Scanning Tunneling Spectroscopy Studies on Strongly Disordered S-Wave Superconductors Close To Metal Insulator Transition

A Thesis

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in Physics

by

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To my parents
DECLARATION

This thesis is a presentation of my original research work. Wherever contributions of others are involved, every effort is made to indicate this clearly, with due reference to the literature, and acknowledgement of collaborative research and discussions.

The work was done under the guidance of Professor Pratap Raychaudhuri, at the Tata Institute of Fundamental Research, Mumbai.

Anand Kamlapure

In my capacity as supervisor of the candidate’s thesis, I certify that the above statements are true to the best of my knowledge.

Prof. Pratap Raychaudhuri

Date:
STATEMENT OF JOINT WORK

The experiments reported in this thesis have been carried out in the Department of Condensed Matter Physics and Material Science under the guidance of Prof. Pratap Raychaudhuri. The results of the major portions of the work presented in this thesis have already been published in refereed journals.

Most of the experiments discussed in this thesis have been conducted by me in the department. For completeness, I have included some of the experiments and data analysis performed by other group members and collaborators.

Some of the scanning tunneling measurements were carried out jointly with Garima Saraswat and Somesh Chandra Ganguli. Transport, Magnetoresistance and Hall effect measurements were carried out in collaboration with Madhavi Chand. Penetration depth measurements were carried out by Mintu Mondal and Sanjeev Kumar. All the Transmission Electron Microscope measurements were carried out by Tanmay Das and Somnath Bhattacharyya. Theoretical work was done in collaboration with Dr. Vikram Tripathi of Department of Theoretical Physics, TIFR and Dr. Lara Benfatto and Dr. Gabriel Lemarié of University of Rome, Rome, Italy.
PREFACE

The work presented in this thesis is on the experimental investigation of the effect of disorder on s-wave superconductor NbN through scanning tunneling spectroscopy (STS) measurements.

Disorder induced superconductor insulator transition (SIT) has been the subject of interest since decades and there have been major advances both experimentally and theoretically in understanding the nature of SIT. Recently new insights have been offered by the numerical simulations which predicts unprecedented phenomena such as persistence of gap across the SIT, spatial inhomogeneity in the gap and order parameter, emergence of superconductivity over much larger length scale than the disorder length scale, which needs to be addressed through sophisticated experiments. The work presented in this thesis unravels many of these novel phenomena near the SIT in s-wave superconductor, NbN, primarily through scanning tunneling spectroscopy measurements and supported by results of penetration depth and transport measurements.

The thesis is organized in following way, In **Chapter 1**, I will introduce the motivation for our experiments on disordered superconductors through the advances in the experimental and theoretical works. I will also introduce our model system: NbN as a perfect system and its characterization through transmission electron microscope at the atomic scale. In **Chapter 2**, I will elaborate on the basics of scanning tunneling microscope (STM), fabrication of low temperature STM, related techniques and the scheme of measurements. **Chapter 3** focuses on our observation of formation of pseudogap state in NbN in presence of strong disorder. We argue that the phase fluctuation is the possible mechanism for the formation of pseudogap state. In **Chapter 4**, we investigate the ground state superconducting properties in strongly disordered NbN through spatially resolved STS measurements. We identify that the coherence peak height is a measure of local order parameter and show that the superconductivity in the disordered NbN emerges over tens of nanometer scale while the structural disorder present in the system is at atomic scale. In this chapter we also show that the order parameter distribution in strongly disordered NbN has a universal behaviour.
irrespective of the strength of disorder present in the system. We end the chapter with the temperature evolution of inhomogeneous superconducting state through spatially resolved STS measurements. In the concluding Chapter 5, I will summarize all our investigation during past 6 years and present a phase diagram showing evolution of various energy scales with disorder.
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I finally thank my family members for their love and patience and I dedicate this thesis to my parents.
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In refereed Journal and related to material presented here.

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   Anand Kamlapure, Tanmoy Das, Somesh Chandra Ganguly, Somnath Bhattacharya and Pratap Raychaudhuri

2. A 350 mK, 9 T scanning tunneling microscope for the study of superconducting thin films and single crystals
   Anand Kamlapure, Garima Saraswat, Somesh Chandra Ganguli, Vivas Bagwe, Pratap Raychaudhuri and Subash P. Pai

3. Universal scaling of the order-parameter distribution in strongly disordered superconductors

4. Phase diagram of the strongly disordered s-wave superconductor NbN close to the metal-insulator transition
   Madhavi Chand, Garima Saraswat, Anand Kamlapure, Mintu Mondal, Sanjeev Kumar, John Jesudasan, Vivas Bagwe, Lara Benfatto, Vikram Tripathi, and Pratap Raychaudhuri

5. Phase Fluctuations in a Strongly Disordered s-Wave NbN Superconductor Close to the Metal-Insulator Transition
   Mintu Mondal, Anand Kamlapure, Madhavi Chand, Garima Saraswat, Sanjeev Kumar, John Jesudasan, L. Benfatto, Vikram Tripathi, and Pratap Raychaudhuri

6. Enhancement of the finite-frequency superfluid response in the pseudogap regime of strongly disordered superconducting films
Mintu Mondal, Anand Kamlapure, Somesh Chandra Ganguli, John Jesudasan, Vivas Bagwe, Lara Benfatto and Pratap Raychaudhuri

7. Temperature dependence of resistivity and Hall coefficient in strongly disordered NbN thin films

8. Tunneling studies in a homogeneously disordered s-wave superconductor: NbN
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**In refereed journals, not related to the work presented here.**

1. Measurement of magnetic penetration depth and superconducting energy gap in very thin epitaxial NbN films
Anand Kamlapure, Mintu Mondal, Madhavi Chand, Archana Mishra, John Jesudasan, Vivas Bagwe, L. Benfatto, Vikram Tripathi, and Pratap Raychaudhuri

2. Andreev bound state and multiple energy gaps in the noncentrosymmetric superconductor, BiPd
Mintu Mondal, Bhanu Joshi, Sanjeev Kumar, Anand Kamlapure, Somesh Chandra Ganguli, Arumugam Thamizhavel, Sudhansu S. Mandal, Srinivasan Ramakrishnan and Pratap Raychaudhuri
3. Role of the Vortex-Core Energy on the Berezinskii-Kosterlitz-Thouless Transition in Thin Films of NbN
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Conference Proceedings
1. Pseudogap state in strongly disordered conventional superconductor, NbN
Anand Kamlapure, Garima Saraswat, Madhavi Chand, Mintu Mondal, Sanjeev Kumar, John Jesudasan, Vivas Bagwe, Lara Benfatto, Vikram Tripathi and Pratap Raychaudhuri

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Madhavi Chand, Anand Kamlapure, Garima Saraswat, Sanjeev Kumar, John Jesudasan, Mintu Mondal, Vivas Bagwe, Vikram Tripathi, Pratap Raychaudhuri.

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5. Evolution of Kosterlitz-Thouless-Berezinskii (BKT) Transition in Ultra-Thin NbN Films
Mintu Mondal, Sanjeev Kumar, Madhavi Chand, Anand Kamlapure, Garima Saraswat, Vivas C Bagwe, John Jesudasan, Lara Benfatto, Pratap Raychaudhuri

6. Effect of Phase Fluctuations on the Superconducting Properties of Strongly Disordered 3D NbN Thin Films
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# TABLE OF CONTENTS

**Synopsis** .......................................................................................................................... 21

**Chapter 1** ............................................................................................................................ 43

1.1 Basics of Superconductivity ............................................................................................ 45
1.1.A The Meissner-Ochsenfeld effect ................................................................................ 45
1.1.B The London equations ................................................................................................ 45
1.1.C Nonlocal Response: Pippard Coherence length (\( \xi_0 \)) ........................................ 46
1.1.D Ginzburg Landau (G-L) model of superconductivity ................................................... 47
   - *Phase stiffness* .................................................................................................................. 48
   - *G-L Characteristic length scales* .................................................................................. 48
   - *Type I and Type II superconductors* ............................................................................. 49
1.1.E BCS theory of superconductivity .................................................................................... 50
   - *The gap function* .......................................................................................................... 51
   - *Temperature dependence of the gap and \( T_c \)* ......................................................... 51
   - *BCS density of states* ..................................................................................................... 52
1.1.F Electron tunneling and measurement of \( \Delta \) ............................................................... 53
1.2 Disordered Superconductors ............................................................................................. 54
1.3 Our model system: NbN .................................................................................................... 56
1.3.A Sample growth and introducing disorder ...................................................................... 56
1.3.B Structural characterization of NbN films ....................................................................... 57
1.3.C Quantification of disorder ............................................................................................ 58
1.4 Effects of disorder ............................................................................................................. 58
1.4.A Resistivity and measurement of \( T_c \) ........................................................................ 59
1.4.B Hall carrier density measurement ............................................................................... 60
1.4.C Upper critical field (\( H_{c2} \)) and coherence length (\( \xi_{GL} \)) ............................ 61
1.4.D Magnetic penetration depth (\( \lambda \)) ....................................................................... 61
1.5 References ......................................................................................................................... 62

**Chapter 2** ............................................................................................................................ 68

2.1 Schematic of STM ............................................................................................................. 69
2.1.A Constant current mode ................................................................................................. 70
2.1.B Constant height mode .................................................................................................. 71
2.2 STM Theory

2.2.A Tersoff–Hamann formalism

2.2.B Other models

2.3 Fabrication of low temperature STM

2.3.A STM Head

- Coarse positioner: .......................................................... 78
- Piezoelectric tube ............................................................ 80
- Mechanical Description of the STM head .......................... 81
- Calibration of Piezo constants ......................................... 83
- Tip preparation ............................................................... 84

2.3.B Sample holder ................................................................ 85

2.3.C Sample Preparation chamber ....................................... 87

2.3.D Load lock and sample manipulators ............................. 88

2.3.E $^3$He Cryostat ............................................................ 89

- Variable temperature insert ............................................... 89
- Liquid Helium Dewar ....................................................... 90
- Temperature control of the sample ................................... 91

2.3.F Vibrational and electrical noise reduction ..................... 91

- Vibrational noise ............................................................. 91
- Electrical noise ............................................................... 93
- Characterization of noise .................................................. 94

2.4 Experimental Methods and results .................................. 94

2.4.A Topography ............................................................... 94

2.4.B Scanning tunneling spectroscopy (STS) ....................... 95

- Normal Superconductor tunneling .................................... 97

2.4.C Linescan .................................................................. 98

2.4.D Spatially resolved STS and conductance map ............... 99

- Conductance map ........................................................... 99

2.5 Reference ........................................................................ 101

Chapter 3

3.1 Experimental strategy and data analysis schemes: ............. 107

3.1.A In-situ preparation of NbN films .................................... 107
3.1.B Line scan and averaged spectrum ........................................ 108
3.1.C DOS evolution with temperature ........................................ 109
3.1.D Background correction for disorder NbN samples ............... 109
3.2 Experimental results ............................................................. 111
3.3 Discussion ............................................................................. 114
   • Regime I: Intermediate disorder level .................................. 116
   • Regime II: Strong disorder level ......................................... 117
   • Regime III Nonsuperconducting regime .............................. 119
3.4 Summary ............................................................................... 120
3.5 References ............................................................................. 121

Chapter 4 ..................................................................................... 125
4.1 Introduction ............................................................................. 125
4.2 Investigation of structural disorder in NbN at the atomic scale.
................................................................................................. 126
4.3 STS Methods .......................................................................... 128
4.4 Evolution of superconducting spectra with increasing disorder
................................................................................................. 129
4.5 Coherence peak height as a measure of local order parameter 130
4.6 Emergence of inhomogeneity in the superconducting state ..... 133
4.7 Universal scaling of the order parameter distribution .......... 135
4.8 Temperature evolution of the inhomogeneous supercond... 137
4.9 Discussion ............................................................................. 141
4.10 Summary ............................................................................. 142
4.11 References ............................................................................. 144

Chapter 5 ..................................................................................... 147
References ..................................................................................... 149
LIST OF SYMBOLS

\( a \)  
  lattice constant or characteristic length scale of phase fluctuations

\( e \)  
  electronic charge

\( E_F \)  
  Fermi energy

\( G \)  
  conductance

\( h=h/2\pi \)  
  \( h \) is Planck's constant

\( H_{c2} \)  
  upper critical field

\( j_s \)  
  Current density due to super-electrons

\( J \)  
  superfluid stiffness

\( k_B \)  
  Boltzmann constant

\( k_F \)  
  Fermi wave-number

\( k_d \)  
  Ioffe Regel parameter

\( l \)  
  mean free path

\( m_e \)  
  mass of electron

\( M_{\alpha\beta} \)  
  Tunneling matrix element between the states \( \alpha \) and \( \beta \)

\( n \)  
  number density/ electronic carrier density

\( n_s \)  
  superfluid density

\( N(0) \)  
  density of states at Fermi level

\( R \)  
  resistance

\( R_H \)  
  Hall coefficient

\( T \)  
  temperature

\( T_c \)  
  superconducting critical temperature

\( v_F \)  
  Fermi velocity

\( \mu^* \)  
  Coulomb pseudopotential

\( \xi \)  
  coherence length

\( \xi_0 \)  
  Pippard Coherence length

\( \xi_{BCS} \)  
  BCS Coherence length

\( \xi_{GL} \)  
  Ginzburg Landau coherence length

\( \rho \)  
  resistivity

\( \lambda \)  
  penetration depth

\( \Phi_0 \)  
  flux quantum

\( \sigma \)  
  conductivity

\( \Theta_D \)  
  Debye temperature

\( \omega_D \)  
  Debye cut-off frequency

\( \Delta \)  
  superconducting energy gap
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>2D</td>
<td>two dimensions</td>
</tr>
<tr>
<td>3D</td>
<td>three dimensions</td>
</tr>
<tr>
<td>AA</td>
<td>Altshuler and Aronov</td>
</tr>
<tr>
<td>ACF</td>
<td>auto correlation function</td>
</tr>
<tr>
<td>BCS</td>
<td>Bardeen, Cooper and Schreiffer</td>
</tr>
<tr>
<td>DOS</td>
<td>density of states</td>
</tr>
<tr>
<td>e-e</td>
<td>electron-electron</td>
</tr>
<tr>
<td>GL</td>
<td>Ginzburg Landau</td>
</tr>
<tr>
<td>HRSTEM</td>
<td>high resolution scanning transmission electron microscope</td>
</tr>
<tr>
<td>HRTEM</td>
<td>high resolution transmission electron microscope</td>
</tr>
<tr>
<td>HTSC</td>
<td>high temperature superconductors</td>
</tr>
<tr>
<td>IVC</td>
<td>inner vacuum chamber</td>
</tr>
<tr>
<td>LT-STM</td>
<td>low temperature scanning tunneling microscope</td>
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<tr>
<td>MIT</td>
<td>metal-insulator transition</td>
</tr>
<tr>
<td>MR</td>
<td>magnetoresistance</td>
</tr>
<tr>
<td>OP</td>
<td>order parameter</td>
</tr>
<tr>
<td>OPD</td>
<td>order parameter distribution</td>
</tr>
<tr>
<td>PID</td>
<td>proportional-integral-derivative</td>
</tr>
<tr>
<td>SIT</td>
<td>superconductor-insulator transition</td>
</tr>
<tr>
<td>STM</td>
<td>scanning tunneling microscope</td>
</tr>
<tr>
<td>STS</td>
<td>scanning tunneling spectroscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TH</td>
<td>Tersoff and Hamann</td>
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<tr>
<td>TW</td>
<td>Tracy Widom</td>
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<tr>
<td>VTI</td>
<td>variable temperature insert</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
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<tr>
<td>ZBC</td>
<td>zero bias conductance</td>
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</table>
Chapter 1. Introduction:

The interplay of superconductivity and disorder is one of the most intriguing problems of quantum many-body physics. Superconducting pairing interactions in a normal metal drives the system into a phase coherent state with zero electrical resistance. In contrast, in a normal metal increasing disorder progressively increases the resistance through disorder scattering eventually giving rise to an insulator at high disorder where all electronic states are localized. Quite early on, it was argued by Anderson\(^1\) that since BCS superconductors respect time reversal symmetry, superconductivity is robust against nonmagnetic impurities and the critical temperature \(T_c\) is not affected by such disorder. However experiments showed that strong disorder reduces \(T_c\) and ultimately drives the system into an insulator\(^2\). Various other phenomena are observed in the vicinity of Superconductor Insulator transition (SIT) which includes the giant peak in the magnetoresistance in thin films\(^3\), magnetic flux quantization in nano-honeycomb patterned insulating thin films of Bi\(^4\), finite high frequency superfluid stiffness above \(T_c\) in amorphous InO\(_x\) films\(^5\), finite spectral gap in the conductance spectra much above \(T_c\) in scanning tunneling microscope (STM) experiments\(^6,7,8\) etc. All of these points towards the existence of finite superconducting correlation persisting in the system even though the global superconductivity is destroyed due to disorder.

In recent times numerous theories and numerical simulations have been carried out in order to understand the real space evolution of superconductivity in presence of strong disorder. In the intermediate disorder limit the effect of disorder is to decrease the pairing amplitude\(^9\) through an increase in the electron-electron Coulomb repulsion which results in decrease in \(T_c\). On the insulating side of SIT, it has been argued that Cooper pair exists even after the single electrons states are completely localized\(^10\). The numerical simulations involve solving Attractive Hubbard model with random on-site energy\(^11,12,13\). Although these simulations ignore the Coulomb interactions and are done on relatively small lattice the end results are instructive. These simulations indicate that in the presence of strong disorder the superconducting order parameter becomes inhomogeneous, spontaneously segregating into superconducting domains, dispersed in an insulating matrix. Consequently the energy gap, \(\Delta\), is not strongly affected but the energy cost of spatially twisting the phase of the condensate, superfluid stiffness \(J\),
decreases rapidly with increasing disorder making the system more susceptible to phase fluctuations. Thus, in presence of strong disorder near SIT, system consists of superconducting islands and their phases are Josephson coupled through insulating regions. Another interesting consequence of these simulations is that in presence of strong disorder with lowering temperature, Copper pairs are formed above the $T_c$ but they are phase incoherent. Therefore one expects a resistive state but finite gap due to superconducting correlations in the local density of states. This gap is termed as pseudogap which resembles well established pseudogap in high $T_c$ Cuprates.

1.1 Our model system: NbN

For our investigation we use thin films of NbN as a model for the study of effect of disorder which can be grown by sputtering Nb in Ar + N$_2$ gas mixture. NbN is s-wave superconductor with relatively high $T_c$ $\sim$16K. Films are grown on single crystalline MgO substrates and are highly epitaxial. All the films grown for the study have thickness $> 50$nm which is much larger than the dirty limit coherence length $\xi \sim$5-8 nm$^{14}$ and can be considered to be 3D as far as superconducting correlations are concerned. Disorder in the film can be tuned by varying the deposition conditions: either by decreasing the sputtering power or by increasing N$_2$ in the gas mixture$^{15,16}$. Disorder in the samples is characterized by Ioffe-Regel parameter, $k_Fl$, using the formula

$$k_Fl = \left\{ \frac{(3\pi^2)^{2/3}\hbar[R_H(285K)]^{1/3}}{\rho(285K)e^{5/3}} \right\}$$

where $R_H$ is the Hall resistance and $\rho$ is the resistivity, both of which are measured using transport measurements. While our most ordered sample shows $T_c$ $\sim$16K, with increasing disorder $T_c$ monotonically decreases all the way down to $<300$mK. The range of $k_Fl$ varies from 1 to 10.2 in our samples.

