_C$ of [Nb(x)/Ni(y)]$_z$ ML from MSU

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NOTE: “UCM” is U. Complutense, Madrid; “MSU” is Michigan State U. SC $T_C$’s are determined by AC or DC SQUID magnetometry. Experiments performed on a given sample may include: FMR, TEM, VR (vibrating reed), NR (neutron reflectivity), XRS (x-ray scattering).

[1] – transition seen as change of slope in m’ data,
[2] – transition seen as another onset in m” data
Significant differences in the $T_c$'s for samples with a Ni capping layer (of the same nominal thickness) may be due to the roughness and transparency of interfaces between the $SC$ and $FM$ layers.

It is of interest to compare the dependence of $T_c$ with $FM$ layer thickness against literature data. In Fig. 3.11 we compare our results to the data of Lazar et. al. [109] obtained from resistivity measurements for Fe/Pb/Fe trilayers. We have a stronger variation in $T_c$ in Nb/Ni, which is closer to an imperfect interface model (solid line on Fig. 3.11b, compared to Fe/Pb/Fe.

Figure 3.11a, left. Superconducting onset temperature ($T_c$) vs. thickness of $FM$ layers for Nb/Ni ML determined by magnetic measurements.

Figure 3.11b, right. Dependence of $T_c$ on the thickness of the Fe layer $d_{Fe}$ in $Al_2O_3/Fe/Pb/Fe$, as determined by resistivity measurements. The dashed line is a fit assuming a perfect interface transparency while the solid line corresponds to an imperfect interface. Adapted from [109].
3.1.5 Switching Anomalies in RSO Magnetization Data

The normal, $FM$ state of $[\text{Nb}(23\text{nm})/\text{Ni}(5\text{nm})]_3$ at $T = 6.5$ K presents the simplest case for data reduction using the standard Quantum Design MPMS software, which assumes ideal point-dipole response. The magnetic moment $m(H)$ exhibits typical $FM$ hysteresis with a coercive field near 20 mT, as shown in Fig. 3.12. The Iterative Regression analysis of magnetic moment data provides excellent fits (Fig. 3.13) of the SQUID voltmeter signal ($R \approx 0.99$, as defined by Eq. (2.2)) for all fields except at the coercive fields where zero crossings of $m(H)$ cause $R$ to go to zero [130]. The best-fit sample position remained fixed at 1.5 cm, as expected for a point dipole undergoing RSO translations of 3-cm amplitude. However, a small reduction of temperature into the $SC$ state produces large, symmetric discontinuities in $m(H)$ located near the normal-state coercive fields, as shown in Fig. 3.12 [130,151]. These anomalies were found to be extremely reproducible on field and temperature cycling, and $R > 0.9$ for data taken over most of the field range, except near the $FM$ coercive fields, where a complex magnetization (i.e., $FM$ domains within the remnant state) might be expected (see Fig. 3.14). Although variations in the effective sample position (“center offset” in Fig. 3.14) were expected, given the extended area (e.g., $4 - 10 \text{ mm}^2$) of $ML$ samples, variations of over 1.5 cm were required in “Iterative Regression” (IR) fits, which is unphysical, given the sample was approximately square with side $\approx 0.3$ cm. On the other hand, the MPMS standard “Linear Regression” (LR) data analysis (which assumes a fixed sample position) generally failed to yield satisfactory fits of data (see Fig. 3.15).
3.1.5.1 Neutron Reflectometry

The inconsistencies in the DC SQUID magnetization data motivated us to conduct direct measurements of the $ML$ magnetization in neutron reflectometry experiments in collaboration with Dr. Michael Fitzsimmons and Dr. Brian Kirby of Los Alamos National Laboratory. The reflectometry data did not reveal any strong differences between the normal and $SC$ states (see Fig. 3.16) in the reversal of the in-plane Ni layer magnetization as the $ML$ was cycled around the hysteresis loop. This apparently contradicts the behaviors shown in Fig. 3.12. A review of MPMS data files showed that moment jumps were only deduced from $SC$ state RSO data analyzed with IR fits, which strongly suggests that the jumps were artifacts of the IR analysis.
Figure 3.12. Errant data for the magnetic moment $m$ for $[\text{Nb(23nm)/Ni(5nm)}]_5$ ML versus applied DC magnetic field $H$ applied parallel to the ML for $T = 6.0$ K (black line, FM state just above $T_C = 5.8$ K) and $T = 5.0$ K (red triangles, SC state). A 3-cm RSO scan amplitude was used with an IR data analysis. After [130,151].
Figure 3.13. $R$ vs. $H$ for multipole (MPF) fits of the SQUID voltmeter data of Figure 2.13b are shown as the thick black curve. $R$-values for the MPMS Iterative Regression are shown as the thin red curve. The MPF are slightly better than the iterative regression fits (IRF); and these data demonstrate a nearly ideal point-dipole behavior of the FM normal state. After [130].
**Figure. 3.14.** Regression Fit parameter $R$ (left axis) versus applied field $H$, obtained from IR fits of the SC state data of *Fig. 3.13*. Values of $R \geq 0.90$ (solid curves) indicate satisfactory agreement with a point-dipole-model for all fields except those in narrow intervals near zero crossings (at the normal-state FM coercive fields $= \pm 20$ mT) of the moment $m$. The best-fit “offset” of the sample position (dashed curve) undergoes unphysically large excursions ($> 0.15$ cm) over the magnetic hysteresis regime (shown in *Fig. 3.12*). After [130].
Figure 3.15. SQUID voltmeter signal $V(z)$ (triangular points) versus sample position $z$ for 5-cm RSO amplitude data for $T = 5.0$ K (see Fig. 7) and decreasing parallel fields $H$ near a zero-crossing ($\mu_{0}H \approx -24$ mT) of the moment $m$. The IR best-fits of $V(z)$ (dashed curves) and corresponding Regression Fit $R$ and effective sample position $z_{\text{eff}}$ ("Off.") are shown. The solid curves are multipole fits (using only dipole and quadrupole terms) of $V(z)$. Note the abrupt change of $z_{\text{eff}}$ to fit the change of the dominant extremum of $V(z)$ at the zero-crossing. After [129,164].
3.1.5.2  Multipole Analysis of SQUID Magnetometer Data

A thorough review of hundreds of data files revealed that moment jumps were only observed in SC state data analyzed with the Iterative Regression fitting option, which strongly suggested that the jumps were artifacts of the fitting method selected. Additional RSO experiments that used the maximal 5-cm RSO amplitude yielded a SQUID voltmeter signal appropriate to two oppositely directed dipoles for applied DC magnetic fields \( H \) near the \( FM \) coercive fields, as shown in Fig. 3.15. The evolutions of the Center Offset and \( R \) showed the moment discontinuities were due to an abrupt shift in the effective sample position \( z_{\text{eff}} \) that occurs when \( R \leq 0 \) and the IR fitting algorithm defaults to the “Linear Regression” algorithm that uses a fixed sample position \( z = 2.5 \) cm (see Eq. (2.2) and Fig. 3.15). The default fits fail completely near the fields for moment reversal, yielding \( R \approx 0 \) and \( m = 0 \).

The failure of the IR algorithm was easy to overlook for two reasons: First, the “double dipole” response is very clean and extremely reproducible on temperature and field cycling [130,151]. Second, the IR provides reasonable point-dipole fits of the voltmeter signal over a restricted 3-cm scan length (\( \pm 1.5 \) cm about \( z_{\text{eff}} \)) by adjusting \( z_{\text{eff}} \). The IR algorithm appears to fail only over narrow field intervals about zero crossings of \( m \), and in the hysteretic regime (\( |H| < \) coercive field) where potentially complex (non-point-dipole) \( FM \) domain patterns and low values of \( R \) are expected for thin-film samples with large areas and shape anisotropies.

In spite of the difficulties encountered in measuring thin-film materials, the SQUID voltmeter signal remains a valid measure of the magnetic flux generated by a
sample moving through the pickup coils. Therefore nonstandard data analyses of the SQUID voltmeter output can in principle be developed to provide valuable information concerning the spatial distribution of magnetization within the sample. We initially were able to fit SQUID voltmeter data such as those shown in Fig. 3.15 using a model with two closely-spaced (“double-dipole”) point dipoles of opposite polarity. Since the double-dipole was essentially a dipole plus a quadrupole, one can naturally consider a multipole expansion to fit an arbitrarily complex voltmeter output. There are a few multipole data analysis methods [135 - 137] appropriate to flux-locked-loop magnetometers extant in the literature, but they are difficult to implement in fully automated data processing packages; in addition, they can yield ambiguous results when applied to the limited information available in uniaxial (versus “vector”, “transverse” or “off-diagonal”) magnetometer measurements. It is therefore not surprising that these methods have not been adapted for routine use in commercial SQUID magnetometers.

Nevertheless, we conduct the order of 1000 SQUID magnetometer runs per year in routine investigations of the magnetic and superconducting properties of thin films and \( ML \). More specifically, we require a practical and accurate fitting algorithm for the MPMS SQUID voltmeter output, and it must converge reliably enough for use with automated measurements that produce large amounts of raw data. These requirements dictate that we develop simplifying approximations that work reliably for thin films and \( ML \). A useful algorithm must also be directly related to a quantitative model that provides insight into the physics of sample materials. To this end, we have formulated a version of a multipolar analysis of the SQUID voltmeter output that has yielded good results for \( SC \) state data for Nb/Ni \( ML \) and Nb films, as discussed below. Our “Multipole
Fit” (MPF) method applies simplifying approximations that we have shown yield meaningful and accurate fits when applied to SQUID voltmeter data from measurements of thin films and \( ML \). Our MPF method [131,164] is based upon the general approach of Ausserlechner et al. [136,164], with some insights on thin films from the very recent work of Stamenov and Coey [135].

The following points concerning the second-order gradiometer of the Quantum Design MPMS are important:

1) A point-dipole shifted radially off the magnetometer z-axis is seen as a point-dipole of the same magnitude plus additional moments of higher order.

2) If a gradiometer is designed to be insensitive to a higher moment of order \( \mathcal{L} \) at a given position \( z \), it is simultaneously most sensitive to the moment of order \( \mathcal{L}-1 \). This means a system cannot be designed to simultaneously avoid “spurious” multipole contributions from both even and odd order.

3) The cylindrical symmetry of the MPMS Magnetometer gradiometer ideally suppresses the influence of all multipole moments \((\mathcal{L}, \mathcal{M})\) with \( \mathcal{M} \neq 0 \).

4) A radially-offset axial dipole moment \((\mathcal{L}=1, \mathcal{M}=0)\) creates additional odd-order multipole contributions in the voltmeter response; and a radially-offset transverse dipole moment \((\mathcal{L}=1, \mathcal{M}=\pm1)\) creates additional even-order multipole contributions in the voltmeter response. These two effects cannot be simultaneously suppressed. (Note that intentional radial offsets of sufficiently small samples can yield information about both the axial
and radial components of the moment without using a second transverse pickup coil set.)