1.2 Structural characterization of disorder

Thin films of NbN grown using sputtering method show high degree of epitaxy revealed through transmission electron microscopy (TEM) images$^{17}$. Fig.1 (a) and (d) show high resolution TEM images probed at the interface of MgO substrate and NbN film along <110> direction for the two samples with $T_c$ = 16K and 2.5K respectively.
The difference between the two films becomes prominent when we take high resolution scanning TEM data (HRSTEM) as shown in Fig. 1. Panels (b) and (e) show HRSTEM image for the two samples with $T_c = 16K$ and 2.5K and panels (c) and (f) show corresponding two dimensional intensity distribution plots. Intensity in the HRSTEM image is primarily contributed by Nb and is proportional to the number of Nb atoms in the probing column. Smooth intensity variation in clean sample ($T_c = 16K$) shows the overall thickness variation produced during ion beam milling while the disordered sample ($T_c = 2.5K$) shows random distribution of intensity in the columns showing random number of Nb atoms in the adjacent columns. This clearly shows that for the disordered films, the lattice contains Nb vacancies but when probed at the large scale it is homogeneous. Thus we have an ideal system in which disorder is present at the atomic length scale and the disorder is homogeneous over entire film.

All the work presented in this thesis on disordered NbN is primarily carried out in our home built STM. Details of the STM and measurement techniques are discussed in the next chapter.
Chapter 2. Scanning tunneling microscope

Scanning tunneling microscope (STM) is a powerful tool to probe the electronic structure of the material at the atomic scale. It works on the principle of quantum mechanical tunneling between two electrodes through vacuum as a barrier. Essential parts consist of a sharp metallic tip which is brought near the sample using positioning units. Small bias applied between tip and sample make the tunneling current flow between them which is amplified and recorded. Tunneling current exponentially depends on the distance between tip and sample. By keeping the current constant, distance between the tip and sample is held constant using feedback loop and by scanning over the sample the topographic image of the sample is generated.

2.1 Setup

The overall schematic of our system is shown in Fig. 2(a). The assembly primarily consists of three units, Sample preparation chamber, load lock and the $^4\text{He}$ dewar$^{18}$. Sample preparation chamber comprises of two magnetron sputtering guns, two

![Figure 2 (a) Schematic view of the home built low temperature scanning tunneling microscope. Cryostat and magnet have been made semi-transparent to show the internal construction. (b) Schematic view of the STM head shown along with the sample holder.](image-url)
evaporation sources, a plasma ion etching gun and a heater to heat the sample during the deposition. Load lock chamber serves as the stage to transfer sample from deposition chamber into the STM chamber using a pair of transfer manipulators. \( ^4 \)He dewar has a 9T magnet which houses \( ^3 \)He insert. Helium cryostat hangs from custom designed vibration isolation table mounted on pneumatic legs and consists of variable temperature insert (VTI) and STM head. STM head (Fig. 2(b)) attached to the VTI consists of sample housing assembly, positioning unit and printed circuit board for the electrical connections. A combination of active and passive vibration isolation systems are used to obtain the required mechanical stability of the tip. The entire system operates in a high vacuum of \( 10^{-7} \) mbar and the base temperature for the measurements is 350mK. Commercially bought control electronics and data acquisition unit (R9, RHK Technology) is used carry out our experiments.

2.2 Methods

Thin films are grown on substrate mounted on specially designed sample holder made of Molybdenum. The Molybdenum holder has threading on side and bottom for holding on the manipulators. Substrate is secured in place on the holder using a cap which also provides electrical contact with the sample for STM measurements. To ensure electrical contact between film and holder (Fig. 3) substrate is pre-deposited with NbN strips in another chamber and the actual film is grown on this strip in STM chamber. Once the film is grown the sample holder attached on horizontal manipulator is pulled back in the load lock and exchanged with the vertical manipulator. Using vertical manipulator the sample holder is transferred into STM head for measurement. To block the room temperature radiation coming from the top, radiation plug which consist of set of metal discs mounted on steel rod is inserted in the annular

**Figure 3 Design of sample holder (a) Molybdenum cap, (b) Substrate with strip deposited at the edge, (c) Molybdenum sample holder, (d) Sample holder assembly, showing substrate fastened with cap. (e) Resulting film on the substrate after the deposition.**
region of VTI. Once all the measurements are completed on the sample it is taken out from the STM and resistivity versus temperature is measured in different cryostat.

2.3 Scanning tunneling spectroscopy

Another powerful technique using STM is to measure local density of states through tunneling conductance measurements and the method is called as scanning tunneling spectroscopy (STS). The tunneling conductance \( G(V) \) between the normal metal tip and the superconductor is given by \(^{19}\)

\[
G(V) \propto \frac{1}{R_N} \int_{-\infty}^{\infty} N_S(E) \left( -\frac{\partial f(E - eV)}{\partial E} \right) dE
\]

(2)

It can be shown that at sufficiently low temperatures Fermi function becomes step function and \( G(V) \propto N_S(V) \) i.e. the tunneling conductance is proportional to the local density of states of the sample at energy \( E = eV \). To measure the tunneling conductance, tip sample distance is fixed by switching off the feedback loop and a small alternating voltage is modulated on the bias. The resultant amplitude of the current modulation as read by the lock-in amplifier is proportional to the \( dI/dV \) as can be seen by Taylor expansion of the current,

\[
I(V + dV \sin(\omega t)) \approx I(V) + \frac{dI}{dV} \bigg|_V . dV \sin(\omega t)
\]

(3)

The modulation voltage used in the measurement is \( V_{mod} = 150 \mu V \) and the frequency used is 419.3Hz.

Temperature evolution of tunneling density of states (DOS) is investigated through STS measurements along a line. Averaged spectra at different temperatures are obtained by taking the average of about 20 spectra each at 32 equidistant points over the line of length 200 nm and then averaging all in once. The ground state superconducting properties and its temperature evolution are measured through spatially resolved STS data. To acquire such data initially topography is imaged at lowest temperature and then by defining a grid of 32×32 STS data is acquired at each location (typically 5 spectra at each pixel and then averaged). For higher temperatures we match the topography before acquiring spatially resolved STS data.
Chapter 3. Emergence of Pseudogap State in Strongly Disordered NbN

One of the most curious and debated state is the pseudogap state observed in high $T_c$ superconductors where finite gap in the DOS at Fermi level is observed much above the superconducting transition temperature which evolves continuously from the superconducting energy gap below $T_c$. Several scenarios based either on peculiarities specific to High $T_c$ Cuprates such as an order competing with superconductivity, or a superconducting transition driven by phase fluctuations have been suggested as possible origin of this feature. In this section we elucidate formation of pseudogap state in NbN using scanning tunneling spectroscopy.

In strong disorder limit all the samples show two distinct features in tunneling spectra: A low bias dip close to Fermi level which is associated with superconductivity and a weakly temperature dependent V-shaped background which extends up to high bias. This second feature which persists up to the highest temperature of our measurements arises from the Altshuler-Aronov (A-A) type e-e interactions in the normal state\textsuperscript{20}. To extract the superconducting information from this data we divide the low temperature spectra by the spectra at sufficiently high temperature where we do not have any soft gap due to superconducting correlations. The temperature up to which the pseudogap persists is defined as $T^*$. 

![Figure 4](image_url) Figure 4 (a) Normalized conductance curves for the sample with $T_c=2.6K$. (b) Derivatives of the conductance curves in panel (a). Few curves are removed for clarity. (c) Normalized conductance curves after dividing curves in panel (a) from 9.35K data. (d) Surface plot of the curves of panel (c).
Representative data for one of the strongly disordered samples ($T_c = 2.6K$) is shown in Fig. 4. Fig. 4(a) shows conductance spectra at different temperatures. We observe that the low bias gap feature disappears above 8K and the spectrum at 9.35K has only the broad background. This is clearly seen in the $dG(V)/dV$ versus $V$ curves (Fig. 4(b)) where the symmetric peak-dip structure associated with the low bias feature completely disappears for the spectrum at 9.35K. Therefore to remove the A-A background from the low temperature spectra we divide the spectrum at 9.35K. Fig. 4(c) shows the divided spectra and Fig. 4(d) shows the colormap of divided data with x-axis as the temperature, y-axis as the bias and the colorscale as the normalized conductance value. The data in panel (d) shows that the pseudogap persists up to 6.5K i.e. $T^* = 6.5K$.

Series of NbN films with increasing disorder were studied using STS. Fig. 5 shows the temperature evolution of tunneling DOS for four samples with $T_c = 11.9K$, 6K, 2.9K and 1.65K in the form of colormap. All the plots in this figure are corrected for Altshuler-Aronov background. R-T data for the same sample is indicated by thick line on top of each colormap. Representative spectra at three temperatures are shown to the right for clarity. Panel (a) $T_c = 11.9K$, shows that at low temperature spectra consist of dip close to zero bias and two symmetric peaks consistent with BCS density of states. The gap in the spectra vanishes exactly at $T_c$ in accordance with BCS theory and flat metallic DOS is restored for $T > T_c$. For the sample with $T_c = 6K$ the gap remains finite upto slightly higher temperature. For strongly disordered samples ($T_c = 2.9K$ and 1.65K) the gap in the electronic spectra at the Fermi level persists all the way upto ~7K showing that it forms the pseudogap state and the corresponding $T^* \sim 7K$. Thus we observe that in presence of weak disorder gap closes exactly at $T_c$ while for strong disorder NbN forms a pseudogapped state above $T_c$.

Observation of pseudogapped state can be explained using phase fluctuation scenario. Superconducting order is characterized by complex order parameter given by $\Delta_0 e^{i\phi}$, where $\Delta_0$ is amplitude of the order parameter (which is proportional to the superconducting energy gap) and $\phi$ is the phase, which is same for the entire sample in the superconducting state. The loss of superconductivity can be because of either vanishing of this amplitude as described by mean field theories like BCS, or because of phase fluctuations which render $\phi$ random. Therefore the superconducting transition is governed by either $\Delta$ or $J$, depending on whichever is lower. In presence
Synopsis

of strong disorder we observe finite gap in the tunneling DOS showing non-vanishing of the amplitude of the order parameter. Therefore the transition is governed by the phase fluctuations. This is further confirmed in our recent penetration depth measurements\textsuperscript{8,22}. Extracting numerical estimate of $J$ from the penetration depth and coherence length, it was observed that for clean samples ($k_F l > 4$) $J \gg \Delta$, showing that phase fluctuations are not important and the superconducting transition happens because of amplitude going to zero. On the other hand, for strongly disordered samples ($k_F l \leq 4$) we observe that $J \leq \Delta$ showing the dominance of phase fluctuations to drive the superconducting transition.

Chapter 4. Emergence of inhomogeneity in the superconducting state of strongly disordered s-wave superconductor, NbN

As discussed in section 2.2, STS measurements give direct access to local density of states. Spatial inhomogeneity can be tracked by acquiring spatially resolved STS data. In this section we study the ground state superconducting properties of NbN through spatial resolved STS measurements. For spatially resolved spectroscopy

Figure 5: (a), (c), (e), (g) Temperature evolution of $G(V)/G_N(V)$ in the form of Colormap for four samples with increasing disorder. (b), (d), (f), (h) shows representative tunneling spectra at different temperatures.
Synopsis

Tunneling conductance was acquired at each location on a 32×32 grid over an area of 200×200 nm at the lowest temperature for films with various disorder levels. Fig. 6 shows the normalized tunneling spectra acquired at 500 mK along line for films of various disorder levels. We observe that with increasing disorder (1) Coherence peaks become progressively diffused, (2) Zero bias conductance value \(G_N(0)\) increases and (3) superconducting spectra becomes highly inhomogeneous.

4.1 Coherence peak height as a measure of local order parameter (OP)

We first concentrate on the nature of individual tunneling spectra. Fig. 7 shows two representative A-A corrected spectra recorded at 500 mK at two different locations on the sample with \(T_c = 2.9\) K. The two spectra show a common feature: a dip close to \(V = 0\) associated with superconducting energy gap, while they differ strongly in the coherence peak heights.

The density of states of a conventional clean superconductor, well described by the Bardeen-Cooper-Schrieffer (BCS) theory, is characterized by an energy gap \(\Delta\), corresponding to the pairing energy of the Cooper pairs and two...
sharp coherence peaks at the edge of the gap, associated with the long-range phase coherent superconducting state. This is quantitatively described by a single particle DOS of the form\(^{23}\),

\[
N_s(E) = \text{Re} \left( \frac{|E| + i\Gamma}{\sqrt{(|E| + i\Gamma)^2 - \Delta^2}} \right)
\]

where the additional parameter \(\Gamma\) phenomenologically takes into account broadening of the DOS due recombination of electron and hole-like quasiparticles. For Cooper pairs without phase coherence, it is theoretically expected that the coherence peaks will get suppressed whereas the gap will persist\(^{13}\). Therefore, we associate the two kinds of spectra with regions with coherent and incoherent Cooper pairs respectively\(^7\). The normalized tunneling spectra with well defined coherence peaks can be fitted well within the BCS-\(\Gamma\) formalism using eq. 1 and 3. Fig 8(a), 8(c) and 8(e) show the representative fits for the three different samples. In all the samples we observe \(\Delta\) to be dispersed between 0.8-1.0 meV corresponding to a mean value of \(2\Delta/k_BT_c \sim 12.7, 7.2\) and 6 (for \(T_c \sim 1.65\) K, 2.9 K and 3.5 K respectively) which is much larger than the value 3.52 expected from BCS theory\(^{19}\). Since \(\Delta\) is associated with the

**Figure 8** Pairing energy and the onset of the soft gap in representative spectra for three samples with \(T_c = 1.65\)K, 2.9K and 3.5K. (a), (c), (e) Normalized tunneling spectra (red) on three different sample exhibiting well defined coherence peaks. Black curves correspond to the BCS-\(\Gamma\) fits using the parameters shown in each panels. (b), (d), (f) Normalized tunneling spectra at a different location on the same samples as shown in (a)-(c) showing no coherence peaks; note that the onset of the soft gap in these spectra coincide with the coherence peak positions in (a)-(c).
pairing energy scale, the abnormally large value of $2\Delta/k_B T_c$ and the insensitivity of $\Delta$ on $T_c$ suggest that in the presence of strong disorder $T_c$ is not determined by $\Delta$. On the other hand, $\Delta$ seems to be related to $T^* \sim 7$-8 K which gives $\Delta/k_B T^* \sim 3.0 \pm 0.2$, closer to the BCS estimate. $\Gamma/\Delta$ is relatively large and shows a distinct increasing trend with increase in disorder. In contrast, spectra that do not display coherence peaks (Fig. 8(b), 8(d) and 8(f)) cannot be fitted using BCS-$\Gamma$ form for DOS. However, we note that the onset of the soft-gap in this kind of spectra happens at energies similar to the position of the coherence peaks, showing that the pairing energy is not significantly different between points with and without coherence.

Since the coherence peaks are directly associated with phase coherence of the Cooper pairs, the height of the coherence peaks provides a direct measure of the local superconducting order parameter. This is consistent with numerical Monte Carlo simulations\textsuperscript{13} of disordered superconductors using attractive Hubbard model with random on-site disorder which show that the coherence peak height in the LDOS is directly related to the local superconducting OP $\Delta_{\text{OP}}(R) = \langle c_R | c_R \rangle$. Consequently, we take the average of the coherence peak height ($\mathcal{h} = (\mathcal{h}_1 + \mathcal{h}_2)/2$) at positive and negative bias (with respect to the high bias background) as an experimental measure of the local superconducting OP (Fig. 7(a)).

### 4.2 Emergence of inhomogeneity in the superconducting state

To explore the emergence of inhomogeneity we plot in Fig. 9(a), 9(b) and 9(c) the spatial distribution of $\mathcal{h}$, measured at 500 mK in the form of intensity plots for three samples over 200 $\times$ 200 nm area. The plot shows large variation in $\mathcal{h}$ forming regions where the OP is finite (yellow-red) dispersed in a matrix where the OP is very small or completely suppressed (blue). The yellow-red regions form irregular shaped domains dispersed in the blue regions. The fraction of the blue regions progressively increases as disorder is increased. To analyse the spatial correlations we calculate the autocorrelation function (ACF), defined as,

$$\rho(\bar{x}) = \frac{1}{n(\sigma_h)^2} \sum_y (\mathcal{h}(\bar{y}) - \langle \mathcal{h} \rangle) (\mathcal{h}(\bar{y} - \bar{x}) - \langle \mathcal{h} \rangle)$$

where $n$ in the total number of pixels and $\sigma_h$ is the standard deviation in $\mathcal{h}$. The circular average of $\rho(\bar{x})$ is plotted as a function of $|\bar{x}|$ in Fig. 9(j) showing that the
Synopsis

Correlation length becomes longer as disorder is increased. The domain size progressively decreases with decrease in disorder and eventually disappears in the noise level for samples with $T_c \geq 6K$. From the length at which the ACF drops to the levels of the base line we estimate the domains sizes to be 50 nm, 30 nm and 20 nm for the samples with $T_c \sim 1.65 K$, 2.9 K and 3.5K respectively. The emergent nature of the superconducting domains is apparent when we compare structural inhomogeneity with the $h$-maps. While the defects resulting from Nb vacancies are homogeneously

Figure 9 (a)-(c) shows colormap of spatial evolution of $h$ for sample with $T_c = 1.65K$, 2.9K and 3.5K respectively, (d)-(f) show the corresponding colormap of ZBC ($G_N(V=0)$) and (g)-(i) show corresponding 2D histogram of $h$ and ZBC. Weak anticorrelation between $h$ maps and ZBC maps can be seen from the two maps and it is further evident from 2D histograms as we see the dense line with negative slope. The values of $T_c$ corresponding to each row for panels (a)-(i) are given on the left side of the figure. (j) Radial average of the 2-dimensional autocorrelation function plotted as a function of distance for the three samples.
distributed over atomic length scales, the domains formed by superconducting correlations over this disordered landscape is 2 orders of magnitude larger.

The domain patterns observed in h-maps is also visible in Fig. 9(d), 9(e) and 9(f) when we plot the maps of zero bias conductance (ZBC), $G_N(0)$, for the same samples. The ZBC maps show an inverse correlation with the h-maps: Regions where the superconducting OP is large have a smaller ZBC than places where the OP is suppressed. The cross-correlation between the h-map and ZBC map can be computed through the cross-correlator defined as,

$$I = \frac{1}{n} \sum_{i,j} \frac{(h(i,j) - \langle h \rangle)(ZBC(i,j) - \langle ZBC \rangle)}{\sigma_h \sigma_{ZBC}} \quad (6)$$

where $n$ is the total number of pixels and $\sigma_{zbc}$ is the standard deviations in the values of ZBC. A perfect correlation (anti-correlation) between the two images would correspond to $I = 1(-1)$. We obtain a cross-correlation, $I \approx -0.3$ showing that the anti-correlation is weak. Thus ZBC is possibly not governed by the local OP alone. This is also apparent in the 2-dimensional histograms of $h$ and ZBC (Fig. 9(g), 9(h) and 9(i)) which show a large scatter over a negative slope.

4.3 Universal scaling of the order parameter distribution

In this section we analyse the statistical properties of OP. For quantitative analysis we define the normalized local order parameter as,

$$S_i = \frac{h_i}{\text{Max}[h]} \quad (7)$$

Fig. 10(a) shows the order parameter ($S$) distribution (OPD) for four samples with $T_c = 1.65K$, 2.9K and 3.5K and 6.4K. We observe that for the sample with $T_c = 6.4K$ OPD peaks around $S = 0.4$. With increasing disorder this weight gradually shifts towards zero and also the OPD gets widen. This is the indication of gradual formation of regions where the superconducting OP is suppressed. We introduce the new scaling variable,

$$R_s = \frac{\ln S - \ln S_{typ}}{\sigma_S} \quad (8)$$

where $S_{typ} = \exp(\ln S)$ and $\sigma_S^2 = \ln^2 S - \ln S^2$. When plotted the probability distribution for rescaled OP (Fig. 10(b)) we see that rescaled OPD for all the samples
Synopsis

35
collapse onto a single curve showing
universality of the OPD The OPD is
also in good agreement with Tracy-
Widom distribution whose relevance
is recently discussed in connection
with directed polymer physics in
finite dimensions \textsuperscript{24,25}. We also
identify similar scaling relation of the
OPD within two prototype fermionic
and bosonic models for disordered
superconductors \textsuperscript{26} showing an
excellent agreement between
experiment and theory. Agreement
between theory and experiments also
confirms the correct identification of
the local OP.