The SQUID pickup coils of our magnetometer are shown in Fig 2.1a. The coil system of the QD MPMS system is axially symmetrical and it is convenient to expand the magnetic moment in spherical coordinates, using spherical harmonics $Y_{l,m}(\theta, \phi)$ [136]. Due to the axial symmetry, the only non-vanishing contributions to flux linking the gradiometer coils will have $m = 0$. The generated voltage response is proportional to the change in flux through the coils during sample motion. The net flux can be written as

$$\Phi(z) = \sum_{l=0}^{l=\infty} \sum_{k=1}^{k_{\max}} \sigma_k G_{k,l}(z_k)$$

(3.2)

Here $k$ is the coil number, $\sigma_k$ denotes the sense of the coil winding ($\pm 1$), $z_k$ is a dimensionless parameter equal to the ratio of (sample position relative to $k_{th}$ coil) / (coil radius), and $G_{k,l}(z_k)$ is the function describing the sample position dependence of the linked flux, and is defined by the following equation [136]:

$$G_{k,l}(z_k) = \frac{(-1)^l \left( \frac{\pi L(2L+1)}{L+1} \right)^{1/2} \frac{\partial^L}{\partial z_k^L} \left( \frac{z_k}{\sqrt{1+z_k^2}} \right)}{L!}$$

(3.3)

In the special case of the Quantum Design MPMS system we have a total of four pickup coils, $k = -1, 0, 0, +1$; $\sigma_{-1}, \sigma_{+1} = +1$, $\sigma_0 = -1$. Then, the flux profile for an individual multipole of order L can be defined as sum over all pick-up coils:
\[ G_L(z) = \sum_k \sigma_k \frac{(-1)^L \left( \frac{\pi L(2L+1)}{L+1} \right)^{1/2}}{L!} \frac{\partial^L}{\partial(z-z_k)^L} \left( \frac{(z-z_k)}{\sqrt{1+(z-z_k)^2}} \right) \]  

(3.4)

Here \( z \) is the sample position relative to the center of the pick-up coil system. The calculated flux profile for the QD MPMS pick-up system is shown in Fig. 3.17 for \( L \leq 4 \). The term with \( L = 1 \) corresponds to an ideal point-dipole response, \( L = 2 \) a quadrupole, \( L = 3 \) an octupole, and so on. The SQUID voltmeter voltage is proportional to the total flux change in the pick-up coil set; therefore we can rewrite equation (3.2) as:

\[ V(z) = (a_0 + a_i z) + \sum_{L=1}^{\infty} m_L G_L(z) \]  

(3.5)

The \( (a_0 + a_i z) \) term is a correction for SQUID drift [140], \( z \) is the sample position, and \( m_L \) is proportional to magnitude of multipole moment with index \( L \). Input data are \( V(z) \) and \( z \), and \( a_0, a_i, \) and \( m_L \) are fit parameters. The original QD regression algorithm utilizes only the lowest-order term of the infinite series in \( L \), and these fits restricted to \( L = 1 \) require 4 parameters: \( a_0, a_i, m_1 \) and a center position. Every additional term in expansion (3.5) will add only one additional fit parameter.
Figure 3.16. Calculated flux profile $G_L$ for the pick-up coil system shown in Figure 2.1. The first four terms of Eq.(3.5) are shown, for $L=1,2,3,4$.

The sample mounting method, sample shape, or any displacement of the sample from the magnetometer field axis may transform an ideal point dipole response into a superposition of multipole responses, as discussed in detail in previous work [135-137]. In general, one cannot distinguish the true sample magnetic moment signal from harmonics generated by errors in positioning or background subtraction. However, in some special cases, fitting to a multipole series may give us critical information about the evolution of the magnetic structure (e.g., domain patterns). A detailed listing of our MPF program (written in Maple©) is given in Appendix A.

As input data we take the “raw” MPMS data – i.e., the SQUID voltmeter voltage $V(z)$ vs. sample position $z$ at a given temperature and field. The output is a set of fit
parameters $a_0$, $a_1$, $m_1$, $m_2$ .. $m_n$ - where $n$ is the maximum multipole index $L$ used in Eq. (3.5), and $a_0$ and $a_1$ are parameters used to correct for instrumental drift [139,140,165], which is assumed to be linear in time.

A general multipole (MP) fit of SQUID voltmeter data acquired for a [Nb(23nm)/Ni(5nm)]$_3$ $ML$ in the SC ($T = 5$ K) state is described in Fig. 3.17. **The improvement in fit quality over the MPMS dipole analysis is striking.** Note that the sample was mounted on the side of a 5.5-mm-diameter drinking straw, which is not expected to be eccentric enough (with respect to the azimuthal symmetry of the MPMS axis) to generate severe multipolar response [135,136]; this expectation is consistent with the near-perfect point-dipole behavior of the $FM$ state (Fig. 3.12). Moreover, small amplitude of the (odd-order) octupolar term in the $SC$ state (Fig. 3.18) and the negligible (even-order) quadrupolar term the normal state [136,164,166] suggest that the huge quadrupolar contribution in Fig. 3.17 probably comes from a **large perpendicular dipole moment** generated by a SC edge current in the $ML$ plane. Since the $ML$ could not have been tilted more than a few degrees with respect to the magnetometer z-axis, the $MP$ fits imply the magnetic response of Nb/Ni ML is **highly anisotropic.** We will present more evidence of a “giant” $SC$ state anisotropy in the next Section.
Figure. 3.17, Top. Regression Fit parameter \( R \) versus \( H \) obtained from MPF fits of the RSO data below. Values of \( R \approx 0.99 \) indicate superb agreement with the data for all fields except where \( R \geq 0.95 \) close to zero-crossings of \( m \) at the normal-state FM coercive fields.