4.4 Temperature evolution of the inhomogeneous superconducting state in NbN

In this section we will focus on temperature evolution of domain structure that
is seen at the lowest temperature as the system is driven across \( T_c \) into pseudogap state.
At high temperatures coherence peaks get diffused due to thermal broadening and the
\( h \)-maps can no longer be used as a reliable measure of the OP distribution. This problem
is however overcome by tracking the zero bias conductance (ZBC) value in the
tunneling spectra to track temperature evolution of domains based on our observation
of weak anticorrelation between \( h \) maps and ZBC maps at lowest temperature.

We investigated the temperature evolution of the domains as a function of
temperature for the sample with \( T_c \sim 2.9 \) K. The bulk pseudogap temperature was first
determined for this sample by measuring the tunneling spectra at 64 points along a 200
nm line at ten different temperatures. Fig.\textsuperscript{11}(a) shows the temperature evolution of the
normalized tunneling spectra along with temperature variation of resistance. In
principle, at the $T^*$, $G_N(V = 0) \approx G_N(V \gg \Delta/e)$. Since this cross-over point is difficult to uniquely determine within the noise levels of our measurements, we use $G_N(V = 0)/G_N(V = 3.5 \text{ mV}) \sim 0.95$ as a working definition for the $T^*$. Using this definition we obtain $T^* \sim 7.2 \text{ K}$ for this sample.

Spectroscopic maps were subsequently obtained at 6 different temperatures over the same area as the one in Fig. 9(e). Before acquiring the spectroscopic map we
corrected for the small drift using the topographic image, such that the maps were taken over the same area at every temperature. Fig. 11(b)-(g) show the ZBC maps as a function of temperature. Below $T_c$, the domain pattern does not show a significant change and for all points $G_N(V = 0)/G_N(V = 3.5mN) < 1$ showing that a soft gap is present everywhere. As the sample is heated across $T_c$ Most of these domains continue to survive at 3.6K across the superconducting transition. Barring few isolated points (< 5%) the soft gap in the spectrum persist even at this temperature. At 6.9K, which is very close to $T^*$, most of the domains have merged in the noise background, but the remnant of few domains, originally associated with a region with high OP is still visible. Thus the inhomogeneous superconducting state observed at low temperature disappears at $T^*$.

These observations provides a real space perspective on the formation of the pseudogap state through phase disordering. Below $T_c$ the coherent superconducting domains get Josephson coupled giving rise to the global zero resistance state. With increase in temperature thermal fluctuations cause this coupling to get weaker. At $T_c$ the weakest coupling is broken and the phase coherence between domains with finite superconducting OP get lost. However, superconducting correlations within domains continue to persist up to much higher temperature $T^*$ giving rise to the pseudogap state in tunnelling measurement.

Chapter 5. Summary

In this chapter we discuss the implication of our results on the nature of the superconducting transition. In a clean conventional superconductor the superconducting transition, well described through BCS theory, is governed by a single energy scale, $\Delta$, which represent the pairing energy of the Cooper pairs. Consequently, $T_c$ is given by the temperature where $\Delta \rightarrow 0$. This is indeed the case for NbN thin films in the clean limit. On the other hand in the strong disorder limit, the persistence of the gap in the single particle energy spectrum in the pseudogap state and the insensitivity of $\Delta$ on $T_c$ conclusively establishes that $\Delta$ is no longer the energy scale driving the superconducting transition. Indeed, the formation of an inhomogeneous superconducting state supports the notion that the superconducting state should be visualized as a disordered network of superconducting islands where global phase
coherence is established below $T_c$ through Josephson tunneling between superconducting islands. Consequently at $T_c$, the phase coherence would get destroyed through thermal phase fluctuations between the superconducting domains, while coherent and incoherent Cooper pairs would continue to survive as evidenced from the persistence of the domain structure and the soft gap in the tunneling spectrum at temperatures above $T_c$. Finally, at $T^*$ we reach the energy scale set by the pairing energy $\Delta$ where the domain structure and the soft gap disappears.

These measurements connect naturally to direct measurements of the superfluid phase stiffness ($J$) performed through low frequency penetration depth and high frequency complex conductivity ($\sigma = \sigma'(\omega) - i\sigma''(\omega)$) measurements on similar NbN samples. Low frequency measurements$^8$ reveal that in the same range of disorder where the pseudogap appears ($T_c \leq 6K$), $J(T\to 0)$ becomes a lower energy scale compared to $\Delta(0)$. High frequency microwave measurements$^{27}$ reveals that in the pseudogap regime the superfluid stiffness becomes strongly frequency dependent. While at low frequencies $J(\propto \omega \sigma''(\omega))$ becomes zero close to $T_c$ showing that the global phase coherent state is destroyed, at higher frequencies $J$ continues to remain finite up to a higher temperature, which coincides with $T^*$ in the limit of very high frequencies. Since at the probing length scale set by the electron diffusion length at microwave frequencies$^{27}$ is of the same order as the size of the domains observed in STS, finite $J$ at these frequencies implies that the phase stiffness continues to remains finite within the individual phase coherent domains. Similar results were also obtained from the microwave complex conductivity of strongly disordered InO$_x$ thin films$^{28}$.

In summary, we have demonstrated the emergence of an inhomogeneous superconducting state, consisting of domains made of phase coherent and incoherent Cooper pairs in homogeneously disordered NbN thin films. The domains are observed both in the local variation of coherence peak heights as well as in the ZBC which show a weak inverse correlation with respect to each other. The origin of a finite ZBC at low temperatures as well as this inverse correlation is not understood at present and should form the basis for future theoretical investigations close to the SIT. However, the persistence of these domains above $T_c$ and subsequent disappearance only close to $T^*$ provide a real space perspective on the nature of the superconducting transition, which is expected to happen through thermal phase fluctuations between the phase coherent
domains, even when the pairing interaction remains finite. However, an understanding of the explicit connection between this inhomogeneous state and percolative transport for the temperature above and below $T_c$ is currently incomplete and its formulation would further enrich our understanding of the superconducting transition in strongly disordered superconductors.

We finally summarize the evolution of various energy scales as a function of disorder for NbN. Superfluid stiffness $J$ was measured using two coil mutual inductance technique and converted to temperature scale using $J/k_B$. $T_c^{BCS}$ is obtained using the BCS relation,

$$T_c^{BCS} = \frac{\Delta(0)}{1.76k_B} \quad (9)$$

where $\Delta(0)$ is ground state superconducting energy gap obtained by fitting tunneling spectra using DOS given by equation (4). It is instructive to note that in the range of disorder where pseudogap appears, $T_c^{BCS}$ is close to $T^*$ as expected from BCS theory. In the same range of disorder $J/k_B$ is smaller than $T_c^{BCS}$ showing that the superconducting transition is governed by phase fluctuations.
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Chapter 1

Introduction

The phenomenon of superconductivity was discovered by Heike Kamerlingh Onnes in 1911 where he observed a sudden drop to zero in the resistivity of Mercury, to an experimental error, at 4.2K. Soon after, many more materials such as aluminium, lead, tin etc. showed the superconductivity on cooling. The temperature below which material turns superconducting is called as critical temperature ($T_c$). In 1933 it was found by Walter Meissner and Robert Ochsenfeld that superconductor expels the weak external applied magnetic field from entering into the bulk. The expulsion of magnetic field would not take place in perfect conductor of free electrons, showing that the superconductor is more than just perfect conductor.

Since the discovery of superconductivity, theorists struggled for several decades to understand the origin of superconductivity although major advances made through phenomenological theories mainly by London in 1935 and Ginzburg-Landau

![Figure 1-1 Basic requirements of superconductivity: (a) Zero resistance state below 4.2K as discovered by Kamerlingh Onnes in 1911, (b) Meissner-Ochsenfeld effect showing expulsion of magnetic field below critical temperature](image-url)
in 1950. It is John Bardeen, Leon Neil Cooper, and John Robert Schrieffer (BCS) who first gave the microscopic theory of superconductivity in 1957. The basic idea in the BCS theory is that in the superconducting state electrons pair through phonon coupling and these pairs, called as Cooper pairs, condense into a single phase coherent ground state which allows the electrons to move without scattering.

For the obvious technological reasons search for the new materials which could superconduct at higher temperatures continued and in 1986 Alex Müller and Karl Bednorz discovered a new class of superconductor known as the doped rare earth cuprates. These materials become superconducting above 30K. In following years a host of new material were found which superconduct at temperatures much higher than the boiling point of liquid N\textsubscript{2}. These new class of materials are called as high temperature superconductors (HTSC). Not much progress is made in understanding the origin of HTSC although there are theories which qualitatively explain the possible mechanism of pairing and symmetry of the gap.

While the quest for new materials continued, there have been also the investigations by some researchers on the effect of disorder on superconducting properties of the material. The problem gives a unique opportunity to study the competition between superconductivity which results from pairing and the pair breaking effects of electron localization and disorder induced Coulomb repulsion. The interest in the field was further increased by the possibility that the disorder driven or magnetic field driven suppression of superconductivity in the limit of zero temperature might be a quantum phase transition.

In this thesis we study the effect of disorder on superconducting properties of s-wave superconductor, NbN, close to metal insulator transition. The study was mainly carried out using home built low temperature Scanning Tunneling Microscopes (STM). The plan of the introduction chapter is as follows. In the first section I will describe the basics of superconductivity and essential concept required to make platform for our study. I will then review the experimental and theoretical advances in the field of disorder/ magnetic field driven superconductor insulator transition (SIT). I will finally introduce to our model system NbN and its characterization through transport measurements and transmission electron microscopy (TEM).
1.1 Basics of Superconductivity

1.1.A The Meissner-Ochsenfeld effect

When a superconductor is cooled below its $T_c$ and kept in a weak external magnetic field then it expels the magnetic flux lines from entering into the bulk so that the field inside a superconductor is zero ($B = 0$). This phenomenon is called as Meissner-Ochsenfeld effect. Although superconductors show the perfect diamagnetism at low fields, strong magnetic fields destroy the superconductivity. The field at which superconductivity breaks down is called as the critical field ($B_c$).

1.1.B The London equations

The phenomenological theory developed by London brothers in 1935 explains the perfect conductivity as well as the Meissner effect where they showed that the superconductor produces screening current at the surface which shields the external magnetic field from entering into the bulk. The two equation governing electromagnetic fields inside a superconductor are,

$$\frac{\partial J_s}{\partial t} = \frac{e^2 n_s}{m} E$$  \hspace{1cm} (1.1)

$$\nabla \times j_s = -\frac{e^2 n_s}{mc} B$$  \hspace{1cm} (1.2)

The first equation essentially explains the perfect conductivity through the free acceleration of charge. Using the identities in vector calculus and Amperes law one can deduce the second equation to,

$$\nabla^2 B = \frac{1}{\lambda_L^2} B$$  \hspace{1cm} (1.3)

Where $\lambda_L$ is called as London penetration depth and is defined as,

$$\lambda_L = \sqrt{\frac{mc^2}{4\pi e^2 n_s}}$$  \hspace{1cm} (1.4)

One can immediately see that on application of magnetic field $B = B_{ap} \hat{y}$ to semi-infinite superconductor (Figure 1-2), the magnetic field inside the superconductor is given by
Figure 1-2 The boundary between superconductor and magnetic field. Blue curve inside the superconductor shows exponential fall characterized by London penetration depth $\lambda_L$. Orange curve show the dependence of the current density with distance inside the superconductor.

$$B(x) = B_{apl} \hat{y} e^{-x/\lambda_L} \quad \text{for } x \geq 0 \quad (1.5)$$

i.e. the magnetic field inside the superconductor decreases exponentially and in the bulk we find $B \to 0$, hence the Meissner effect. Also from the second London equation (Equ. 1.2) along with equation of continuity ($\nabla \cdot j_s = 0$) it follows that,

$$j_s(x) = -\frac{e}{4\pi\lambda_L} B_{apl} \hat{z} e^{-x/\lambda_L} \quad \text{for } x \geq 0 \quad (1.6)$$

Thus the supercurrents flow in the direction parallel to the surface and perpendicular to $B$ and decrease into the bulk over the same scale $\lambda_L$.

1.1.C Nonlocal Response: Pippard Coherence length ($\xi_0$)

The nonlocal generalization of the London equations was proposed by Pippard\(^2\). He argued that the superconducting wavefunction has a characteristic dimension $\xi$. Superconducting properties such as superfluid density changes over the length scale of $\xi$ which can be estimated using uncertainty principle and is given by,
\[ \zeta = \alpha \frac{\hbar v_F}{k_B T_c} \quad (1.7) \]

Where \( \alpha \) is a numeric constant of the order of unity. BCS theory predicts that the value of \( \alpha \approx 0.18 \). It also has a physical significance in BCS theory that it represents the size of the Cooper pairs.

### 1.1.1. D Ginzburg Landau (G-L) model of superconductivity

The phenomenological theory of superconductivity was introduced by Ginzburg and Landau\(^3\) in 1950 which describes superconducting phase transition within Landau’s general theory of second order phase transition. They introduced a complex pseudo-wave function \( \psi = |\psi|e^{i \varphi} \) as an order parameter to describe superconducting electrons.

G-L equation can be obtained using the variational principle to minimize the free energy and it has the form analogous to Schrodinger’s equation,

\[
\frac{1}{2m^*} \left( \frac{\hbar}{i} \nabla - \frac{e^*}{c} A \right)^2 \psi + \beta |\psi|^2 \psi = -\alpha(T) \psi \quad (1.8)
\]

The corresponding equation for supercurrent is,

\[
J_s = e^* \frac{\hbar}{2m^*} (\psi^* \nabla \psi - \psi \nabla \psi^*) - \frac{e^*}{m^* c} |\psi|^2 A \quad (1.9)
\]

With \( \psi = |\psi|e^{i \varphi} \) and using equ. 1.8 we can get the equation for supercurrent velocity as,

\[
\nu_s = \frac{\hbar}{2m^*} \left( \nabla \varphi - \frac{2e}{\hbar c} A \right) \quad (1.10)
\]

It can be shown that G-L order parameter can be related to local density of superelectrons as,

\[
n_s^* = |\psi(x)|^2 = -\frac{\alpha}{\beta} \quad (1.11)
\]
• **Phase stiffness**

Bulk superconducting ground state is described by a constant order parameter, $\psi$, where the phase of the order parameter, $\varphi$, has a constant value everywhere. There is an energy cost associated with changing $\varphi$ from one part of the superconductor to another. This energy cost is called as phase stiffness or superfluid stiffness and denoted as $J$. From equ. 1.10, the velocity of the superfluid is given by,

$$v_s = \frac{\hbar}{2m}(\nabla \varphi) \quad (1.12)$$

Now the increase in kinetic energy by phase twist is given by $n_s \int d^3r \left(\frac{1}{2}mv_s^2\right) = \frac{1}{2}\frac{\hbar^2}{4m} \int d^3r(\nabla \varphi)^2$. In analogy with XY model\textsuperscript{4,5} in statistical physics we define $J$ over the cut-off distance $a$ as\textsuperscript{6,7},

$$J = \frac{\hbar^2 n_s a}{4m} \quad (1.13)$$

For all our analysis we take the minimum cut-off distance $a$ equal to coherence length $\xi$ as it is a characteristic length scale over which the superconducting parameters changes. It is important to note that $J \propto n_s$ which is related to $\lambda_L$ (equ. 1.4) which is experimentally measureable quantity.

• **G-L Characteristic length scales**

Solving G-L equation at the interface of superconductor introduces a characteristic length called as G-L coherence length given by $\xi = \left(\frac{\hbar^2}{4m^*|\alpha(T)|}\right)^{1/2}$ and it is the measure of the distance over which order parameter respond to a perturbation. To the first order approximation in $\alpha$, it can be written as, $\xi(T) = \xi(0)|t|^{-1/2}$, where $t = \frac{T_c - T}{T_c}$.

Also the London penetration depth can be written as,

$$\lambda = \sqrt{\frac{mc^2}{4\pi e^2 n_s}} = \sqrt{\frac{mc^2}{8\pi e^2 \left(-\frac{\alpha}{\beta}\right)}} \quad (1.14)$$
The ratio $\kappa = \frac{\xi}{\lambda}$ is called as G-L parameter is an important parameter and is independent of temperature within G-L theory.

- **Type I and Type II superconductors**

The superconductors with G-L parameter $\kappa < \frac{1}{\sqrt{2}}$ are called as Type-I superconductors. These materials show a perfect diamagnetism at all fields below a critical field $H_c$ where the superconductivity is completely destroyed. Most elemental superconductors are Type-I superconductors. In 1957 Abrikosov\(^8\) showed that for superconductors with $\kappa > \frac{1}{\sqrt{2}}$, there exist an equilibrium state in presence of magnetic field where the field lines penetrate the superconductors to form vortices. These materials are called as Type-II superconductors. Vortices in Type-II superconductors are formed above the lower critical field $H_{c1}$ and there is continuous increase in the flux penetration till the upper critical field $H_{c2}$ where the superconductivity is completely destroyed.

These vortices in Type-II superconductors form a triangular lattice\(^9\) and each vortex contains exactly one quantum of flux, $\Phi_0 = \hbar/2e = 2.07 \times 10^{-15}$ Wb. The nearest neighbour distance for the vortex lattice is given by,

$$a_\Delta = 1.075 \left( \frac{\Phi_0}{B} \right)^{1/2}$$  \hspace{1cm} (1.15)

Figure 1-3(a) shows the contour diagram for $|\psi|^2$ in presence of magnetic field for

Figure 1-3 Abrikosov Flux lattice: (a) theoretically calculated contour diagram of $|\psi|^2$ just below the upper critical field (b) triangular lattice of flux lines on the surface of Pb. The black dots are cobalt particles.
type-II superconductor. Figure 1-3(b) shows the results of first experiment to visualize the vortex lattice\textsuperscript{10}.

### 1.1. E BCS theory of superconductivity

Microscopic theory of superconductivity given by Bardeen, Cooper and Schrieffer\textsuperscript{11} (BCS) in 1957 explains the superconductivity in many metals and predicts many properties. The idea behind the theory is that ground state of free electrons is unstable against the small attractive interaction between electrons\textsuperscript{12}, no matter how small is the interaction and the electrons pair to form bound state. The attractive interaction between the electrons is provided by electron phonon exchange which can be understood as follows: an electron with negative charge \(-e\) attracts the positively charged ions as it moves in the crystal and the lattice distortion locally induces excessive positive charge. This positive charge is in turn attracts another electron forming a bound state with the first one. The cartoon picture showing the phonon mediated attraction is as shown in Figure 1-4.

![Cartoon picture of Cooper pair, pair of electrons with equal and opposite momenta.](image)

Cooper showed in that the bound state energy of the electron pair with equal and opposite momenta and spin is given by,

\[
\varepsilon = -2\hbar \omega_D e^{-(2/N(0)V)} \tag{1.16}
\]
where $\omega_D$ is the cut-off frequency corresponding to the Debye temperature. Next we will briefly review the BCS theory.\(^\text{11}\)

BCS took the form for the ground state as,

$$|\psi_G\rangle = \prod_{k=k_1,...k_M} (u_k + v_k c_{k\uparrow} c_{-k\downarrow}) |\phi_0\rangle$$

Where $|u_k|^2 + |v_k|^2 = 1$ and $|\phi_0\rangle$ is the vacuum state. Coefficients $u_k$ and $u_k$ are chosen so as to minimize the expectation value of the energy using the so called reduced Hamiltonian,

$$\mathcal{H} = \sum_{k\sigma} \epsilon_k n_{k\sigma} + \sum_{kl} V_{kl} c_{k\uparrow} c_{-k\downarrow} c_{l\downarrow} c_{-l\uparrow}$$

(1.17)

BCS assumed the simple form for the attractive interaction $V_{kl}$ as,

$$V_{kl} = \begin{cases} -V, & |\xi_k| \text{ and } |\xi_l| \leq \hbar \omega_D \\ 0, & \text{Otherwise} \end{cases}$$

(1.18)

Where $\xi_k$ is the single particle energy of the electrons with respect to Fermi energy. Following are the important key results of BCS theory,

- **The gap function**

$$\Delta(0) = 2\hbar \omega_D e^{-1/N(0)V}$$

(1.19)

Where $\Delta$ is the superconducting energy gap formed at the Fermi level and $N(0)$ is Fermi level density of states.

- **Temperature dependence of the gap and $T_c$**

Temperature dependence of the gap can be numerically calculated using,

$$\frac{1}{N(0)V} = \int_0^{\hbar \omega_D} \frac{\text{tanh} \frac{1}{2} \beta (\xi^2 + \Delta^2)^{1/2}}{(\xi^2 + \Delta^2)^{1/2}} d\xi$$

(1.20)

where $\beta = (k_B T)^{-1}$. Figure 1-5 shows the temperature dependence of $\Delta$ which holds in good approximation for most of the conventional superconductors.
The critical temperature is the temperature at which $\Delta(T) \to 0$. Thus the integral 1.16 can be evaluated by substituting $\Delta = 0$ and it yields,

$$k_B T_c = 1.13 \hbar \omega_D e^{-1/N(0)}$$

(1.21)

Comparing with Equ. 1.15 we get,

$$\Delta(0) = 1.764 k_B T_c$$

(1.22)

![Figure 1-5. Temperature dependence of energy gap within BCS theory.](image)

- **BCS density of states**

  The quasiparticles excitation energy $E_k$ within BCS theory is given by $E_k^2 = \Delta^2 + \xi_k^2$ which shows the minimum excitation to be $\Delta$, i.e. there is a gap in the energy spectrum. The single particle density of states (DOS) is given by,

$$\frac{N_s(E)}{N(0)} = \frac{d\xi}{dE} = \begin{cases} \frac{E}{\sqrt{E^2 - \Delta^2}}, & E > \Delta \\ 0, & E < \Delta \end{cases}$$

(1.23)
1.1.F Electron tunneling and measurement of $\Delta$

In 1960 Giaever$^{13}$ introduced a method to measure the $\Delta$ for the superconductor based on the principle of quantum mechanical tunneling. The measurements involves tunnel junction which consists of a normal metal and a superconductor separated by very thin insulating layer. The tunneling current between normal metal and a superconductor is given by,

$$I_{ns} = \frac{G_{nm}}{e} \int_{-\infty}^{\infty} \frac{N_{2s}(E)}{N_2(0)} \left[ f(E) - f(E + eV) \right] dE$$  \hspace{1cm} (1.24)

Where $N_{2s}(E)$ is the BCS density of states and $f$ is the Fermi function. More direct comparison between theory and experiments can be made through the tunneling differential conductance,

$$G_{ns} = \frac{dI_{ns}}{dV} = G_{nn} \int_{-\infty}^{\infty} \frac{N_{2s}(E)}{N_2(0)} \left[ -\frac{\partial f(E + eV)}{\partial eV} \right] dE$$  \hspace{1cm} (1.25)

It can be seen that as $kT \to 0$ the tunneling conductance mimics the density of states for the superconductors,
\[ G_{ns} \bigg|_{T=0} = G_{nn} \frac{N_{2s}(e|V|)}{N_2(0)} \]  

(1.26)

Figure 1-7(a) shows the tunneling differential conductance spectra plotted as a function of \( V \) for the NbN-oxide-Ag tunnel junction at various temperatures. Solid lines shows the fits using BCS density of states (Equ. 1.18) with additional broadening parameter \( \Gamma \) which takes into account the additional broadening due to finite lifetime of the superconducting quasiparticles.

\[ N_s(E) = Re \left( \frac{|E| + i\Gamma}{\sqrt{(|E| + i\Gamma)^2 - \Delta^2}} \right) \]  

(1.27)

Figure 1-7(b) shows the temperature evolution of \( \Delta \) and \( \Gamma \) plotted along with resistivity Vs temperature curve.

**Figure 1-7.** Tunneling measurements on NbN/oxide/Ag planar tunnel junction with \( T_c = 14.9K \). (a) \( G(V) \)-V spectra at different temperatures along with the BCS-\( \Gamma \) fits, (b) Temperature dependence of \( \Delta \), \( \Gamma \) and \( \rho \).

### 1.2 Disordered Superconductors

The interplay of superconductivity and disorder is one of the most intriguing problems of quantum many body physics. Superconducting pairing interactions in a normal metal drives the systems into a phase coherent state with zero electrical resistance. In contrast, in a normal metal increasing disorder progressively increases the resistance through disorder scattering eventually giving rise to an insulator at high disorder where all electronic states are localized. Quite early on, it was argued by Anderson that since BCS superconductors respect time reversal symmetry,
superconductivity is robust against nonmagnetic impurities and the critical temperature $T_c$ is not affected by such disorder. Anderson’s idea however applies only to weakly disordered systems, with their extended electronic states. In presence of strong disorder experiments showed that it reduces $T_c$ and ultimately drives the system into an insulator\cite{17,18,19,20}. This suppression of superconductivity could be thickness driven\cite{21,22,23}, magnetic field driven\cite{24} or disorder driven\cite{25,26}. Various other novel phenomena are observed in the vicinity of superconductor insulator transition (SIT). The two key observations are (i) persistence of finite superconducting correlations above $T_c$ through measurements of finite high $J$ stiffness above $T_c$ in amorphous InO$_x$ films\cite{27,28}, finite spectral gap at zero bias in the conductance spectra much above $T_c$ in scanning tunneling microscope (STM) experiments\cite{29,30,31} etc., and (ii) presence of superconducting correlations/ Cooper pairing through the measurements of activated temperature dependence of resistance on the insulating side\cite{32}, the giant peak in the magnetoresistance in thin films\cite{33,34,35}, magnetic flux quantization in nano-honeycomb patterned insulating thin films of Bi\cite{36}, a more recent transport\cite{37,38} and tunneling experiments\cite{39}.

Although the complete theoretical understanding of the nature of SIT is lacking, in recent times numerous theoretical and numerical advances have been made. It is shown that in the intermediate disorder limit the effect of disorder is to decrease the pairing amplitude\cite{40,41} through an increase in the electron-electron ($e$-$e$) Coulomb repulsion which results in decrease in $T_c$. In presence of strong disorder experimental observations are understood qualitatively through number of prototype models of disordered superconductors which are based on either fermionic\cite{42,43,44,45,46} or bosonic\cite{47,48,49} description. The fermionic models demonstrated the survival spectral gap across SIT and the transition is driven by phase fluctuation between superconducting islands. Bosonic models indicated that the SIT is driven by quantum phase fluctuations between localized Cooper pairs.

In particular here I would like to highlight on the recent numerical simulations which have direct relevance to the work presented in this thesis. These simulations involve solving Attractive (negative-$U$) Hubbard model with random on-site energy\cite{43,50,45}. While these studies ignore Coulomb interactions and are done on relatively small systems compared to real superconductors, they nevertheless support
key aspects of the basic scenario of the disordered superconductors namely (i) Single particle spectral gap in the DOS at lowest temperature survives through SIT and is finite everywhere though it is highly inhomogeneous. However $J$, decreases rapidly with increasing disorder making the system more susceptible to phase fluctuations. (ii) Coherence peak heights at the gap edge are directly correlated to the local superconducting order and vanish with increasing temperature and disorder. (iii) Near SIT, pseudogap appears in the DOS at low energies above $T_c$ and also on the insulating side. These results are indeed in good agreement with our results on disordered NbN presented in this thesis.

In spite of the fact that the field of disordered superconductors has produced variety of novel phenomena and interesting theoretical results which has enriched our understanding of SIT to a great extent, more experimental works are needed for complete understanding and resolving the open questions in the field. More specifically, in regard of theoretical propositions, suggesting the emergence novel phenomena beyond the ambit of BCS theory, there is very little direct experimental evidence confirming the predictions made. In this thesis we address most of the experimental remedies through our investigation on NbN which can be grown with larger atomic defects by tweaking growth parameters.

### 1.3 Our model system: NbN

For our investigation we use NbN as a model system to study the effect of disorder. NbN is a conventional s-wave superconductor with optimum $T_c \sim 17$K. Bulk NbN has the $\lambda$ of $\sim 250$ nm, electronic mean free of $l \sim 4$nm and the $\xi \sim 5$nm. It has face centred cubic structure similar to NaCl. Band structure calculations show that Fermi level lies within the 4d band and these electrons contribute to the conduction.

#### 1.3.A Sample growth and introducing disorder

Epitaxial thin films of NbN are grown using reactive DC magnetron sputtering in Ar+N$_2$ gas mixture on (100) oriented single crystalline MgO substrate which is heated to 600$^\circ$C. The optimum conditions to get the highest $T_c$ of 17K are sputtering power =200W, Ar:N$_2$ ratio = 84:16. The disorder in the system is tuned by varying deposition conditions: either by decreasing the sputtering power keeping the partial gas pressures constant or by increasing the N$_2$ partial pressure$^{51,52}$. In both these cases Nb
flux relative to N₂ in the plasma is reduced which results in the Nb vacancies in the crystal hence the disorder. For our study all the films are deposited with thickness ≥ 50nm which is much larger than the dirty limit coherence length $\xi \sim 5$-8 nm⁵³ and can be considered to be 3D as far as superconducting correlations are concerned.

### 1.3.B Structural characterization of NbN films

X-ray diffraction (XRD) study on films grown using above method show the formation of crystalline NbN on MgO substrates.⁵⁴ All our films show high degree of epitaxy as seen from the $\phi$-scans using a four circle goniometer. This is further confirmed directly through the high resolution transmission electron microscope (HRTEM). Figure 1-8(a) and (b) show HRTEM images probed at the interface of MgO

Figure 1-8 TEM images (a), (b) High resolution TEM images for two samples with $T_c \sim 16K$ and 2.5K at the interface of NbN-MgO. (c), (d) corresponding high resolution scanning TEM images.

substrate and NbN film along <110> direction for the two samples with $T_c \sim 16K$ and 2.5K respectively. The difference between two samples at the atomic scale is revealed
in Figure 1-8(c) and (d) which shows the high resolution scanning transmission (HRSTEM) images for same samples respectively. Intensity in the HRSTEM image is primarily contributed by Nb and is proportional to the number of Nb atoms in the probing column. Smooth intensity variation in clean sample ($T_c \sim 16$K) shows the overall thickness variation produced during ion beam milling while the disordered sample ($T_c \sim 2.5$K) shows random distribution of intensity in the columns showing random number of Nb atoms in the adjacent columns. This clearly shows that for the disordered films, the lattice contains Nb vacancies but when probed at the large scale it is homogeneous. Thus we have an ideal system in which disorder is present at the atomic length scale and the disorder is homogeneous over entire film.

1.3.C Quantification of disorder

To quantify disorder we use the Ioffe Regel parameter $k_F l$ which is the measure of mean free path $l$ in units of de-Broglie wavelength ($\lambda_F$). In clean system $l \gg \lambda_F$ and therefore $k_F l$ has a large value. With increasing disorder $l$ decreases steadily due to disorder scattering and therefore the quantity $k_F l$ also decreases. At $k_F l \leq 1$ all the bloch states are completely localized which corresponds to Anderson metal insulator transition (MIT). $k_F l$ values are extracted from resistivity and Hall measurements and calculated using free electron formula,

$$k_F l = \frac{(3\pi^2)^{2/3} \hbar [R_H(285K)]^{1/3}}{\rho(285K) e^{5/3}}$$

(1.28)

Here $R_H = -\frac{1}{ne}$ assumes absence of e-e interaction which is not the case for our disordered samples. Therefore we calculate $k_F l$ at highest temperature of our measurements (i.e. at 285K) where the effects of interaction is believed to be smaller. $k_F l$ in our samples ranges from 10 ($T_c = 16$K) to all the way down to 0.42 ($T_c < 300$mK) and we observe that $k_F l \sim 1$ is the critical disorder where superconductivity is completely destroyed.

1.4 Effects of disorder

In this section we will review our recent work on disordered NbN through the transport and $\lambda$ measurements.
1.4.A Resistivity and measurement of $T_c$

Figure 1-9(a) shows resistivity Vs temperature curves ($\rho - T$) for full range of disorder. The inset of Figure 1-9(a) shows the expanded view of $\rho - T$ in the transition region. Figure 1-9(b) shows the plot of $T_c$ values with increasing disorder, $T_c$ being the temperature at which resistivity becomes 1% of its normal state value. Here we see that $T_c \to 0$ as $k_F l \to 0$. Most disordered samples with $k_F l < 1$ do not show superconducting downturn all the way down to 300mK. For these samples $T_c$ is taken as 300mK. From $\rho - T$ curves we observe that except the least disordered sample with $k_F l = 10.12$, all the samples show negative temperature coefficient which gets more and more pronounced with increasing disorder.

Figure 1-9. (a) $\rho - T$ for NbN films with different $k_F l$, the inset shows the expanded view in the transition region. (b) Variation of $T_c$ with $k_F l$, (c) Conductivity $\sigma - T$ at low temperature for the three samples with $k_F l = 0.82$, 0.49 and 0.42. Extrapolations to $\sigma$ as $T \to 0$ are shown with lines of different colour.
Figure 1-9(c) shows the conductivity Vs temperature $\sigma - T$ curves for three most disordered samples with $k_Fl < 1$. When extrapolated as $T \to 0$ the $\sigma$ has finite value which implies that our most disordered samples are not insulators but are bad metals. Conventionally $k_Fl = 1$ is associated with Anderson metal insulator transition. The inconsistency between $k_Fl$ values and the observed metallic behaviour shows that in presence of strong $e-e$ interaction free electronic theory cannot be applied to measure accurately $k_Fl$ values.

1.4.B Hall carrier density measurement

Carrier density ($n$) for the samples with various disorder is obtained by Hall resistance measurement. Figure 1-10(a) shows $\rho_{xy}$ plotted as a function of applied magnetic field. Carrier density $n$ is given by $n = -1/R_H e$ where $R_H$, the Hall coefficient is extracted from the slope of $\rho_{xy} - H$ curves. Above relation for $n$ is valid only in the absence of $e-e$ interactions therefore $n$ is determined at 285K following argument from section x. The measured carrier density for the stoichiometric NbN with $T_c \sim 16$K is in good agreement with the band structure calculations. Figure 1-10(b) shows the $n(285K)$ for films with increasing disorder.

Figure 1-10. Hall measurements, (a) $\rho_{xy} - H$ measured at 285K for samples with different $k_Fl$. (b) carrier density $n$ extracted from $\rho_{xy}$ and plotted as function of $k_Fl$. 
1.4.C Upper critical field \((H_{c2})\) and coherence length \((\xi_{GL})\)

Figure 1-11 shows experimentally measured \(H_{c2}\) and \(\xi\) for samples with varying levels of disorder. We observe the non-monotonic behaviour in these quantities with increasing disorder which can be explained by noting the competition between BCS coherence length \((\xi_{BCS} = \hbar v_F / \pi \Delta, v_F\) being Fermi velocity) and \(l\) which are related as \(\xi_{GL} = \sqrt{\xi_{BCS} l}\). In the low disorder regime \(\xi_{BCS}\) does not change much but \(l\) rapidly decreases hence \(\xi_{GL}\) also decreases. However in strong disorder regime \(\xi_{BCS}\) increases rapidly which explains the increase in \(\xi_{GL}\) and hence decrease in \(H_{c2}\).

![Figure 1-11. \(H_{c2}(0)\) and \(\xi_{GL}\) as a function of \(k_F l\). These two parameters show the non-monotonic behaviour with increasing disorder.](image)

1.4.D Magnetic penetration depth (\(\lambda\))

\(\lambda\) was measured for various levels of disorder using two coil mutual inductance technique operating at 60 kHz. This technique operates on the principle that the thin superconducting film will partially shield the secondary coil from the magnetic field produced by the primary, the degree of shielding being dependent on \(\lambda\). The detailed experimental methods are given in ref. 57. Figure 1-12(a) shows \(\lambda\) measured at the lowest temperature for films with various disorder levels. \(\lambda(0)\) for the least disordered sample is 250nm which is much larger than \(\xi_{GL}\) which is \(\sim\) 5nm, thus NbN is a type II superconductor.
Figure 1-12(b) shows corresponding $\lambda^2(0)$ which is proportional to the $J$. It is evident from the plot that as disorder increases $J$ decreases rapidly making it susceptible to phase fluctuations.

![Graphs showing penetration depth and inverse square of penetration depth as functions of $T_c$.](image)

Figure 1-12 Penetration depth measurements, (a) measured magnetic penetration depth ($\lambda$) for films with different $T_c$, (b) inverse square of $\lambda$ from panel (a), which is proportional to superfluid stiffness plotted as a function of $T_c$.

### 1.5 References


Chapter 1. Introduction


Chapter 1. Introduction


Chapter 2

Scanning tunneling microscope

The Scanning Tunneling Microscope (STM) invented in 1983 by Binnig and Rohrer\textsuperscript{1,2,3} at IBM Zurich has been proven to be the most important tool for surface investigations. The first experiment showing atomically resolved Si(111) which confirmed $7 \times 7$ surface reconstruction\textsuperscript{4} and later experiments demonstrated the unsurpassed spatial power of STM. Using the combination of scanning tunneling microscopy and scanning tunneling spectroscopy (STS), number of interesting experiments have been carried demonstrating the capability of the instrument. These include building structures at the atomic level using the technique of atom manipulation\textsuperscript{5}, visualising standing wave pattern formed by electron surface states in an artificial quantum corral\textsuperscript{6,7}, first direct evidence of Kondo resonance at the magnetic impurity on metal surface\textsuperscript{8}, spectroscopic mapping of vortex core in Abrikosov lattice in Type-II superconductors\textsuperscript{9} etc.

Spatially resolved spectroscopy measurements performed at the atomic scale has provided the excellent insight into the physics of strongly correlated electron systems, especially high temperature cuprate superconductors. Other related techniques include spin polarized scanning tunneling microscope\textsuperscript{10} (SP-STM) which is powerful tool to determine spin texture of the surface at the atomic level. Recently combination of STM and non-contact atomic force microscopy (nc-AFM) has provided the unprecedented spatial resolution\textsuperscript{11,12} along with spectroscopic information which enabled imaging of single molecules and real space evolution of organic reactions. In this chapter I will summarize the operating principles of STM and STS and then describe the development and characterization of low temperature, high vacuum scanning tunneling microscope (LT-STM).
2.1 Schematic of STM

Scanning tunneling microscope essentially consists of a very sharp metal tip which is brought very close to the sample under investigation (< 10 Å) so that there is an overlap between the tip and sample wavefunctions. If the bias voltage is applied to the sample, electrons tunnel from tip to sample or vice versa which establish a very small tunneling current of the order of nano-ampere range (typically from 10pA to few nA) which can be measured using current preamp. The tunneling current exponentially depends on the tip-sample separation $d$,

$$I \propto e^{-\kappa d} \quad (2.1)$$

Figure 2-1 shows the schematic view of the simplest design for STM. Essentially the STM consist of following components,

![Diagram of STM components](image)

**Figure 2-1. Schematic of typical Scanning tunneling Microscope. It essentially consists of (a) tip, (b) Scanning unit made of coarse positioner and piezo tube, (c) Sample, (d) Preamp for measuring tunneling current, (e) Control electronics which controls piezo motion and communicate with computer and (f) display unit.**
1) Piezo electric scanning unit which bears the tip at the end and consist of (a) coarse positioner which brings the tip sample separation to within tunneling regime, (b) Piezoelectric tube which fine controls the vertical (Z) and lateral (X, Y) movement of the tip.

2) Vibration isolation stage (not shown in the Figure) which eliminates the vibrations coming from the ground.

3) Control electronics which controls the motion of piezo tube with feedback and drives the coarse positioner. The controller also communicates with the computer to change the experimental settings such as bias voltage, tunneling current set point scanning speed, scanning range, the gains of feedback loop etc., and sends the feedback signal and tunneling current signal to generate topographic images and tunneling spectra.

The tunneling process is initiated by bringing the tip close to the sample within few angstrom from the sample surface using suitable approach method. Once the tip is in tunneling region the feedback loop takes over and the current is maintained to its set value by moving the tip in Z direction. Figure 2-2 shows the cartoon diagram illustrating the two modes to get the topographic image as described below.