**Figure. 3.17, bottom.** MP (dipole, quadrupole, octupole) moments for \([\text{Nb}(23\text{nm})/\text{Ni}(5\text{nm})]_5\) ML versus applied DC magnetic field \( H \parallel \text{ML} \) for \( T = 5.0 \text{ K} \) (SC state; \( T_C \approx 5.8 \text{ K} \); starting from \( \pm 100 \text{ mT} \)). A 5-cm RSO scan amplitude was used with the MPF data analysis. Note that abrupt switching anomalies near \( \pm 24 \text{ mT} \) are absent. After [164,166].
3.1.6 Extreme Magnetic Anisotropy and Transverse AC Moment Data

Our inference of strong magnetic anisotropy of the [Nb(23nm)/Ni(5nm)]$_5$ ML in the SC state was confirmed in measurements of the angular dependences of $m''$ and $m'$ at $T = 4.5$ K, as shown in Figs. 3.18a and 3.18b, respectively. These data provide important clues concerning the anomalous magnetic properties of Nb/Ni ML by taking into account the fact that both the AC drive amplitude perpendicular to the ML and the detected sample flux linked to the SQUID voltmeter are proportional to $\cos(\theta)$. The strong decrease of $m''$ (a measure of dissipative flux motion) for $\theta > 70^\circ$ signals strong FL pinning (“lock-in” [167-169]) by the Ni layers. The crossover toward $m' \propto \cos^2 \theta$ for $\theta > 70^\circ$ SC indicates that SC diamagnetic currents become strongly confined within Nb layers. The sharp decrease of $m'$ below detectability within about 5 degrees of perfect parallel orientation provides a likely explanation for the inconsistent observations of the occurrence of superconductivity in SQUID experiments involving only slightly different sample mountings near 90$^\circ$ (see Sec. 3.1.5.2, above).

The strong angular anisotropy implies most of the SC diamagnetic moment is oriented perpendicular to the ML, which makes it **undetectable in the experimental geometries employed in our previous neutron reflectometry experiments**. On the other hand, VR magnetometry is **optimal** for probing the perpendicular diamagnetic response in a parallel DC magnetic field. We determined the SC onsets in field-cooled-warming (FCW) sweeps from either the VR frequency $f$ or amplitude $A$ for a [Nb(23nm)/Ni(5nm)]$_5$ ML sample mounted approximately 5$^\circ$ off the DC field direction, using a piezoelectric drive of 100 mV (see Fig. 3.19). The data define **two reversible phase boundaries** that coincide remarkably well, except where they exhibit thermal hysteresis near large down-
shifts of the SC onset at 0.22 and 0.62 T, and smaller shifts at 0.1, 0.36 and 0.58 T, as shown in Fig. 3.20.

**Figure 3.18a.** MPMS SQUID Rotator data (triangles) for the imaginary ($m''$) part of the AC magnetic moment of a [Nb(23nm)/Ni(5nm)]$_S$ ML in the SC state at $T = 4.5$ K. Data were collected using an AC frequency $f = 10$ Hz and amplitude $h_0 = 3.0$ Oe, with DC applied field $H$ at an angle $\theta$ with respect to the normal to the ML plane. Dashed and solid lines denote data multiplied by $\cos \theta$ and $\cos^2 \theta$, respectively, and indicate the onset of strong FLL pinning for $\theta > 60^\circ$. The logarithmic scale that shows the AC losses rapidly decrease below detectability (MPMS noise floor $\approx 5 \times 10^{-8}$ emu) within about 10 degrees of perfect parallel orientation. After [166].
Figure 3.18b. MPMS SQUID Rotator data (triangles) for the real ($m'$) part of the AC magnetic moment data for a [$\text{Nb}(23\text{nm})/\text{Ni}(5\text{nm})$]$_5$ ML in the SC state at $T = 4.5$ K (parameters and notation as in a), above). The cross-over to $m' \propto \cos^2 \theta$ dependence indicates the SC diamagnetic currents become strongly confined within Nb layers for $\theta > 70^\circ$. The logarithmic scale that shows the AC diamagnetic moment sharply decreases to the MPMS noise floor within about 5 degrees of perfect parallel orientation. After [166].
Figure 3.19. VR frequency $f$ and amplitude $A$ versus temperature $T$ for a $[\text{Nb}(23\text{nm})/\text{Ni}(5\text{nm})]_5$ ML in a parallel magnetic field $\mu_0 H = 0.12$ T with VR drive $V = 100$ mV. Open symbols denote initial field-cooled (FC) data, and solid symbols denote subsequent FC-warming cycle (FCW) data (only slight hysteresis is apparent). Red lines indicate the assumed normal-state baselines in $f(T)$ and $A(T)$, and vertical arrows denote the temperatures of the SC onset near 6.6 K. Note the slope changes that are apparent near 6.0 and 5.6 K. After [131].

Abrupt slope changes in $f(T)$ and $A(T)$ were also identified well below the upper SC onset (see Fig. 3.19), and were generally found (almost independent of $H$) near characteristic temperatures of 5.1, 5.6 and 6.0 K. These anomalies could be grouped into two other trajectories that closely tracked the behavior of the SC onsets, as shown in Fig. 3.20.
Figure 3.20. Field ($H$) – temperature ($T$) “phase boundaries” determined from abrupt changes in slope of the VR amplitude $A$ and frequency $f$ in FCW experiments with piezoelectric drive = 100 mV for the VR oriented approximately 5° off the field axis (1<sup>st</sup>-3<sup>rd</sup> onsets). Open squares denote data for the VR oriented nearly parallel to the field axis. Vertical dashed lines indicate tentative phase transition lines, and solid lines are guides to the eye showing the temperature sequence of VR anomalies observed at fixed $H$. After [131].