![Figure 2-2. Modes of operation for topographic imaging. In constant height mode z is fixed and current is recorded. In constant current mode z is varied to keep current constant using a feedback loop](image)

**2.1.A Constant current mode**

In this mode the current is kept constant using the feedback loop throughout the image acquisition. During the image scanning the output of the feedback loop to Z
electrode of the piezo tube are transformed to get the vertical position as a function of lateral position \( Z(X, Y) \). Corrugation amplitude is defined as difference between smallest and largest tip sample-distance in constant current image. Since the tunneling current exponentially depends on the separation between tip and sample, the corrugation amplitudes < 0.1 Å can be obtained using STM.

### 2.1.B Constant height mode

In this mode the vertical position of the tip is kept fixed throughout the scan and the current is measured as at each location to get the topographic image. This mode is suitable only for small area with flat surface as there is risk of tip crashing. This mode has an advantage that the images can be acquired with extremely high scan speeds thereby reducing the time for acquiring the image.

### 2.2 STM Theory

As a first approximation STM can be modelled as a finite barrier potential problem in 1D with an electron with mass \( m \) and energy \( E \) incident from left on the rectangular potential barrier of width \( d \) and height \( V_0 \) (Figure 2-3). The solution of Schrödinger wave equation for the three regions is given by,

\[
\begin{align*}
\psi_I &= A_I e^{ikx} \\
\psi_{II} &= A_{II} e^{kx} + A_{II}' e^{-kx} \\
\psi_{III} &= A_{III} e^{kx} + A_{III}' e^{-ikx}
\end{align*}
\]

where,

\[
k = \sqrt{\frac{2mE}{\hbar^2}} \quad \text{and} \quad \kappa = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}
\]

The coefficients \( A \)'s are found using appropriate boundary conditions. The transmission coefficient \( T \) which is proportional can be given as \(^{13}\),

\[
T = \left| \frac{A_{III}}{A_I} \right|^2 = \frac{4E(V_0 - E)}{4E(V_0 - E) + V_0^2 \sinh^2 \kappa d}
\]

We see that for STM \( d \sim 5 \text{ Å} \), \( V_0 = 4 \text{ eV} \), only the \( \sinh \) term dominates and one gets,
Figure 2-3. Quantum tunneling through the barrier potential of width $d$ and height $V_0$. The energy of the tunnelled particle is the same but the amplitude has decreased showing the exponential dependence on tip sample separation as stated in Equ. 2.1.

For proper theoretical treatment of the tunneling problem we require the correct description of the barrier potential, a detailed description of electronic states of sample and tip and a determination of wave function tail of the tunneling electron in the region between the tip and sample. This problem is very difficult to address as the tip is poorly characterized and calculations of tip wave functions is extremely difficult. Also in real systems the tip and sample may interact strongly and cannot be considered to be independent. However there exists several models based on the perturbative transfer Hamiltonian formalism introduced by Bardeen$^{14}$. The main assumptions in the theory, which led to explain the experimental data$^{15}$, are (1) the interaction between the two electrodes is sufficiently weak so that one can neglect and treat the two electrodes independent, (2) Each of the wavefunctions have exponential tail in the tunneling...
barrier and falls off to zero within the barrier, (3) The overlap is negligibly small so that each electrode wavefunctions are not influenced by the tail of the other. Following is the brief summary of the Bardeen’s approach.

According to Fermi’s Golden rule the probability of tunneling of an electron from state $\Psi_t$ with energy $E_t$ to the state $\Psi_s$ with energy $E_s$ is given by,

$$ W = \frac{2\pi}{\hbar} |M|^2 \delta(E_t - E_s) \quad (2.8) $$

Here the delta function ensures that the electron does not lose energy during tunneling (elastic tunneling) and $M$ is the tunneling matrix element between the two states and is given by the following integral over the surface $S$ in the barrier region,

$$ M_{st} = \frac{\hbar}{2m} \int [\Psi_s^* \nabla \Psi_t - \Psi_t^* \nabla \Psi_s^*] \cdot dS \quad (2.9) $$

Using this we can write the expression for the tunneling current from the tip to sample for the states with energy $\varepsilon$ and when bias $V$ is applied to the sample as,

$$ I_{ts} = -2e \frac{2\pi}{\hbar} |M|^2 \frac{\rho_t(\varepsilon) \cdot f(\varepsilon)}{\text{Number of states of the tip}} \cdot \frac{\rho_s(\varepsilon - eV) \cdot [1 - f(\varepsilon - eV)]}{\text{Number of empty states of the sample}} \quad (2.10) $$

where $f$ is the Fermi function given by $f = \left[1 + e^{\varepsilon/k_B T}\right]^{-1}$ and $\rho_s (\rho_t)$ is the local density of states (LDOS) for the sample (tip).

also the tunneling current from the sample to tip is given by,

$$ I_{st} = -2e \frac{2\pi}{\hbar} |M|^2 \frac{\rho_s(\varepsilon - eV) \cdot f(\varepsilon - eV)}{\text{Number of states of the sample}} \cdot \frac{\rho_t(\varepsilon) \cdot [1 - f(\varepsilon)]}{\text{Number of empty states of the tip}} \quad (2.11) $$

To get the total current we subtract Equ. 2.11 from Equ.2.10 and integrate over all the energy states,

$$ I_{ts} = -\frac{4\pi e}{\hbar} \int |M|^2 \rho_t(\varepsilon)\rho_s(\varepsilon - eV)f(\varepsilon) $$

$$ - f(\varepsilon - eV)d\varepsilon \quad (2.12) $$
Figure 2-4. Schematic diagram of the tunneling process. Energy is along vertical axis while the density of states is indicated along horizontal direction. For simplicity, in this case the sample is applied with the bias $-V_0$ with respect to tip. Therefore the Fermi level for sample shifts up by $eV_0$ allowing the electron from the filled states of the sample tunnel into the empty states of the tip.

Now all that one needs is to calculate the matrix elements given by Equ. (2.9).

### 2.2.A Tersoff–Hamann formalism

Tersoff and Hamann\textsuperscript{16,17} (TH) were the first who applied the transfer Hamiltonian approach to STM. They considered the limit of small bias and made simplified assumption (Figure 2-5) that tip is spherical with a radius of curvature $R$ located at $r_0$, and can be described by a spherically symmetric s-wavefunction given by,

$$
\Psi_t \propto e^{i\kappa R} \frac{e^{-\kappa|r-r_0|}}{\kappa|r-r_0|} \quad \text{with} \quad \kappa = \sqrt{\frac{2m\phi}{\hbar^2}} (2.13)
$$

where $\phi$ is the work function. With these assumptions and the known values of the parameters, TH obtained the expression for the tunneling conductance which is given by,
Figure 2-5. Schematic view of the tunneling geometry within Tersoff – Hamann model. Tip may have arbitrary shape but it is spherical at the end. Radius of curvature of the tip is $R$ and the center of the curvature is at $r_0$. Nearest distance between the tip and sample is $d$.

\[ G_t \equiv \frac{I_t}{V_t} \approx 0.1R^2 \cdot e^{2\kappa R} \rho_S (r_0, E_F) \]  \hfill (2.14)

with

\[ \rho_S (r_0, E) = \sum_s |\Psi_s|^2 \delta(E_s - E) \]  \hfill (2.15)

where $\rho_S (r_0, E_F)$ is the LDOS of the sample at Fermi level evaluated at the centre of the tip $r_0$. Therefore within TH model, constant current mode image has simple interpretation as contours of constant $\rho_S (r_0, E_F)$ of the surface and it reflect only the sample properties.

### 2.2.B Other models

With known experimental parameters: $R = 9$ Å, tip center to top layer distance $= 15$ Å and with low bias it was shown that\textsuperscript{16,17} s-wave tip model is not sufficient to resolve features smaller than 6 Å and it fails to explain previously observed atomically resolved images. However it has been shown that the atomically resolved imaging of
closed packed structures can be obtained by using the tip which has more directed wavefunction (e.g. $d_z^2$ state)\textsuperscript{18}. In 1988 Chen\textsuperscript{19,20,21} proposed simpler way to approximate the tunneling matrix elements where he showed that by expanding vacuum tail of the tip wave functions in terms of spherical harmonics, tunneling matrix elements can be expressed as a derivative of the sample wave functions at the centre of the apex atom. Following table shows the tunneling matrix elements evaluated for different tip wave functions,

<table>
<thead>
<tr>
<th>State</th>
<th>$M \alpha$ value at $r_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s$</td>
<td>$\psi$</td>
</tr>
<tr>
<td>$p [z]$</td>
<td>$\frac{\partial\psi}{\partial z}$</td>
</tr>
<tr>
<td>$d [z^2 - \frac{1}{3}r^2]$</td>
<td>$\frac{\partial^2\psi}{\partial z^2} - \frac{1}{3}\kappa^2\psi$</td>
</tr>
</tbody>
</table>

Table 2.1 Tunneling matrix elements for different tip states

### 2.3 Fabrication of low temperature STM

Over the past few years there are reports of construction of STM\textsuperscript{22,23,24,25,26,27,28,29,30,31} which can reach temperatures below 1K incorporating in-situ cleaving and surface cleaning of single crystals and thin film deposition capabilities. However, a design that allows measurements to be performed on in-situ grown superconducting films on insulating substrates has remained a challenge. The study of superconducting thin films on insulating substrates is important for several reasons. The two important reasons are,

- Single crystalline substrates of insulating MgO, SrTiO$_3$ and LaAlO$_3$ remain the most popular choice for growing lattice matched high-quality epitaxial thin films of several superconductors used for basic studies and applications, such as YBa$_2$Cu$_3$O$_7$, (La,Sr)$_2$CuO$_4$ and NbN.
- The superconducting transition temperature of a superconductor in contact with a normal metal is suppressed through proximity effect up to a depth of the order of the coherence length, $\xi$, from the interface. Since $\xi$ (few nanometers to a few hundred nanometers), is in the same range of the
thickness as most epitaxial films it is important to use insulating substrates in order to study the intrinsic properties of superconducting films.

In this following subsections I describe the construction of low temperature STM with base temperature of 350mK specifically designed for spectroscopic investigations of in-situ superconducting thin films grown on insulating substrates in a deposition chamber connected to the STM. In addition, our design also incorporates a

![Diagram of LT-STM assembly](image)

**Figure 2-6.** 3D view of the LT-STM assembly consisting of three primary sub-units: (i) The sample preparation chamber, (ii) the load lock chamber to transfer the sample from the deposition chamber to the STM and (iii) the 4He Dewar with 9T magnet housing 3He cryostat on which the STM head is attached. The 4He Dewar hangs from a specially designed vibration isolation table mounted on pneumatic legs. The Dewar, cryostat and magnet have been made semi-transparent to show the internal construction.
crystal cleaving assembly for the study of superconducting single crystals. The highlights of our STM are a simple stable design of STM head and a molybdenum sample holder which allows deposition of superconducting thin films on insulating substrates up to a deposition temperature of 800°C. While most of our measurements are restricted below 12 K the temperature of the LT-STM can be precisely controlled from 350 mK – 20 K with temperature drift < 10 mK below 3K for about 8 hours and < 20 mK in the range 3 - 20 K over several hours.

The overall schematic of our system is shown in Figure 2-6. The LT-STM assembly consists of three primary sub-units: (i) The sample preparation chamber, (ii) the load lock chamber to transfer the sample from the deposition chamber to the STM and (iii) the 4He dewar with 9T magnet housing 3He cryostat on which the STM head is attached. The 4He dewar hangs from a specially designed vibration isolation table mounted on pneumatic legs. A combination of active and passive vibration isolation systems are used to obtain the required mechanical stability of the tip. Data acquisition is done using the commercial R9 SPM controller from RHK technology, Inc., USA. (Model: R9 SPM Control system). In following subsections we describe the mechanical details of various components of the setup.

2.3.A STM Head

Over the years, several designs of STM heads have been adopted for operation at low temperatures based on the requirement of stability and convenience of sample or tip exchange. Some of the popular designs include the Pan type and Besocke Beetle-type, which involve coordinated control of multiple piezo elements for coarse positioning. In contrast, the design of our STM head, which is directly mounted below the 3He pot is relatively simple. In this design both coarse approach as well as scanning is achieved through movement of the tip whereas the sample is static. We use commercially bought coarse positioner for the coarse approach of the tip and for fine positioning we use the piezoelectric tube scanner. Following is the brief of the working principle of two.

- **Coarse positioner:**

  Before the start of experiments the tip is brought near the sample in tunneling region using a coarse positioner called as piezo walker. We use piezo walker from
Attocube Systems AG (model ANPz51). It works on the principle of slip stick motion where the motion is due to controllable use of the inertia of a sliding block. The essential components of the piezo walker are, (a) Fixed frame which is rigidly fixed to the main body of STM head, (b) piezoelectric actuator which expand on application of voltage in perpendicular direction and is rigidly glued to the fixed frame, (c) Guiding rod and (d) clamped table or the sliding block which is frictionally held on the guiding rod. Other parts of the positioning unit is screwed on this clamped table.

To obtain the net step (see Figure 2-7) initially the guiding rod is moved slowly by applying a ramp (B) where the sliding block sticks to the guiding rod. Subsequently the guiding rod is accelerated very rapidly over a short period of time (typically microseconds) so that the inertia of the sliding block overcomes the friction. This way, the sliding block disengages from the accelerated rod and remains nearly non-displaced and thus it made a net step. Periodic repetition of this sequence leads to a step-by-step motion of the sliding block in one direction. A piezo electric ceramics pushes or pulls the guiding rod and the exact sequence in the slip and stick motion is controlled by an appropriate triangular voltage signal.

**Figure 2-7.** Schematic explaining working principle of a coarse positioner. It mainly consist of fixed frame, piezoelectric actuator, sliding block which slides on the guiding rod. On application of triangular wave voltage as shown in the right side, the sliding block moves upward.
• **Piezoelectric tube**

A piezoelectric tube scanner normally consists of a thin-walled cylindrical tube of a piezoelectric material with a thin coating of gold, silver or nickel in its inner and outer walls, (see Figure 2-8). The copper coating on the inner and outer walls of the piezoelectric tube acts as the scanner electrodes. The outer electrode is axially quartered into four equal sections. A pair of the opposite sections of the quartered electrode is referred to as the X, –X electrodes and other pair as Y, –Y electrodes.

![Figure 2-8. (a) Schematic sketch of the operation of the piezo tube scanner. (b-c) For our case when a positive voltage is applied to all the four quadrants, the tube contract in z direction while with negative voltages, it extends. (d) When opposite polarity voltages are applied to X,–X (or Y,–Y) then the tube deforms laterally to produce along X (Y) direction.](image)

When a voltage is applied between inner electrode and one outer electrode, the material between the electrodes stretches/contracts in the tube's longitudinal direction. By applying the same voltage (for our case negative voltage) to all four outer electrodes, the whole tube can be stretched, for Z tracking (see Figure 2-8). The tube can also be bent to produce lateral deformation by applying some voltage to one outer segment only and optionally the opposite voltage to the opposing electrode segment, for symmetrical deformation (see Figure 2-8(d)). Thus by controlled application of various voltages the tip can be positioned to very fined position. Total extension or lateral deformation is given by following formulae

\[38\]
\[ \Delta Z = \frac{d_{31} VL}{t} \]
\[ \Delta X = \Delta Y = \frac{0.9 \ d_{31} VL^2}{d_m t} \] (2.16)

where \( d_{31} \) = Piezoelectric strain constant,
\( V \) = applied voltage,
\( L \) = Length of the electrode,
\( d_m \) = mean diameter of the tube, \((\text{OD}+\text{ID})/2\),
\( t \) = thickness of the tube.

- **Mechanical Description of the STM head**

The outer body is made of single piece of gold plated oxygen free high conductivity (OHFC) Copper (see Figure 2-9). The sample holder, coming from the top...
with the sample facing down, engages on a Gold plated Copper part which is electrically isolated from the main body using cylindrical Macor\textsuperscript{39} machinable ceramic part. Both these parts are glued together using commercially available low temperature glue\textsuperscript{40}. The copper part has 45° conical cut at the top matching with sample holder. In the conical region, there are two nonmagnetic stainless steel studs where sample holder gets locked and it can be disengaged from vertical manipulator. The copper part also has two leaf springs made of phosphor bronze which grab the sample holder and also provide better thermal contact and prevent mechanical vibration of the sample holder. Electrical contact to this copper part is given by soldering a stud which extrude from the lower side.

Positioning unit is located in the cuboidal cavity in the lower part of STM head. One of the sides of the cavity is open to get access for mounting the positioning unit and changing tip. The positioning unit consists of a coarse approach positioner and a piezoelectric tube on which the STM tip is fixed. The coarse positioner is fixed to a copper bottom plate using a pair of titanium screws which are in turn screwed to the main body. Fine positioning and scanning is performed using a 1 inch long piezoelectric tube\textsuperscript{41} which has gold plated electrodes inside and outside (see Figure 2-10). Outside gold plating is divided into two segments. The lower half is used for Z motion while upper segment has four quadrants and used for XY motion. Inner electrode is grounded and wrapped out on the upper side to avoid the build-up of any static charge. The piezo-tube is electrically isolated from coarse positioner at the bottom and the copper tip carrier on the top through Macor\textsuperscript{39} pieces which are glued to the tube so as to reduce differential thermal expansion. The copper tip holder is glued on the upper side of top Macor piece and has a bore of diameter 400µm

![Figure 2-10. Image of the scan tube used in our STM. Gold plated electrodes have two segments. Lower segment is used for Z motion. Upper segment is subdivided into four quadrants for X-Y movement. Inner electrode is wrapped around at the top which helps to discharge the static charges if any.](image-url)
for mounting the tip. Printed circuit boards screwed on the three sides of the cuboid serve as the connecting stage for electrical connection to the piezo units, sample and tip. Temperature of STM head is measured using two Cernox\textsuperscript{TM} sensors\textsuperscript{42} mounted on the bottom plate of the STM as well as on the $^3$He pot. The entire STM head is enclosed in gold plated copper can ensuring temperature homogeneity over the entire length of the head. We observe that after achieving a stable temperature for about 10 min the temperature of the STM head and $^3$He pot differ at most by 20mK.

- **Calibration of Piezo constants**

The piezo-constants for X and Y movement for the scanning head were initially calibrated using lithographically patterned Au lines of width 100 nm and separation of 100 nm on a metallic substrate and subsequently fine-tuned using atomically resolved topographic image on NbSe\textsubscript{2} (see Figure 2-20). The piezo constant for Z movement was calibrated in two steps. Since we use the same piezo for X-Y and Z motion, the piezo constants obtained from the X-Y calibration were used to obtain an approximate calibration for Z (see Equ. 2.16). The Z calibration of the piezo tube was fine-tuned using the observed atomic step edge on an NbSe\textsubscript{2} single crystal (see Figure 2-11). The crystal structure of NbSe\textsubscript{2} is composed of stacks of tri-layers where an Nb layer is sandwiched between two Se layers. The bonding between Nb and Se layer is covalent whereas that between two Se layers is van der Walls type. Therefore during the cleaving process the exposed surface consists of Se atoms. When an atomic step forms the height of the step edge is $\sim$6.36 Å corresponding to the distance between two Se layers.

**Figure 2-11.** Calibration of z movement of piezo using atomic step. (a) large area (1μm×1μm) topographic image on NbSe\textsubscript{2} single crystal showing single atomic step. (b) Zoomed view (100nm×100nm) of the topography near the step. (c) Line profile of the image near the step edge showing the step height =6.3 Å.
Following table summarizes the values of piezo constant for our STM head calibrated at 4K.

<table>
<thead>
<tr>
<th>Axis</th>
<th>Piezo constant in nm/volt</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>4.49</td>
</tr>
<tr>
<td>Y</td>
<td>4.49</td>
</tr>
<tr>
<td>Z</td>
<td>0.84</td>
</tr>
</tbody>
</table>

Table 2.2 Piezo constants for the piezoelectric tube used in our STM head

The high voltage amplifier output of our controller is ±215 V. This gives the total scan size of ~ 1.93 μm.

- **Tip preparation**

  We use Pt-Ir wire (80-20%) of diameter 300 μm as a tip which is held frictionally in the tip holder. Tip is prepared by cutting the Pt-Ir wire using sharp scissor at an angle. While cutting, the wire is pulled back so that there is tension in the wire which makes the tip sharp. The cut tip is cleaned and further sharpened using field emission described below.

Figure 2-12. Potential energy diagram for electron at the interface of metal. Φ is the work function of the metal. Curve 1 represents resultant potential experienced due to image potential. When a electric field is applied (shown by dashed curve 2) the resultant potential experience by electron is shown by continuous blue line.
At the interface of the metal electrons experience the effective potential as shown in Figure 2-12 indicated by curve 1. Here $\Phi$ is the work function of the metal. When an electric field is applied, it tilts the barrier making it thinner and therefore increasing the tunneling probability. This phenomenon is called field emission. In STM when very high electric field is applied between tip and sample we get the current due to field emission. Field emission removes the adsorbates on the tip such as oxide layer and other impurity resulting in clean tip surface. Also when the tip is subject to very high positive potential with respect to sample (~200V) then atoms of the tip are emitted resulting in the sharpening the tip\textsuperscript{21}. The tip-sample separation is typically few nanometers.

Figure 2-13 shows the schematic of Field emission circuit where a series resistance $R = 660 \, k\Omega$ is used to limit the current through the circuit in case tip crashes with the sample.

![Figure 2-13. Schematic circuit diagram for field emission. In this case tip is applied with positive voltage.](image)

### 2.3.B Sample holder

The main challenge in the study of superconducting films grown in-situ on insulating substrates is in establishing the electrical contact with the sample for doing STM experiments. We overcome this problem by using a design of a sample holder...
where the film can be directly grown in-situ on the insulating substrate fixed on the holder, and subsequently transferred to STM head for measurement. The sample holder made of molybdenum is shown in Figure 2-14. The choice of the material is given by a trade-off between the need of high thermal conductivity to ensure temperature homogeneity during measurements and the capacity to withstand temperatures up to 800°C during deposition in reactive atmosphere (e.g. oxygen and nitrogen). The substrate is mounted with silver epoxy on the top flat surface and fixed in position by fastening a cap having 4.3 mm diameter hole in the center. The edge of the cap makes direct contact with the top surface of the sample and brings it in electrical contact with the rest of the sample holder. The lower part of the sample holder ends in a 45° slant which mates with the corresponding part on the STM head as shown in Figure 2-9. The sample holder has a horizontal M4 threads on the side for mounting on the horizontal manipulator and M6 threads at the bottom for mounting it on the vertical manipulator. It has two diametrically opposite cuts at the bottom side which fits on the studs on STM
head and locks the circular movement while disengaging the sample holder from the vertical manipulator after the sample is mounted on the STM head.

For STM measurements on films grown on insulating substrates, first two contact strips are deposited ex-situ on two edges of the substrate as shown in Figure 2-14 (b). The width of the strips is adjusted such that when the substrate with contact pads is mounted on the sample holder, a small portion of the strip on either side is exposed through the hole in the cap (Figure 2-14 (d)). When the superconducting film is deposited on the substrate in the in-situ chamber, the edge of the film is in contact with the strip and is therefore electrically connected to the entire sample holder. In principle, the strips could be made of any material that can withstand the deposition temperature of the superconducting film. However, in most cases we found it convenient to make the strips of the same material as the material under study. Since our STM head is symmetric, the tip engages at the center of the sample which ensures tip to strip distance ~ 1 mm. This is much larger than the length over which we would expect superconducting proximity effects from the contact pads to play any role in the measurements.

For the study of single crystals a single piece sample holder of similar shape without the cap is used. The crystal is mounted on the flat surface using a two component conducting silver epoxy. Depending on the hardness, the crystal is cleaved in vacuum (in the load lock cross) alternatively by gluing a small rod on the surface using the same silver epoxy and hitting it with a hammer or by gluing a tape on the surface and pulling the tape using one of the manipulators.

### 2.3.C Sample Preparation chamber

The sample preparation chamber, fitted with a turbo molecular pump and with a base pressure ~ 1×10^{-7} mbar, is located on the top of table and is connected to load lock through a gate valve (Figure 2-15). The chamber consists of two magnetron sputtering guns facing down at an angle, to the substrate heater. The confocal arrangement of guns allows for co-sputtering. The substrate heater consists of a resistive heating element made of a patterned molybdenum plate. Sample holder is inserted using the horizontal manipulator in the chamber through the load-lock and held above the heater. It is heated radiatively and its temperature is measured using thermocouple (PT100) located inside, at the tip of the horizontal manipulator. In addition, the
Figure 2-15. Schematic 3D view of the sample preparation chamber and load-lock cross. The deposition chamber incorporates two magnetron sputtering guns, a substrate heater for heating the substrate up to 800° C, a plasma ion etching gun and two thermal evaporation sources. The substrate in inserted inside the deposition chamber using the horizontal manipulator.

The load-lock, located at the top of the 3He cryostat, has six CF35 ports and it is connected to sample preparation chamber and STM chamber through gate valves. Typical time to pump the load-lock chamber from ambient pressure to 1×10⁻⁶ mbar is about 20 minutes. Sample manipulators (Figure 2-16) are made of seamless steel tubes (closed at one end) and have matching threads at the end to engage on the corresponding threads on the sample holder. A thermocouple is fitted inside the horizontal sample manipulator to measure the temperature of the sample during deposition. Once the sample is deposited horizontal manipulator is pulled back bringing the sample holder
in the cross, and the sample holder is transferred to vertical manipulator and inserted into the STM head.

![Diagram of sample manipulator with thermocouple and Wilson seals]

Figure 2-16. Design of the horizontal sample manipulator with in-built thermocouple for measuring the temperature during sample deposition. A differential pumping arrangement between two Wilson seals is used to remove any leaked gas during movement. The end of the manipulator is made transparent to show the position of the thermocouple. The vertical manipulator is similar in construction but does not have the thermocouple.

### 2.3.E $^3$He Cryostat

The low temperature stage consists of an internally fitted charcoal sorption pump based $^3$He cryostat from Janis Research Company[^45] (Figure 2-17). The cryostat essentially consists of variable temperature insert and a liquid helium Dewar with superconducting magnet.

- **Variable temperature insert**

  We use a custom designed insert which consists of annular shaped sorption pump, 1K pot and $^3$He pot which give us direct line of site access from the top of the cryostat to the STM head mounted below the $^3$He pot. To ensure thermal stability the STM head is bolted to $^3$He pot using 6 screws which ensures good thermal contact between the two. To prevent radiative heating, a radiation plug is inserted in the cryostat after loading the sample using the same vertical manipulator as the one used to insert the sample. The radiation plug (not shown) sits just above the STM head. The $^3$He pot and sorption pump are fitted with resistive heaters. Top flange have many feedthroughs
for electrical wires. All the electrical wires coming from the top are thermally anchored at the 1K pot and the $^3$He pot.

- **Liquid Helium Dewar**

  The cryostat is mounted in a 65 liters capacity Al-Fibreglass Dewar with retention time of approximately 5 days. The superconducting magnet with maximum of 9 T aligned along the STM tip hangs from the top flange of the cryostat. Exhaust line of the cryostat is connected with one way valve which maintains a constant pressure slightly above atmosphere. This allows us to flow liquid $^4$He in a capillary wrapped around the sorption pump such that the sorption pump can be cooled without using an external pump.
Chapter 2. Scanning tunneling microscope

- **Temperature control of the sample**

  STM head is connected to the $^3$He pot as described in VTI section. Therefore we control the temperature of $^3$He pot to set temperature of the sample. $^3$He pot can be cooled either by condensing liquid $^3$He in the pot and pumping over the liquid or through exchange gas from 1K pot. To condense $^3$He, sorption pump is initially heated to 45K and 1K pot is pumped down to 1.6K. $^3$He condenses in the inner walls tubes passing through 1K pot and gets collected in $^3$He pot in about 45 minutes. Once $^3$He is regenerated sorption pump cooling valve is opened and sorption pump temperature is set to 6K. In about 20 min $^3$He pot temperature reaches the base temperature of 350mK where it stays for approximately 8 hours.

  To set the temperature between 350mK to 2.5K we again use the same regeneration procedure as described above but the only difference is we use reduced sorption pump cooling power. This is achieved by setting the sorption pump to a higher temperature. Typically for getting the sample temperature of 1K the sorption pump temperature is set to 20K. Heater power given to the sorption pump is controlled through computer program so as to get desired $^3$He temperature. The reason for not using the heater on the $^3$He pot is it boils off the $^3$He very fast and the longish experiments are not possible to carry out. For temperature above 3K we use cooling power from 1K pot. Here the sorption pump temperature is set to 30K so that there is some exchange gas to cool $^3$He pot and the desired temperature at the $^3$He pot is achieved by heating $^3$He pot using the PID control.

2.3.F **Vibrational and electrical noise reduction**

Most crucial part of any STM design is the vibrational and electrical noise reduction as it is directly reflected in the ultimate noise level in the tunneling current. We have adopted following schemes to reduce eventual noise level.

- **Vibrational noise**

  For sound isolation, the entire setup is located in a sound proof enclosure made of sound proofing perforated foam. To reduce vibrational noise mainly coming from the building, the entire setup rests on a commercial vibration isolation table\textsuperscript{46} (Newport SmartTable\textsuperscript{®}) (see Figure 2-17) with integrated active and passive stages with horizontal and vertical resonant frequency < 1.7 Hz. Finally, since in our cryostat the
1K pot pump has to be on during STM operation, special precaution has to be taken to isolate the system from the pump vibrations which get transmitted in two different ways: (i) Direct pump vibration transmitted through vibration of the connecting bellows and (ii) indirect vibration transmitted through the sound propagated through the $^4\text{He}$ gas in the pumping line. The first source is isolated by keeping the pumps on a different floor in the basement and a rigid section of the pumping line is embedded in a heavy concrete block before connecting to the pump.

To isolate the second source of vibration a special pumping scheme is adopted. The 1K pot is connected to the pump through two alternate pumping lines (See Figure 2-18). While condensing the $^3\text{He}$ and cooling the STM head from 4.2K to the base temperature, the 1K pot is cooled to 1.6 K by pumping through a 25.4 mm diameter pumping line directly connected to the pump (pumping line A). Once the base temperature of 350 mK is reached on the STM head, the pumping line A is closed and the pumping line B is opened. This line has a 30 cm long 10 cm diameter intermediate section packed with high density polystyrene foam which isolates the STM from the sound generated by the pump. Since the polystyrene foam reduces the pumping speed, the 1K pot warms up to 2.8 K, with no noticeable increase in the temperature of the STM head. During the steady-state operation of the STM at 350 mK the pumping is

![Figure 2-18 Cartoon diagram showing isolation of vibration coming from the pump. Pumping line pass through a solid concrete block which removes the vibrations. To remove the sound noise from the line the pumping line passes through a high density foam (path B). For regeneration of $^3\text{He}$ pumping is done though path A.](image)
Figure 2-19. Noise characterization (a) Spectral density of the velocity vs. frequency on the top of the cryostat measured using an accelerometer. The spectral densities with and without the 1K pot pump on are nearly identical. (b) Spectral density of the tunneling current with the tip out of tunneling range, within tunneling range with feedback on and with feedback off. (c) Spectral density of Z height signal with feedback on. Measurements in (b) and (c) were performed at 350 mK on a NbSe2 single crystal with tunneling current set to 50 pA and bias voltage to 20 mV.

further reduced by partially closing a valve to keep the 1K pot at a constant temperature of ~ 3.5K. While operating in this mode we do not observe any difference in vibration level on the top of the cryostat with the 1K pot pump on or off.

- **Electrical noise**

To reduce the electrical noise coming from the 50Hz line signal, ground connection of all instruments, table and Dewar are made to a separate master ground. RF noise is further reduced by introducing 10 MHz low pass filter before each
Chapter 2. Scanning tunneling microscope

connection that goes into the STM. The tunneling current is detected using a Femto DLPCA-200 current amplifier placed at the top of the cryostat with gain of $10^9$ V/A. While the bandwidth of the DLCPA-200 amplifier is 500 kHz, the measurement bandwidth is set digitally restricted to 2.5 kHz in the R9 SPM controller.

- **Characterization of noise**
  
  In our system we have low Z-height and current noise that allows us to get very good signal to noise ratio in spectroscopic measurements as discussed in next sections. Figure 2-19 (a) shows the vibration noise spectrum recorded using the accelerometer on the table while the 1K pot pumping line is on and off. The two profiles show practically no difference in the vibration levels. The final test of isolation performance is obtained from the spectral density (SD) in the current and Z-height signals. We recorded these signals at 350 mK in actual operating condition. Figure 2-19(b) shows the SD of the current (i) when the tip is out of tunneling range (background noise of the electronics), (ii) at a fixed tunneling current with feedback on condition, and (iii) after switching off the feedback for 5 s. The SD with tip out of tunneling range is below 300 fA Hz$^{-1/2}$. At fixed tunneling current (feedback on) additional peaks appear in the SD at 25.5 Hz and 91.5 Hz but the peak signal is only marginally larger than 300 fA Hz$^{-1/2}$. Even after switching off the feedback the peak signal is less than 1 pA Hz$^{-1/2}$. Similarly, the Z-height SD at fixed tunneling current with feedback on (Figure 2-19(c)) is less than 2 pm Hz$^{-1/2}$ at all frequencies and less than 50 fm Hz$^{-1/2}$ above 150 Hz.

### 2.4 Experimental Methods and results

In this section we discuss experimental techniques and the scheme of experiments we use in this thesis. In our STM for applying bias and tunneling current measurements we use the same master ground. We can measure the tunneling current as a function of X, Y, Z and V (bias).

#### 2.4.A Topography

Topography is the most common mode STM measurement employed all around. To acquire topographic image the tip is raster scanned across the surface of the sample in constant current mode and the Z variations are recorded as a function of position, $Z(X, Y)$. As seen in section 2.2.A constant current topography represents contours of constant electronic density of states at the surface.
Figure 2-20. (a) Atomically resolved topographic image of NbSe2 obtained in constant current mode; the charge density wave modulation is also visible. The tunneling current was set to 150 pA, the bias voltage to 20 mV and the scan speed was 13 nm/s. (b) Line cut along the line shown in (a).

Figure 2-20 shows the topographic image taken on 2H-NbSe2 single crystal acquired at 350mK. with Bias $V = 20$ mV and $I_{set} = 150$ pA. Having a hexagonal closed packed layered structure this crystal can be easily cleaved in-plane. We cleaved the crystal in-situ by attaching a tape on the surface and subsequently pulling the tape in vacuum in the load-lock chamber using the sample manipulators. The figure clearly reveals the hexagonal lattice structure along with the charge density wave modulation. The lattice spacing of 0.33 nm is in good agreement with the lattice constant of NbSe2 known from literature.28,47,48

2.4.B Scanning tunneling spectroscopy (STS)

In section 2.2 we saw that tunneling current gives direct access to the local density of states. However it is in the integrated form. In the following subsection we show that tunneling conductance, which is experimentally measurable quantity, indeed is proportional to local density of states. From Equ. 2.12 we write
\[ I = A \int_{-\infty}^{\infty} |M|^2 \rho_t(\epsilon) \rho_s(\epsilon - eV) [f(\epsilon) - f(\epsilon - eV)] d\epsilon \]  

(2.17)

where \( A \) is constant. If we use normal metal tip then the LDOS for tip has a constant value for small window of bias (< 100mV) and assuming constant tunneling matrix element \( M \) \textsuperscript{49,52} we get,

\[ I = A \rho_t(0)|M|^2 \int_{-\infty}^{\infty} \rho_s(\epsilon - eV) [f(\epsilon) - f(\epsilon - eV)] d\epsilon \]  

(2.18)

where \( \rho_t(0) \) is Fermi level density of states for tip. If both tip and sample are metal then tunneling equation becomes,

\[ I_{nn} = A|M|^2 \rho_t(0)\rho_s(0) \int_{-\infty}^{\infty} [f(\epsilon) - f(\epsilon - eV)] d\epsilon \]

\[ = A|M|^2 \rho_t(0)\rho_s(0)eV \equiv G_{nn}V \]  

(2.19)

Which shows that the tunneling junction is purely ohmic and has well defined conductance \( G_{nn} \), independent of \( V \) and temperature. Figure 2-21 shows the tunneling spectrum obtained on silver single crystal which shows ohmic behaviour. This also confirms that the tip density of states is flat within the range of bias.

![Figure 2-21. Raw IV spectra acquired on silver single crystal using Pt-Ir tip. The spectroscopy set point before switching off the feedback was \( V = 100 \) mV, \( I = 500 \) pA, and the lock-in modulation voltage was 500 \( \mu \)V with frequency of 419.3 Hz.](image-url)
When the sample is not normal metal (e.g. superconductor), Eqn. 2.17 becomes\footnote{49,52},

\[
I = A\rho_t(0)|M|^2 \int_{-\infty}^{\infty} \rho_s(\varepsilon)[f(\varepsilon) - f(\varepsilon - eV)]d\varepsilon
\]

\[
= \frac{G_{nn}}{e} \int_{-\infty}^{\infty} \frac{\rho_s(\varepsilon)}{\rho_t(0)}[f(\varepsilon) - f(\varepsilon - eV)]d\varepsilon
\]

(2.20)

For more direct comparison between theory and experiment, we write Eqn. 2.20 as,

\[
G(V) = G_{nn} \int_{-\infty}^{\infty} \frac{\rho_s(\varepsilon)}{\rho_t(0)} \left[-\frac{\partial f(\varepsilon - eV)}{\partial (eV)}\right]d\varepsilon
\]

(2.21)

It can be shown that at sufficiently low temperatures Fermi function becomes step function and \(G(V) \propto N_S(V)\) i.e. the tunneling conductance is proportional to the local density of states of the sample at energy \(\varepsilon = eV\). To measure the tunneling conductance, tip sample distance is fixed by switching off the feedback loop and a small alternating voltage is modulated on the bias. The resultant amplitude of the current modulation as read by the lock-in amplifier is proportional to the \(dI/dV\) as can be seen by Taylor expansion of the current,

\[
I(V + dV \sin(\omega t)) \approx I(V) + \left.\frac{dI}{dV}\right|_V . dV \sin(\omega t)
\]

(2.22)

The typical modulation voltage used in the measurement is \(V_{\text{mod}} = 150\mu V\) which is \(\sim 2\%\) of the bias value. The modulation frequency used is 419.3Hz which is selected based on the minimum noise in the current spectral density. We obtain the conductance as a function of voltage by sweeping bias from negative value to positive value which we refer to as tunneling conductance spectra or tunneling DOS.

- **Normal Superconductor tunneling**

  If we use the superconducting sample then we write the density of states for the sample within BCS theory is given by,

  \[
  \rho_s(\varepsilon) = \text{Re} \left[ \frac{\varepsilon}{\sqrt{(|\varepsilon|)^2 - \Delta^2}} \right]
  \]

(2.23)
Figure 2-22. Tunneling spectroscopy on Pb single crystal acquired with Pt-Ir tip at 500mK (red circle) along with BCS fit with fit temperature \(=500\)mK. The spectrum is averaged over 10 voltage sweeps at the same point. The spectroscopy set point before switching off the feedback was \(V = 6\) mV, \(I = 500\) pA, and the lock-in modulation voltage was 150 \(\mu\)V with frequency of 419.3 Hz.

Figure 2-22 shows the typical spectrum acquired at 500mK at a single point on polished Pb single crystal. The spectrum shows two distinct peaks called as coherence peaks and a dip close to Fermi level indicating the gap. Figure 2-22 also shows the fit using BCS density of states (Eqn. 2.20 and 2.22). We have taken into account broadening due to the finite modulation voltage which is used for lock-in measurements by doing adjacent averaging of points in the theoretical curve over a sliding voltage range of 150 \(\mu\)V. BCS fit gives an energy gap \(\Delta=1.3\) meV which is in good agreement with reported values of the energy gap in Pb.

2.4.C Linescan

In the previous section we saw the spectroscopy at single point on the surface of the sample. Since we have \((X, Y)\) control we can acquire the density of states anywhere on the surface within the scan range. Some samples with no impurity may have uniform DOS but for some interesting samples tunneling DOS may be inhomogeneous. To study the inhomogeneity we can measure the conductance spectra along a line at equispaced interval. We call this data as a linescan.
Figure 2-23. 3D plot for the line scan acquired on disordered NbN with $T_c = 1.65K$ along a line of length 200 nm at 350mK.