Additional VR data were acquired at reduced piezoelectric drives of 5, 10, 26, and 50 mV at selected DC fields $\mu_0 H = 0.08, 0.10, 0.36$ and 0.62 T (where thermal hysteresis was observed). The SC onsets exhibited large, abrupt down-shifts of 0.5-1.0 K with increasing VR drive, indicating drive-dependent instabilities within the SC state: One of two lines of onsets near 6.5 K was found to extend to at least 0.62 T for drives of 5-26
mV, but disappeared at $\mu_0H \approx 0.2$ T for piezo transducer drives $\geq 50$ mV; whereas a line of anomalies near 6.0 K was found to terminate at 0.62 T for drives $\geq 26$ mV (see Fig. 3.21). These observations finally confirmed that the SC state does persist to a maximal $T_C \approx 6.5$ K in parallel DC fields, which places the VR results in tentative agreement with AC SQUID data in Fig. 3.5.

The VR was finally re-oriented very close to $H \parallel ML$ for another set of experiments that revealed a near-vertical upper line of onsets (Fig. 3.21) to at least 0.7 T, which implies an initial slope of at least $-dH_c/dT \approx 14 T/K$, which is three times larger than observed for the extreme high-field Chevrel phase, PbMo$_6$S$_8$ [170]. The down-shift of the SC onset near 0.2 T (0.62 T) therefore marks a hysteretic jump from the 6.5 K to 6.0 K (6.0 K to 5.5 K) “phase boundary”, possibly due to increasing in-plane or inter-plane SC currents that drive the flux line lattice, and have the potential (for critical current densities $J_c \approx 10^7$ A/cm$^2$) to switch the magnetization direction of Ni domains.

3.2. Summary and Conclusions

We have completed a thorough study of Nb/Ni SC/FM multilayer system and observed a number of interesting properties.

We emphasize that great care must be taken in measuring SC thin films with SQUID magnetometers such as the Quantum Design MPMS. We have found Nb/Ni ML exhibit extreme two-dimensional anisotropy (strong perpendicular moment) in the SC state. Presumably, this happens due to confinement effects when the SC layer thickness $x \ll \xi$, $\lambda$. This is at least in qualitative agreement with previous neutron reflectometry data on
Nb films that were interpreted in terms of a SC state magnetization that was strongly oriented perpendicular to the film plane [171].

In spite of the failure of the standard Quantum Design data processing algorithms, we have demonstrated that the MPMS SQUID voltmeter signal contains useful information describing the complex magnetization of non-point-dipole samples. We have developed a new algorithm that yields excellent fits of SQUID voltmeter data for SC Nb/Ni ML. The method helps explain the anomalous behavior of the SC onsets in AC SQUID moment data in applied magnetic fields parallel and perpendicular to the ML plane, the paradox between abrupt switches in SQUID magnetometry, and the lack of anomalies in neutron reflectometry data for the in-plane magnetization profile in the SC state [138, 151]. We find multipole contributions introduced into the SC state SQUID voltmeter data are much bigger than suggested by recent analyses [135-137,164] of SQUID data reduction algorithms. Our VR measurements of the transverse AC response reveal SC onsets as high as 6.5 K that reproducibly down-shift by ~0.5 K at certain DC fields, depending on the VR piezo drive and field orientation. This clarifies observations of $H_{C2}$ and $T_C$ “inconsistencies” in SQUID data taken using various DC field orientations and AC drives and frequencies [138,151].

The VR signals in FC and FCW runs near DC fields where jumps occur are hysteretic and depend upon drive level, but are otherwise reproducible, implying they mark irreversible transitions between near-vertical $H$-$T$ “phase boundaries”. A huge value, $-dH_{C2}/dT > 14$ T/K ($\sim 3$ PbMo$_6$S$_8$ value) was observed for aligned ML and $H < 0.7$ T, which implies the existence of suppressed orbital pairbreaking, and may be the signature of exotic SC pairing states (FFLO state, triplet pairing, etc.[43-44,91-92,97-
99,102-108,172]) in Nb/Ni $ML$. The existence of phase transitions between $SC$ states with unconventional order parameters and/or FLL rearrangements is also supported by the discovery of slope anomalies in the VR data for $A$ and $f$ that generally agree in both $FC$ and $FCW$ data.

Here we summarize major findings of this work concerning Nb/Ni $ML$:

- Multipole SQUID magnetometer data analysis methods can reveal complex $SC$-normal phase boundaries.
- SQUID experiments are consistent with VR data and lack of anomalies observed in neutron reflectance results.
- AC moment data for $ML$ oriented near-parallel to the $ML$ plane suggest extremely strong anisotropy, restricting the $SC$ current to in-plane flow.
- Vibrating reed data reveal $SC$ onsets in the transverse moment jump by up to 0.5 $K$ with increasing applied $DC$ field $H$, depending on the VR drive and field orientation.
- $-dH_{c2}/dT > 14 \ T/K$ ($\sim 3 \times \text{PbMo}_6\text{S}_8$) for $\mu_0 H < 0.7 \ T$ was observed in VR data for a $ML$ well aligned with the magnetic field, implying supercurrent response is confined to Nb layers and orbital pairbreaking is suppressed.
- Our results provide evidence for the existence of exotic $SC$ pairing states (FFLO, triplet superconductivity, etc.) in Nb/Ni $ML$.

Appendix A

Here we give a detailed listing of the Maple© program used for our Multipole Fitting procedure (MPF). Italic font is used for actual Maple input, and normal font is used for comments. Red “$>$” indicates Maple command prompt and blue font indicates output result of command execution. Italic font also is a result of Maple command execution.
First, we import data from a file 06-09-21_III116_2_T5.0.csv (*.csv is a “comma separated file”--- i.e., data columns are separated with a “,”). The file format assumed for the input file is described below:

- the first column is an external magnetic field “H”
- the second column is a current sample position from a “raw” file
- the third column is a “scaled voltage” from a “raw” file.

This particular program was used to fit RAW data output using the RSO option; it needs to be changed if applied to DC data. The RSO option always involves taking 64 measurements during every scan. Each of this measurement is a voltage measured at specified transport position. For each temperature/field data point there will be 1 voltage measurement for each of 64 transport positions, the dipole moment of the sample is then extracted from this voltage vs. position measurement set. However, this is not true for DC transport measurements, for which the user has an option to vary the number of measurements per scan and this program has to be adjusted accordingly.

The variable, DataPoints, is controlled by the number of measurements per scan. The variable, InputData, contains input data that are read from the input file.

The parameter $Ar$ is a constant that is calculated based upon the size of the input data array, it will be used to define the output data array size and is calculated dynamically.

The variables $X$ and $Y$ are vectors that contain input data for the fitting function. Variable $sp$ is the separation distance between the SQUID pickup coils. Variable $r$ is the radius of the SQUID pick-up coils as described in [165].

The last two variables are actual physical characteristics of our particular device and have to be adjusted if the program is intended to be used for different SQUID systems. The dimensionless parameter $zk = l/r$ determines the geometry of the pick-up coils.

\[
> \quad Ar := 0; \text{DataPoints} := 64;
\]

\[
Ar := 0
\]

\[
\text{DataPoints} := 64
\]

We import data into variable InputData:
> InputData
> := ImportMatrix("d:/_docs/nbni//nbni/III116H/06-09
>                   -21_III116H_2_T5.0.csv", source = delimited, delimiter = ",",
>                   format = rectangular, datatype = float8, transpose = false,
>                   skiplines = 0);

Continue with linear algebra module:
>
> with(LinearAlgebra):
>
Now, we determine the number of measurements stored in the InputData from its size and number of position measurements per data point:
>
> Ar := RowDimension(InputData)/DataPoints - 1;

\[
Ar \ := 302
\]

So, in this sample file we have 302 measurements, with 64 position measurements per data point. We can verify the value for magnetic field at last measurement point, which should be 5000 Oe:
>
> InputData[(Ar + 1)·DataPoints, 1];

5000.

Define another matrix that will be used to store intermediate calculation results.
>
> M4 := Matrix(1..(Ar + 1)·DataPoints, 1..4);

\[
M4 \ := \begin{bmatrix}
19392 \times 4 \ Matrix \\
Data \ Type: \ \text{anything} \\
Storage: \ \text{rectangular} \\
Order: \ \text{Fortran_order}
\end{bmatrix}
\]

Next, we copy area of interest from InputData into matrix M4:
>
> M4[1..(Ar + 1)·DataPoints, 1..3] := InputData[1..(Ar + 1)
>                   ·DataPoints, 1..3];

\[
M4_{1..19392, 1..3} \ := \begin{bmatrix}
19392 \times 3 \ Matrix \\
Data \ Type: \ \text{float8} \\
Storage: \ \text{rectangular} \\
Order: \ \text{Fortran_order}
\end{bmatrix}
\]
Define output matrix $Res1$:

$$Res1 := \text{Matrix}(1..(Ar + 1) \cdot DataPoints, 1);$$

Define two vectors used in fitting function $(X,Y)$:

$$X := \text{Matrix}(1..DataPoints);$$

$$Y := \text{Matrix}(1..DataPoints);$$

Define physical parameters of the pickup coils, $sp$ equals coil separation in centimeters and $R$ equals coil radius in centimeters.

$$R := 0.97; \quad sp := 1.519;$$

$$zk := \frac{sp}{R};$$

$$zk := 1.56597938$$

$$with(\text{Statistics});$$

In the next line we define placeholders for our input and output data:

$$R1 := \text{array}(1..Ar + 1); \quad R2 := \text{Matrix}(1..Ar + 1, 2); \quad R3 := \text{Matrix}(1..Ar + 1, 3); \quad R4 := \text{Matrix}(1..Ar + 1, 2);$$
Now, we define a generating function $G$ that will be used to generate a geometry factor for our particular SQUID coil configuration. Variable $l$ is the derivative order; it controls order of generated multipoles.

\[
G := (x, l) \to (-1)^l \cdot \left( \frac{\pi \cdot l \cdot (2 \cdot l + 1)}{(l + 1)} \right)^{0.5} \cdot \frac{1}{l!} \frac{\text{diff}}{\sqrt{(1 + x^2)}}, x^l ;
\]

\[
G := (x, l) \to \frac{(-1)^l \left( \frac{\pi l (2 l + 1)}{l + 1} \right)^{0.5} \left( \frac{d^l}{dx^l} \left( \frac{x}{\sqrt{1 + x^2}} \right) \right)}{l!}
\]

Since flux-locked loop sensor is essentially a set of three coils connected in series, the final generating function is also a sum of three terms with parameters $z1, z2, z3$ that determine coil position relative to the sample, the middle coil has two turns and orientation opposite to others, hence factor of -2:

\[
sl := (z1, z2, z3, l) \to G(z1, l) - 2 \cdot G(z2, l) + G(z3, l);
\]

\[
sl := (z1, z2, z3, l) \to G(z1, l) - 2 \cdot G(z2, l) + G(z3, l)
\]

\[
x0 := 3.0;
\]

Parameters $z1, z2, z3$ are not independent, and we can express them as:

\[
z1 = - sp - z, \\
z2 = - z,
\]
$z^3 = + sp - z$, where $z =$ position of the sample versus the center of coordinates, and $sp =$ position of the coil vs. center of origin. The fitting is done to the function $W$, which is defined as a sum of individual multipoles plus a constant offset and an additional linear term responsible for sensor drift in time. $W$ can be any linear combination of $F00$... $FN0$, depending on which of those terms is expected to give the highest contributions to the total signal.