Figure 2-23 shows the line scan acquired on strongly disordered NbN shown in the form of 3D plot. Transition temperature $T_c$ of the sample is 1.65K and it can be seen that the sample is highly inhomogeneous with large variation coherence peaks and the value of conductance at zero bias.

2.4.D Spatially resolved STS and conductance map

Similar to linescan we can acquire conductance spectra over an area. For this we define a grid and acquire STS data at each point as a function of $(X, Y)$. This method is very powerful to obtained spatial information of tunneling DOS as the inhomogeneous domains or regions can be directly visualized.

- **Conductance map**

We can visualize the spatially STS data as 3-dimensional data set: 2 spatial dimensions namely X and Y and one energy dimension. Therefore we can make plots of conductance value as a function of bias (energy) and we call this plot as conductance
map. Due to experimental constraints (time limit of 8 hours) we cannot acquire very high resolution spatially resolved STS data therefore we are limited with resolution of conductance map (64x64). Alternately we can acquire high resolution conductance at a given energy by fixing the bias and recording the conductance value using lock-in while topographic imaging.

**Figure 2-24.** Spatially resolved STS data on NbSe2 single crystal acquired at 350mK in magnetic field of 0.2T. (a) 3D plot of line scan where the line passes through the center of the vortex. (b-c) Conductance map obtained by slicing the spatially resolved STS data at zero bias and 1.4mV respectively. The maps show Abrikosov vortex lattice. (d) High resolution conductance map acquired by recording lock-in signal during the topographic scan. The bias applied was 1.4mV and the current was set to 50pA during the imaging.

Figure 2-24 shows the spatially resolved STS data acquired on NbSe2 single crystal at 350mK in magnetic field of 0.2 T. Spectra were recorded at each point on 64x64 grid over area of 352x352 nm by sweeping the bias from –6mV to 6mV. Figure 2-24 (b) and (c) shows the conductance map for $V = 0V$ and $V = 1.4 mV$ which clearly reveals hexagonal Abrikosov vortex lattice\(^{51}\). The lattice constant, $a \approx 109.8$ nm is in excellent agreement with the theoretical value expected from Ginzburg Landau theory\(^{52}\). For voltages below $\Delta/e$ the vortices appear as regions with larger conductance whereas for voltages close to the coherence peak the vortices appear as regions with lower conductance. Figure 2-24 (a) shows the line scan sectioned on the line shown in panel (b). Three representative spectra are highlighted in the figure. Spectra 1 and 3 correspond to the superconducting region while the spectrum 2 is at the vortex core and has a zero bias conductance peak which is the signature of Andreev bound state inside
the vortex core. In Figure 2-24(d) we show a high resolution (128 × 128) conductance map obtained by measuring $dI/dV$ at a fixed bias voltage of 1.4mV while scanning over the same area.

### 2.5 Reference


14 J. Bardeen, *Tunnelling from a Many-Particle Point of View*, Phys. Rev. Lett. 6, 57 (1961)


Low temperature glue, STYCAST 2850FT, from Emerson and Cuming.

Piezo electric tube from EBL Products, Model EBL#2

Cernox sensor from LakeShore Cryotronics Inc., USA.

We found the two component silver epoxy EPO-TEK® E4110 from Epoxy Technology, Inc to have adequate mechanical strength for cleaving most single crystals.

Ion source from Tectra GmbH, Frankfurt, Germany. Model: IonEtch sputter Ion Gun, Gen II


Custom built SmartTable® with central hole from Newport Corporations, USA.


Superconducting state is characterized by a gap in the electronic spectrum which indicates pairing of electrons into Cooper pairs and a phase coherence of these Cooper pairs which manifests in resistanceless flow of current. For conventional superconductors this gap vanishes at $T_c$, as described by Bardeen-Cooper-Schrieffer (BCS) and Eliashberg mean-field theories. In contrary the case is very different for high $T_c$ cuprate superconductors (HTSC) where the gap in the electronic spectrum exists much above $T_c$ and it is called as pseudogap. The origin of pseudogap and its relationship with superconductivity has been the field of active research for more than two decades. Several scenarios based either on peculiarities specific to High $T_c$ Cuprates such as an order competing with superconductivity, or a precursor to superconducting energy gap where the superconducting transition driven by phase fluctuations have been suggested as possible origin of this feature.

In case of conventional disordered superconductors, it is know from dirty limit BCS relation that disorder scattering reduces superfluid stiffness ($J$). At sufficiently strong disorder $J$ can become smaller than the superconducting energy gap which renders the superconductor more susceptible to phase fluctuations to suppress superconductivity leaving finite local pairing amplitude. This implies that in presence of strong disorder there is a possibility of finite gap due to pairing above $T_c$ in the local electronic spectra similar to HTSC. Indeed in this chapter we demonstrate systematically the formation of such gapped state in NbN above $T_c$ and present a temperature disorder ($T-k_F$) phase diagram. Borrowing term from HTSC we call this gap as pseudogap.

The chapter is organized as follows. In section 3.1, I will present the experimental methods and the scheme of analysis of the STS data. Section 3.2 focusses
on the experimental results on the effect of disorder on superconducting properties of NbN. In section 3.3 we will discuss various possible mechanisms behind our experimental observations. The experimental data presented in this chapter is the combination of data acquired on STM’s, one operating down to 2.6K and other down to 350mK (section 2.3).

3.1 Experimental strategy and data analysis schemes:

In this section we will discuss the details of the sample growth conditions, data acquisition method and data analysis scheme.

3.1.A In-situ preparation of NbN films

For growing NbN thin films we use (100) oriented MgO single crystalline substrates. Before mounting it on sample holder we deposit strips of ordered NbN having \( T_c = 16K \). Epitaxial thin films of NbN are then grown in-situ in a deposition chamber by sputtering high purity niobium target in Ar-N\(_2\) mixture and then transferred

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deposition power (W)</th>
<th>Ar:N(_2) ratio</th>
<th>Time of deposition (min)</th>
<th>( T_c ) (K)</th>
<th>( k_F l )</th>
</tr>
</thead>
<tbody>
<tr>
<td>DONbN-2</td>
<td>120</td>
<td>82:18</td>
<td>5</td>
<td>13.5</td>
<td>5.8</td>
</tr>
<tr>
<td>DONbN-3</td>
<td>100</td>
<td>82:18</td>
<td>5</td>
<td>11.9</td>
<td>4.8</td>
</tr>
<tr>
<td>DONbN-17</td>
<td>40</td>
<td>82:18</td>
<td>10</td>
<td>8.9</td>
<td>3.5</td>
</tr>
<tr>
<td>DONbN-7</td>
<td>40</td>
<td>65:35</td>
<td>20</td>
<td>6</td>
<td>2.6</td>
</tr>
<tr>
<td>DONbN-21</td>
<td>20</td>
<td>60:40</td>
<td>40</td>
<td>2.6</td>
<td>1.66</td>
</tr>
<tr>
<td>DOSTM-26</td>
<td>75</td>
<td>84:16</td>
<td>6</td>
<td>6.4</td>
<td>2.7</td>
</tr>
<tr>
<td>DOSTM-73</td>
<td>13.6</td>
<td>56:44</td>
<td>50</td>
<td>3.5</td>
<td>1.88</td>
</tr>
<tr>
<td>DOSTM-19</td>
<td>18</td>
<td>60:40</td>
<td>40</td>
<td>2.9</td>
<td>1.74</td>
</tr>
<tr>
<td>DOSTM-30</td>
<td>15.2</td>
<td>60:40</td>
<td>40</td>
<td>2.1</td>
<td>1.55</td>
</tr>
<tr>
<td>DOSTM-7</td>
<td>14</td>
<td>60:40</td>
<td>40</td>
<td>1.65</td>
<td>1.45</td>
</tr>
<tr>
<td>DOSTM-14</td>
<td>10.2</td>
<td>32:68</td>
<td>45</td>
<td>(&lt; 300m)</td>
<td>(\sim 1.1)</td>
</tr>
</tbody>
</table>

Table 3.1 Sample growth conditions and corresponding \( T_c \) values for the important samples
into the STM head using pair of sample manipulators. Disorder in the system is introduced by varying the deposition conditions. (For details see section 1.3A). All the samples used in this study have the thickness greater than 50nm. Once the sample is transferred into the STM head, before we start the measurements a radiation plug is put on top of the STM head which blocks the radiations coming from the top. Once all the STM measurements are completed, the sample is taken out of STM head and four probe resistivity measurements are carried out on the sample in different cryostat. Table 3.1 describes the sample deposition conditions and other details for the samples used for our study.

3.1.B Line scan and averaged spectrum

All the data presented in this chapter is based on the average of the tunneling conductance spectra acquired on the line of length 200 nm. As the coherence length ($\xi$) for all the films is < 10 nm, the averaged spectrum is a measure of spatially averaged tunneling density of states (DOS). To acquire such data (see Figure 3-1) we define a line of length 200 nm over the topographic image and acquire several conductance spectra (typically 5-10) over each point on the grid of 32 equispaced points. Figure 3-1(b) shows conductance spectra plotted in the form of colormap along a line of length 200 nm over 32 points for the sample with $T_c = 11.9K$. Here each point is the average of 5 spectra. Figure 3-1(c) shows the average of all the spectra acquired on 32 points. We do not observe significant difference between averaged spectra acquired along different lines.

![Figure 3-1](image-url)

Figure 3-1 Line scan procedure (a) Topographic image showing the line (b) STS data acquired along a line shown in panel a plotted in the form of colormap. (c) Average of the spectra shown in panel (b).
3.1.C DOS evolution with temperature

To study temperature evolution of tunneling DOS the line scan averaged spectra are acquired at different temperatures, starting from lowest upto the temperature where the tunneling DOS is flat or is temperature independent. The care is taken such that the spectra are acquired on the same line for which the topographic image is taken every time and the previous line is identified. Figure 3-2(a) shows the conductance spectra normalized at high bias value \((G(V)/G_N)\) at different temperatures for the sample with \(T_c=11.9K\). Figure 3-2(b) shows the evolution of tunneling DOS with temperature plotted in the form of colormap. Colormap shows that at lowest temperature (3.1K) conductance spectra has a dip in the centre (blue) and two symmetric peaks (red) which slowly evolve with the temperature. The dip in the DOS disappears at 11.9K indicating the closer of superconducting energy gap at \(T_c\).

![Figure 3-2](image.png)

Figure 3-2. (a) Temperature evolution of conductance spectra for the sample with \(T_c = 11.9K\). Spectra are acquired with bias = 6mV and \(I_{set} = 400pA\) (b) Colormap of the data in panel a.

3.1.D Background correction for disorder NbN samples

Samples in low disordered regime shows the typical BCS like spectra in the superconducting state and the dip at zero bias vanishes at \(T_c\) where it attains the flat
density of states corresponding to normal metallic state (see Figure 3-3(a)). However with increasing disorder we see two prominent features in the superconducting spectra: (a) dip close to zero bias due to superconducting energy gap and (b) a broad, temperature independent V shaped background extending upto high bias. The second feature in the tunneling spectra arises from Altshuler-Aronov (AA) type electron-electron interaction and becomes progressively prominent with increasing disorder\(^9,10,11\) (Figure 3-3(b-e) ). The superconducting contribution from these spectra is extracted by dividing the low temperature spectra by the spectrum obtained at high temperature (typically 9K) where the superconducting correlations are absent and we have only the background due to AA interaction (black curves in Figure 3-3(a-e)). Here onward we will refer the background corrected spectra \( (G(V)/G_{9K}(V)) \) as normalized conductance spectra and denote them as \( G_N(V) \). Figure 3-3(f) shows the normalized spectra for the three samples with \( T_c=6.4K \), 3.5K and 1.65K.

Figure 3-3. AA correction (a-c) Conductance spectra for the three films in the intermediate disorder level with \( T_c=13.5K \), 11.9K and 6.4K acquired at lowest temperature and at the temperature just above \( T_c \) showing gradual formation of background due to AA type interactions. (d-e) Conductance spectra for two films in strong disorder regime acquired at lowest temperature and at 9K. (f) background corrected spectra for the films in panels c-e.
Figure 3-4. (a) Normalized conductance curves for the sample with $T_c=2.6K$. (b) Derivatives of the conductance curves in panel (a). Few curves are removed for clarity. (c) Normalized conductance curves after dividing curves in panel (a) from 9.35K data.

The temperature evolution of $G_N(V)$ is illustrated in Figure 3-4 for the disordered NbN sample with $T_c = 2.6K$. Panel (a) shows the raw conductance spectra at different temperatures and panel (b) shows the derivative of the spectra in panel (a). It is very clearly seen in the $dG(V)/dV$ versus $V$ curves that the symmetric peak-dip structure associated with the low bias feature completely disappears for the spectrum at 9.35K and therefore it is the natural choice to take as the background spectrum. Figure 3-4(c) shows normalized conductance spectra obtained using spectrum at 9.35K as a background spectrum.

3.2 Experimental results

In this section we present our study on the effect of disorder on superconducting properties of NbN through the combination of STS and transport measurements. Disorder in our films can be varied over a very wide range: $T_c$ ranges from 16K ($k_F l \sim 10$) in the cleanest sample to $< 300$mK ($k_F l < 1$). Our study essentially brings out three distinct regimes of disorder as discussed in the subsequent sections.

At the moderate to intermediate disorder ($k_F l > 2.7$), $T_c$ is gradually suppressed with increasing disorder while the system follow conventional BCS behaviour\[^{12}\]. Figure 3-5 shows the temperature evolution of normalized spectra for four samples in this disorder regime plotted in the form of colormap ($T_c = 13.5K, 11.9K, 8.9K, 6.4K$). All the spectra here are spatially averaged over the line of length 200nm. The resistance Vs. temperature curves are plotted superimposed on top of the colormap for clarity. Also in corresponding right panels are plotted the normalized spectra for three temperatures for clarity which includes spectra at lowest temperature (blue), below $T_c$ (green) and one at just above the $T_c$ (red). We observe that for all the samples the spectra
Figure 3.5. (a), (c), (e), (g) Colormap of temperature evolution of spatially averaged normalized tunneling conductance for the samples in the intermediate disorder regime with $T_c=$13.5K, 11.9K, 8.9K, and 6.4K. Corresponding resistivity Vs temperature is plotted on top of the colormap. We observe that the gap in the tunneling spectra closes at $T_c$. (b), (d), (f), (h) Representative spectra at different temperatures.
Chapter 3. Emergence of Pseudogap ....  113

Figure 3-6. (a), (c), (e), (g), (i) Colormap of temperature evolution of spatially averaged normalized tunneling conductance for the samples in the strong disorder regime with $T_c = 6\, K$, 3.5K, 2.9K, 1.65K and <300mK. Corresponding resistivity Vs temperature is plotted on top of the colormap. We observe the formation of pseudogap in the tunneling spectra above $T_c$. (b), (d), (f), (h) Representative spectra at three temperatures: (i) at lowest measurable temperature (blue) (ii) near the transition (green) and in the pseudogap regime (red).
at low temperature show a prominent gap and two symmetric coherence peaks. The superconducting gap vanishes exactly at $T_c$ as expected from BCS theory and a flat metallic DOS is restored above $T_c$.

With further increase in disorder ($2.7 > k_F l > 1$) $T_c$ continue to decrease monotonically while we observe the emergence of pseudogap state where the finite gap above $T_c$ is revealed though STS measurements. The temperature at which pseudogap vanishes is denoted by $T^*$. For practical purposes we define $T^*$ as the temperature at which the zero bias conductance (ZBC) value in the normalized conductance spectra become 95% of the value at high bias. Figure 3-6 shows colormap of temperature evolution of normalized conductance spectra for five samples with $T_c = 6K, 3.5K, 2.9K, 1.65K$ and $< 300mK$. Three spectra are shown on the corresponding right side panels for clarity which include the spectra at lowest temperature (blue), near $T_c$ (green) and one in the pseudogap region (red). Figure 3-6 reveals that with increasing disorder $T^*/T_c$ increases. For sample with $T_c = 1.65$, $T^* > 4T_c$ while for the sample with $T_c < 300mK$, $T^* >> T_c$. Interesting thing to notice in all our strongly disordered samples is that $T^*$ has the value $\sim 6 - 7K$ irrespective of the value of $T_c$. The pseudogap state has also been observed in other strongly disordered conventional s-wave superconductors like TiN$^{13}$ and InO$^{14}$ consistent with our results.

All the above results are summarized in the Figure 3-7 in the form of phase diagram where we plot evolution of $T_c$ and $T^*$ as a function of $k_F l$. The phase diagram brings out three distinct regimes: the intermediate regime (regime I) where the superconducting state is characterized by a single energy scale $T_c$, strong disorder regime (regime II) which is characterized by the emergence of the pseudogap state and a nonsuperconducting regime (regime III) where the samples remain nonsuperconducting down to 300mK.

### 3.3 Discussion

Before we understand the effect of disorder to decrease $T_c$ and emergence of pseudogap state we will discuss the possible mechanisms responsible for the destruction of superconductivity. The superconducting state is characterized by a complex order parameter,

$$\Psi = |\Delta|e^{i\varphi}$$ (3.1)
where $\Delta$ is a measure of the binding energy of the Cooper pairs and $\varphi$ is the phase of the macroscopic condensate. It is important to note that a finite $\Delta$ manifests as a gap in the electronic energy spectrum and is proportional to $T_c$ in the BCS framework (Equ. 1.21). In the superconducting state $\varphi$ has same value everywhere and the zero resistance state results from the phase coherence of the Cooper pairs over all length scales. This means also that there is a phase stiffness or energy cost associated with changing $\varphi$ from one place to another. Superconductivity can be suppressed mainly through following two routes. The first route is by a decrease in $\Delta$ caused by a weakening of the pairing interactions. In such a situation, $T_c$ will get suppressed but the superconductor will continue to follow conventional BCS behaviour with the superconducting energy gap disappearing at $T_c$. However, a second, less explored route for the suppression of $T_c$ is through a decrease in the phase stiffness$^{15,16,17}$. When the phase stiffness becomes sufficiently small the superconducting state will get destroyed due to a loss of global phase coherence resulting from thermally excited phase...
fluctuations, leaving pairing amplitude $\Delta$ finite above $T_c$. In this situation the gap continue to persist above $T_c$ up to the temperature where the pairing amplitude vanishes. We now discuss in details the role of disorder in three regimes shown in the phase diagram.

- **Regime I: Intermediate disorder level**

  We observe that in our samples in the regime $I$, $T_c$ monotonically decreases with increase in disorder, but continues to follow conventional BCS behaviour. Figure 3-8 shows conductance spectra and corresponding BCS fits for the sample in this disorder regime with $T_c = 11.9$K. Therefore, we expect the decrease in $T_c$ to be caused by a weakening of the pairing interaction. This weakening can result from two effects. First, with increase in disorder, the diffusive motion of the electron results in an increase in the repulsive $e-e$ Coulomb interactions, which partially cancels the phonon mediated attractive pairing interaction. It is interesting to note that some of the early works attributed the complete suppression of superconductivity in several disordered superconductors, solely to this effect. The second effect comes from the fact that disorder, in addition to localizing the electronic states close to the edge of the band also increases the one electron bandwidth, thereby decreasing the density of states ($N(0)$) close to the middle of the band. While this effect alone cannot result in complete

![Figure 3-8](image)

**Figure 3-8.** (a) Temperature evolution of conductance spectra for the sample with $T_c = 11.9$K along with BCS-$\Gamma$ fits. (b) Temperature variation of $\Delta$ obtained from the best fits plotted along with expected BCS behaviour (solid black line).
suppression of superconductivity, it can have a noticeable effect in the intermediate disordered regime\textsuperscript{23}. Both these effects are captured at a qualitative level using the modified BCS relation\textsuperscript{24},

\[
T_c = 1.13 \Theta_D \exp \left( -\frac{1}{N(0)V - \mu^*} \right)
\]

where \(\Theta_D\) is a temperature scale of the order of Debye temperature, \(V\) is the attractive electron-phonon potential and \(\mu^*\) is the Coulomb pseudopotential which accounts for the disorder enhanced \(e-e\) interactions. The available theoretical model on the dependence of the \(\mu^*\) on disorder in a 3-D superconductor is currently not developed enough to attempt a quantitative fit of our data. However the combination of the two effects mentioned above qualitatively explains the suppression of \(T_c\) in the intermediate disorder level, where the superconducting energy gap in the tunneling DOS vanishes exactly at \(T_c\).