Here we demonstrate how to substitute actual coil physical dimensions into generating functions and calculate the first five terms of the multipole expansion $s10...s50$ by substituting $z1,z2,z3$ from expressions above:

```plaintext
> s10 := s1(z1,z2,z3,1) : s1 := (z) -> subs(z1 = -sp - z, z2 = -z, z3 = sp - z, s10)
> s20 := s1(z1,z2,z3,2) : s2 := (z) -> subs(z1 = -sp - z, z2 = -z, z3 = sp - z, s20)
> s30 := s1(z1,z2,z3,3) : s3 := (z) -> subs(z1 = -sp - z, z2 = -z, z3 = sp - z, s30)
> s40 := s1(z1,z2,z3,4) : s4 := (z) -> subs(z1 = -sp - z, z2 = -z, z3 = sp - z, s40)
> s50 := s1(z1,z2,z3,5) : s5 := (z) -> subs(z1 = -sp - z, z2 = -z, z3 = sp - z, s50)
```

Construct $F00$, which contains the constant offset and linear term:

```plaintext
> F1 := (a0, b0, a1, z) -> a0 + b0 * z + a1 * s1(z);
    F1 := (a0, b0, a1, z) -> a0 + b0 * z + a1 * s1(z)
> F00 := F1(a0, b0, 0, (z - x0) / R);
    F00 := a0 + b0 * (1.030927835z - 3.09278350z)
```

Construct $F10$, the first order term, which corresponds to ideal dipole response:

```plaintext
> F10 := F1(0, 0, a1, (z - x0) / R);
```

Construct the remaining higher order multipoles, $F20...F50$:

```plaintext
> F2 := (a2, z) -> a2 * s2(z);
    F2 := (a2, z) -> a2 * s2(z)
> F20 := F2(a2, (z - x0) / R);
> F3 := (a3, z) -> a3 * s3(z);
    F3 := (a3, z) -> a3 * s3(z)
```

108
F30 := F3(a3, \frac{(z - x0)}{R})

F4 := (a4, z) \rightarrow a4 \cdot s4(z)

F40 := F4(a4, \frac{(z - x0)}{R})

F5 := (a5, z) \rightarrow a5 \cdot s5(z)

F50 := F5(a5, \frac{(z - x0)}{R})

Now, we can write down our final expression for the fitting function as a sum of the linear term F00 and the multipole terms F10...F50.

W := F00 + F10 + F20 + F30 + F40 + F50

In the following section of code we perform a non-linear fitting procedure and save R1, R2, R3, R4, Res1 to the disk storage (see end of this program listing). Variable R1 contains plotted graphs for random fit quality control, R2 and R3 contain regression fit quality data, R4 contains the fit coefficients (a0, a1...an), and Res1 holds the signal reconstructed from fit coefficients substituted into the fit function W.

In the next block of code we go through all the data points in InputData. The first column is the external magnetic field H (Oe), the second column is the sample position, and the third column is the measured response voltage in Volts. We take blocks of data of length DataPoints (= 64 in this example) and perform a non-linear fit to the function W.

We store fit quality indicators into array R3, where the first column is the external field H, the second column is the normalized residuals (difference between input data and reconstructed data), and the third column is the Regression Fit Quality calculated the same way as described in reference [139].

We store Maple graphs into array R1, so that after the fitting is done we can quickly compare data to the reconstructed functions.
for $i$ from 0 by 1 to $Ar$ do
  $k := i$;
  $X := InputData[k \cdot DataPoints + 1 .. (k + 1) \cdot DataPoints, 2]$:
  $Y := InputData[k \cdot DataPoints + 1 .. (k + 1) \cdot DataPoints, 3]$:
  $V1 := InputData[k \cdot DataPoints + 1 .. (k + 1) \cdot DataPoints, 2 .. 3]$:
  $V2 := convert(V1, listlist)$:
  $F := NonlinearFit(W, X, Y, z, output = parametervalues, \# iterationlimit = 100000)$:
  $R2[i + 1, 1] := InputData[DataPoints \cdot k + 1, 1]$:
  $Pl := subs(F, W)$:
  $mA := 0$:
  $mDelta := 0$:
  $maxV := 0$:
  for $j$ from 1 by 1 to $DataPoints$ do
    $M4[DataPoints \cdot k + j, 4] := evalf(subs(z
      = InputData[DataPoints \cdot k + j, 2], Pl))$:
    $mA := mA + abs(M4[DataPoints \cdot k + j, 4])$:
    if $(maxV < abs(M4[DataPoints \cdot k + j, 4]))$ then $maxV := abs(M4[DataPoints \cdot k + j, 4])$ end if:
    $mDelta := mDelta + (abs(InputData[DataPoints \cdot k + j, 3]) - abs(M4[DataPoints \cdot k + j, 4]))^2$:
  end do:
  $R3[i + 1, 1] := InputData[DataPoints \cdot k + 1, 1]$:
  $R3[i + 1, 2] := \frac{mDelta}{maxV^2 \cdot (DataPoints - 1)}$:
  $R3[i + 1, 3] := 1 - \frac{mDelta}{maxV^2 \cdot (DataPoints - 1)}$:
  $R1[i + 1] := plot([[Pl, V2], z = 0 .. 5])$:
  $H := InputData[k \cdot DataPoints + 1, 1]$:
  $Res1[i + 1, 1] := F$:
end do:

> Copy some of the data into $R4$ and $R1$ so we can easily plot them:

> $R4[1 .. Ar, 1] := R3[1 .. Ar, 1]$:
$R4[1 .. Ar, 2] := R3[1 .. Ar, 3]$:
$R2[1 .. Ar, 2] := R3[1 .. Ar, 2]$:
$R2[1 .. Ar, 1] := R3[1 .. Ar, 1]$:
We now plot the residuals in order to confirm the quality of the fit:

> `plot(convert(R2, listlist)[1..Ar], x = -0..1000);`

![Graph showing residuals over a range of x-values](image)

**Figure A.1.** Fit quality control. Y axis is the normalized difference between input data and fit function v. X-axis is the applied magnetic field in gauss. The zero on Y-axis means a perfect fit, and one means the fit failed completely.

We also plot the regression fit quality:

> `plot(convert(R4, listlist)[1..Ar], x = -5000..5000, y = 0.995..1);`
Figure A.2. Fit quality control, (y = 1-A.1 data). A y-axis value equal to 1 indicates a perfect fit, a zero value indicates that the fit has failed.

One can see that the quality of the fit is excellent, since a regression fit quality better than 0.998 indicates a very good fit. We can examine some random data points simply by displaying plots stored in array \( R1 \):

\[ > R1[250]; \]
Figure A.3. Experimental data vs. fit function. The y-axis represents the SQUID voltmeter signal strength, the x-axis represents the sample position relative to the center position of the SQUID coils. The green curve indicates the fit function, and the red curve indicates the data.

Now we compute the dipole moment of the sample, which is defined by the coefficient $a I$. In order to simplify plotting, we will create a new variable $dl$, which will have the array dimensions 2xAr, and we assign the first column to be field $H$, and the second column to be the dipole moment:

```plaintext
> for j from 1 by 1 to Ar do
dl[j, 2] := subs(Res1[j, 1], a1)
dl[j, 1] := R2[j, 1];
end do:
```

Now we can easily plot the dipole moment vs. external magnetic field $H$:

```plaintext
> plot(convert(dl, listlist)[1..Ar], x = -5000..5000);
```
Figure A.4. Result of fitting a multipole of first order (dipole moment). The y-axis represents signal strength in (emu), the x-axis is the magnetic field (gauss) acting on the sample.

In the next section of code we prepare our data for output to a text file and save it to disk. Data are saved in two files: one (06-09-21_III116_2_T5.0_fit_a1a2a4) contains fit coefficients, that is, the magnetic multipole moments. The second file (06-09-21_III116_2_T5.0_fit_details_a1a2a4a5) holds the predicted values of the SQUID voltmeter signal (volts), which can be compared to the actual RAW SQUID output. The output variable Out1 will have:
- column (1) = external field $H$
- column (2) = coefficient $a1$, dipole term
- column (3) = coefficient \(a_2\), quadrupole term
- column (4) = coefficient \(a_3\), octupole term
- column (5) = coefficient \(a_4\)
- column (6) = coefficient \(a_5\)
- column (7) = magnetic center position, as computed by fitting algorithm
- column (8) = "regression factor" – fit quality indicator

First line will be column headers:

```plaintext
> Out1[1, 1] := "H":
Out1[1, 2] := "dipole":
Out1[1, 3] := "quadrupole":
Out1[1, 4] := "octupole":
Out1[1, 5] := "a4":
Out1[1, 6] := "a5":
Out1[1, 7] := "center_position":
Out1[1, 8] := "Reg_factor":
```

Lines two through \(Ar\) will be variable values:

```plaintext
>
for j from 2 by 1 to Ar do
Out1[j, 1] := R2[j, 1]:
Out1[j, 2] := subs(Res1[j, 1], a1) \cdot 2 :
Out1[j, 3] := subs(Res1[j, 1], a2) \cdot 2 :
Out1[j, 4] := subs(Res1[j, 1], a3) \cdot 2 :
Out1[j, 5] := subs(Res1[j, 1], a4) \cdot 2 :
Out1[j, 6] := subs(Res1[j, 1], a5) \cdot 2 :
Out1[j, 7] := subs(Res1[j, 1], x0) :
Out1[j, 8] := R4[j, 2]:
end do:
```

Now examine line 65:

```plaintext
> Out1[65, 1..5];

\[
\begin{bmatrix}
4250, & 0.0001829761166 & -0.0009588206542 & -0.00009353891900 & -0.0000391892384
\end{bmatrix}
\]
```

One can see coefficients \(a1\) and \(a2\) are of the same order of magnitude, that is, the quadrupole contribution is comparable to the dipole contribution to the magnetic multipole moment of the sample. The next step is to save the results of the fitting procedure to the disk. We have chosen a plain text format for compatibility with other software.
We save two variables – \textit{Out1}, which contains fitting coefficients, and \textit{M4} – which contains original \textit{InputData} (columns one through three) with the addition of the predicted data (column four).

\begin{verbatim}
> ExportMatrix
   ("d:/_Sergiy/nbni/III116H/06-09-21_III116H_2_T5.0_fit_a1a2a4a
    txt", Out1);

> M4[1, 1] := "II ";
M4[1, 2] := "position";
M4[1, 3] := "V, data";
M4[1, 4] := "V, fit";

> ExportMatrix
   ("d:/_Sergiy/nbni/III116H/06-09
    -21_III116H_T5.0_fit_details_a1a2a4a5.txt" M4);

>
\end{verbatim}
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Masters, Physics, 2004
University of Kentucky, Kentucky, USA

Specialist, Physics, 1999
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