- **Regime II: Strong disorder level**

Strong disorder regime is characterized by two temperature scales, namely, \(T_c\), which corresponds to the temperature at which the resistance appears and \(T^*\), the pseudogap temperature where the gap in the local tunneling spectra disappears. \(T_c\) continues to decrease monotonically with increasing disorder, whereas \(T^*\) remains almost constant down to \(k_F l \sim 1\), where the superconducting ground state is completely destroyed. It would be natural to ascribe these two temperature scales to the phase stiffness of the superfluid (\(J\)) and the strength of the pairing interaction (\(\Delta\)) respectively. \(J\) can be estimated using the relation\textsuperscript{15,16},

\[
J = \frac{\hbar n_s}{4m^*}
\]

where \(a\) is the length scale over which the phase fluctuates and \(m^*\) is the effective mass of the electron. A rough estimate of \(J\) is obtained from \(n_s\) derived from the low temperature penetration depth\textsuperscript{25} \((\lambda(T \to 0))\) and setting \(a \approx \xi\) in the equation,

\[
n_s = \frac{m^*}{\mu_0 e^2 \lambda^2}
\]
In conventional “clean” superconductors, $J$ has value several orders of magnitude larger than $\Delta$, and therefore phase fluctuations play a negligible role in determining $T_c$. However, disorder enhanced electronic scattering decreases $n_s$, thereby rendering a strongly disordered superconductor susceptible to phase fluctuations.

Figure 3-9. Magnetic penetration depth at lowest temperature $\lambda(T \to 0)$, superfluid stiffness ($J/k_B$) and experimentally measured $\Delta(0)$ plotted as a function of $T_c$ for different NbN films. In the strong disorder regime we cannot fit spectra with BCS DOS therefore the green line extrapolated such that $\Delta/k_B$ is equal to pseudogap temperature.

In Figure 3-9, we summarize the values of $J$ for NbN films with different $T_c$ estimated from Equ. 3.3 using experimental values of $n_s$ measured from penetration depth (Ref. 25) and the values of $\xi$ obtained from the upper critical field, $H_{c2}^{8,26}$. Apart from some small numerical factor of the order of unity arising from the choice of the cut-off $a \approx \xi$ in Equ. 3.3, we see that for the samples in the regime $I$, $J \gg k_B T_c$ such that phase fluctuations play a negligible role in determining $T_c$. As we enter regime $II$, ...
$J$ becomes of the order of $k_B T_c$. Also the crossover from regime I to regime II occurs on the same samples where we observe a deviation of $n_s(T)$ from the dirty-limit BCS theory, both at zero temperature and finite $T$. Both effects can be attributed to phase fluctuations in the presence of disorder. As it has been recently discussed in Ref.27, as disorder increases, the superfluid stiffness is lower than in the dirty-BCS scenario since the phase of the superconducting order parameter relaxes to accommodate to the local disorder, leading to an additional paramagnetic reduction of the superfluid response of the system. At the same time the enhanced dissipation lowers the temperature scale where longitudinal phase fluctuations can be excited, leading to a linear decrease of $n_s(T)$ in temperature, as observed in our samples. Also from Figure 3-10, which shows the lowest temperature linescan plotted with increasing disorder level, we observe the spontaneous inhomogeneity in the superconducting spectra in strong disorder regime. In light of all these observations, we therefore conclude that the superconducting state in strongly disordered NbN samples is destroyed at $T_c$ due to phase fluctuations between superconducting domains. However, even above this temperature, $\Delta$ remains finite due to phase incoherent Cooper pairs which continue to exist in these domains and giving rise to pseudogap state. The relative insensitivity of $T^*$ to disorder and the gradual decrease in $T_c$ suggests that increase in phase fluctuations is responsible for the decrease in $T_c$ in this regime, while the pairing amplitude remains almost constant. Eventually, at a critical disorder ($k_F l \approx 1$), the superconducting ground state is completely suppressed by quantum phase fluctuations, that are themselves enhanced by disorder. The overall physical picture and the phase diagram obtained in our experiments share many analogies with recent theoretical calculations on disordered superconductors.

- **Regime III Nonsuperconducting regime**

In nonsuperconducting regime, superconductivity is completely suppressed due to disorder. The insensitivity of $T^*$ to disorder in regime II suggests the persistence of finite local pairing correlation in this regime, where the system is comprised of inhomogeneous superconducting islands and the global superconductivity is suppressed due to quantum phase fluctuations between inhomogeneous regions. Indeed the recent experiments on NbN samples in this regime indicated this scenario through magnetoresistance measurements.
Figure 3-10. Line scans acquired at lowest temperature for 8 films with different levels of disorder. We can see that for the samples with $T_c \leq 6K$ superconductivity becomes inhomogeneous supporting phase fluctuation scenario.

3.4 Summary

We have shown that with increasing disorder a 3D conventional superconductor, NbN, evolves from a BCS superconductor in a moderately clean limit to the situation where the superconductivity is completely destroyed through phase fluctuations. We constructed a temperature-disorder ($T-k_Fl$) phase diagram.
summarizing various temperature scales based on the transport and STS measurements. We identify three distinct regimes of disorder on the phase diagram: (i) the intermediate disorder regime where $T_c$ monotonically decreases due to weakening of pairing interaction, (ii) strong disorder regime where the decrease in $T_c$ is governed by phase fluctuations and (iii) nonsuperconducting. It would be interesting to explore the analogy with underdoped high-$T_c$ cuprates, which share many similarities with strongly disordered s-wave superconductors.

3.5 References


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Chapter 3. Emergence of Pseudogap ….


Chapter 4

Emergence of inhomogeneity in the superconducting state of strongly disordered s-wave superconductor, NbN

4.1 Introduction

In recent times numerous theories and numerical simulations have been carried out in order to understand real space evolution of superconductivity in presence of strong disorder. The starting Hamiltonian for the superconductor is normally the attractive Hubbard model with random on-site energy\(^1,2,3\). Although these simulations ignore the Coulomb interactions and are done on relatively small lattice the end results are instructive. These simulations indicate that in the presence of strong disorder the superconducting order parameter becomes inhomogeneous, spontaneously segregating into superconducting domains, dispersed in an insulating matrix. Consequently the energy gap \(\Delta\) is not strongly affected but the energy cost of spatially twisting the phase of the condensate, the superfluid stiffness \(J\), decreases rapidly with increasing disorder making the system more susceptible to phase fluctuations. Thus in presence of strong disorder and below the critical disorder system consists of superconducting islands and the phases are Josephson coupled through insulating regions in the superconducting state. These superconducting islands lose phase coherence above \(T_c\) but persists upto much higher temperatures.

While the formation of an inhomogeneous superconducting state has been invoked to explain a variety of phenomena close to the critical disorder for the destruction of the superconducting state e.g. magnetic field tuned superconductor-insulator transition\(^4,5\), finite superfluid stiffness\(^6\) above \(T_c\) and Little-Parks oscillations in a disorder driven insulating film\(^7,8\), a direct experimental proof of emergent
inhomogeneity in a system where the structural disorder is indeed homogeneously distributed over typical length scale of superconducting domains is currently lacking.

In this chapter we use a low temperature scanning tunneling microscope (LT-STM) to explore the inhomogeneity formed in the superconducting ground state in homogeneously disordered NbN. In combination we also use high resolution scanning transmission electron microscope (HRSTEM) to study the structural disorder at the atomic length scale. Indeed we see the emergence of inhomogeneity in the local order parameter in the form of domains of size over tens of nanometer while the structural disorder is distributed uniformly over atomic scale. We also observe the striking universality in the order parameter distribution when we rescale the order parameter by taking logarithm and normalizing to its variance.

The plan of the chapter is as follows, in section 4.2 we first explore the structural disorder in NbN at the atomic scale probed through HRSTEM. In next few sections we discuss the general trend in the superconducting spectra with increasing disorder through scanning tunneling spectroscopy (STS) measurements and define the order parameter for the disordered superconducting state. In section 4.6 we discuss the emergent inhomogeneity and its spatial correlation. In section 4.7 we explore the universality in the order parameter distribution. We report the temperature evolution of the inhomogeneous superconducting state across $T_c$ in section 4.8. Finally we discuss the implication of our results in concluding section.

**4.2 Investigation of structural disorder in NbN at the atomic scale.**

To characterise the disorder at the atomic scale HRSTEM measurements were performed on two films: one with low disorder having $T_c \sim 16$K and other is strongly disordered sample having $T_c \sim 2.5$K ($k_Fl \sim 1.7$). To make the interfaces 'edge on', i.e, perpendicular to the incoming electron beam, both the samples were tilted along $<110>$ in this present study. The structure of NbN projected along $<110>$ is shown in the inset of Figure 4-1(a) which reveals that atomic columns contain either Nb or, N i.e, atomic columns with mixed atoms are not present while viewing through this direction. High resolution Z-contrast images of MgO/NbN thin film interfaces of both samples (Figure 4-1(a) and (g)) shows that the films grow epitaxially on MgO (100) substrate. At low
Figure 4-1 Structural characterization of NbN films. (a),(g) HRTEM images at the interface of NbN-MgO for samples with $T_c \sim 16K$ and 2.5K respectively. Crystal structure of NbN projected along <110> is shown in the inset of (a) where blue and green circles represent Nb and N atoms resp. (b),(h) low magnification images for same samples as in (a) and (g). (c)-(f) and (i-l) are HRSTEM images at two different locations plotted along with surface plots of the two dimensional intensity distribution for two samples with $T_c \sim 16K$ and 2.5K. Intensity distribution in each image is normalized with respect to the minimum intensity value in the corresponding imaged region.
magnification (Figure 4-1(b) and 4-1(h)) the two samples look similar: After a distance of columnar kind growth the films grow uniformly.

The essential difference between the two samples is brought out when disorder is investigated at atomic length scales. For this purpose HRSTEM images were acquired at several locations for each sample in the uniform regions of the films shown in Figure 4-1(b) and 4-1(h). Figure 4-1(c-f),(i-l) shows the HRSTEM images at two locations on each sample along with the corresponding surface plots of two dimensional intensity distributions. For all experiments, small camera length was purposefully selected, which allowed the high angle annular dark field (HAADF) detector to collect mainly electrons scattered at high angles which are mostly contributed by atomic columns containing Nb (Z=41). In this case, the intensity ($I$) of an atomic column in HRSTEM image is proportional to the number of Nb atoms ($n$) in the column$^9,10$. Therefore, the intensity variation in these images reflects the variation of number of Nb atoms in respective columns resulting from Nb vacancies in the crystalline lattice. The smooth intensity variation in the low disordered sample (Figure 4-1(e) and 4-1(f)) is primarily due to the overall thickness variation of TEM sample produced during ion milling. In contrast, in the strongly disordered sample (Figure 4-1(k) and 4-1(l)) we observe large intensity variation even in adjacent columns, showing that Nb vacancies are randomly distributed in the crystalline lattice. Thus even in strongly disordered NbN thin films, structural disorder stems from randomly distributed Nb vacancies, while the films remains homogeneous when averaged over length scales larger than few nm.

### 4.3 STS Methods

Sample growth conditions for the NbN films is described in section 3.1.A. In this chapter we mainly concentrate on samples with names starting from DOSTM (see table 3.1). The data presented in this chapter mainly consists of spatially resolved tunneling conductance spectra acquired at each location on 32×32 grid over an area of 200×200 nm at a given temperature. Temperature evolution of spatially resolved superconductivity is investigated through STS data acquired at different temperature intervals upto ~ 9K, where the superconducting correlations are completely suppressed. All the spectra presented here is corrected for background due to $e$-$e$ interaction using
the averaged spectrum over all the spectra at ~ 9K. We will refer to these spectra as normalized spectra and are denoted as $G_N(V)$.

### 4.4 Evolution of superconducting spectra with increasing disorder

Since STS gives direct access to the local density of states of the surface, the spatial inhomogeneity in the superconducting state can be studied using spatially resolved STS data. Figure 4-2 shows the 3D view of line scans at lowest temperatures (~ 500mK) plotted with increasing disorder.

![Figure 4-2. Line scan for four samples in strong disorder regime. The scans show that with increasing disorder, spectra becomes progressively inhomogeneous.](image)

Also the histograms for the zero bias conductance (ZBC) value, $G_N(0)$, at lowest temperature is shown in Figure 4-3 for six samples. We observe from these two figures that with increasing disorder,

- All the tunneling spectra show the gap at zero bias associated with superconducting energy gap.
- Coherence peaks becomes progressively diffused.
- We observe in each line scan that the onset of the gap has approximately the same value but the coherence peak heights has large variation.
- ZBC value, $G_N(0)$, continuously increases.
- Superconducting spectra highly inhomogeneous evidenced through both spatial variation of coherence peak heights and zero bias conductance.
Figure 4-3. Histograms of zero bias conductance (ZBC) for various levels of disorder. Plots shows that with increasing disorder from clean to strongly disordered regime, peak value in the ZBC increases.

In the following sections we will investigate in details on the inhomogeneity in the superconducting properties of disordered NbN.

4.5 Coherence peak height as a measure of local order parameter (OP)

We first concentrate on nature of individual tunneling spectra for the three samples in strong disorder regime. Figure 4-4 shows the two representative spectra recorded at two different locations at 500mK for three samples with $T_c = 1.65K$, 2.9K and 3.5K. The spectra shows a dip at zero bias associated with superconducting energy gap but they differ strongly in the heights of the coherence peak. The spectra in Figure 4-4(a-c) shows well defined coherence peaks at the gap edge while for those in Figure 4-4(d-f) coherence peaks are completely suppressed. Also unlike the ordered NbN where the spectrum is fully gapped, we observe significant ZBC. This is the general feature observed in all strongly disordered NbN thin films that we have measured.
The density of states for a conventional clean superconductor, well described by the Bardeen-Cooper-Schrieffer (BCS) theory, is characterized by an energy gap ($\Delta$), corresponding to the pairing energy of the Cooper pairs and two sharp coherence peaks at the edge of the gap, associated with the long-range phase coherent superconducting state. This is quantitatively described by a single particle DOS of the form

$$N_S(E) = \text{Re} \left( \frac{|E| + i\Gamma}{\sqrt{|E| + i\Gamma)^2 - \Delta^2}} \right)$$

where the additional parameter $\Gamma$ phenomenologically takes into account broadening of the DOS due to recombination of electron and hole-like quasiparticles.

For Cooper pairs without phase coherence, it is theoretically expected that the coherence peaks will get suppressed whereas the gap will persist. Therefore, we associate the two kinds of spectra with regions with coherent and incoherent Cooper pairs respectively. The normalized tunneling spectra only with coherence peaks can be fitted well within the BCS-$\Gamma$ formalism using Equ. (1). Figure 4-4(a-c) show the representative fits for the three different samples. In all the samples we observe $\Delta$ to be dispersed between 0.8-1.0 meV corresponding to a mean value of $2\Delta/k_B T_c \sim 12.7, 7.2$
and 6 (for $T_c \sim 1.65$ K, 2.9 K and 3.5 K respectively) which is much larger than the value 3.52 expected from BCS theory. Since $\Delta$ is associated with the pairing energy scale, the abnormally large value of $2\Delta/k_BT_c$ and the insensitivity of $\Delta$ on $T_c$ suggest that in the presence of strong disorder $\Delta$ is unrelated to $T_c$ thereby suggesting that it is not relevant energy scale determining $T_c$. On the other hand, $\Delta$ seems to be related to $T^* \sim 7$-8 K which gives $2\Delta/k_BT^* \sim 3.0\pm0.2$, closer to the BCS estimate. $\Gamma/\Delta$ is relatively large and shows a distinct increasing trend with increase in disorder. In contrast, spectra that do not display coherence peaks (Figure 4-4(d-f)) cannot be fitted using BCS-$\Gamma$ form for DOS. However, we note that the onset of the soft-gap in this kind of spectra happens at energies similar to the position of the coherence peaks. This shows that the pairing energy is not significantly different between points with and without coherence.

Since the coherence peaks are directly associated with phase coherence of the Cooper pairs, the height of the coherence peaks provides a direct measure of the local superconducting order parameter. This is consistent with numerical Monte Carlo simulations\(^3\) of disordered superconductors using attractive Hubbard model with random on-site disorder which show that the coherence peak height in the LDOS is directly related to the local superconducting OP, $\Delta_{OP}(R) = \langle c_{R\downarrow}c_{R\uparrow}\rangle$. Consequently, we take the average of the coherence peak height ($h = (h_1 + h_2)/2$) at positive and negative bias (with respect to the high bias background) as an experimental measure of the local superconducting OP (Figure 4-5).

![Figure 4-5. Representative normalized spectra for sample with $T_c \sim 2.9$K recorded at two different locations at 500mK. $h$ is the average of the coherence peak heights at positive ($h_1$) and negative bias ($h_2$), calculated with respect to line passing through high bias region (black line).](image_url)
4.6 Emergence of inhomogeneity in the superconducting state

To study the spatial evolution of superconducting order parameter we plot in Figure 4-6, the spatial distribution of $h$, measured at lowest temperatures in the form of intensity plots for six samples. Figure 4-6(a) is the colormap for the sample with $T_c = 11.9K$ acquired over $150 \times 150$ at $3.1K$ while Figure 4-6(b-f) shows the colormaps for the samples with $T_c = 6.4K$, $3.5K$, $2.9K$, $2.1K$ and $1.65K$ respectively, acquired at $500mK$ over $200 \times 200$ area. The plots shows that for sample with $T_c = 11.9K$, $h$ is uniform while with increasing disorder $h$ becomes progressively inhomogeneous. For strongly disordered samples (Figure 4-6(c-f)) we see large variation in $h$ forming regions where the OP is finite (yellow-red) dispersed in a matrix where the OP is very small or completely suppressed (blue). The yellow-red regions form irregular shaped domains dispersed in the blue regions. The fraction of the blue regions progressively increases as disorder is increased.

![Colormap of spatial evolution of $h$ for sample with $T_c$ = 11.9K, 6.4K, 3.5K, 2.9K, 2.1K and 1.65K respectively.](image-url)
To analyze the spatial correlations we calculate the autocorrelation function (ACF), defined as,

\[
\rho(\bar{x}) = \frac{1}{n(\sigma_h)^2} \sum_y (h(\bar{y}) - \langle h \rangle) (h(\bar{y} - \bar{x}) - \langle h \rangle)
\]  

(4.2)

Figure 4-7(d-f) shows the ACF plotted as a function of positions for the peak height maps showed in respective panels (a-c). We also plot the circular average of \(\rho(x)\) as a function of \(|\bar{x}|\) in Figure 4-7(g) which shows that the correlation length

![Figure 4-7. 2D Autocorrelation analysis (a-c) Colormap of h for three samples with \(T_c = 2.5K, 2.9K\) and 1.65K respectively. (d-f) Corresponding 2D Autocorrelations of h-maps plotted as function of positions x and y. (g) Radial average of the 2-dimensional autocorrelation function plotted as a function of distance for the three samples.](image-url)
becomes longer as disorder is increased. The domain size progressively decreases with
decrease in disorder and eventually disappears in the noise level for samples with $T_c \geq 6K$. From the length at which the ACF drops to the levels of the base line we estimate
the domains sizes to be 50 nm, 30 nm and 20 nm for the samples with $T_c \sim 1.65$ K, 2.9
K and 3.5 K respectively. The emergent nature of the superconducting domains is
apparent when we compare structural inhomogeneity with the $h$-maps. While the
defects resulting from Nb vacancies are homogeneously distributed over atomic length
scales, the domains formed by superconducting correlations over this disordered
landscape is 2 orders of magnitude larger.

4.7 Universal scaling of the order parameter
distribution

Previous section indicated that the OP, $h$, becomes progressively in-
homogeneous with increasing disorder and it has a large distribution. In this section we
analyse the statistical properties of OP. In Figure 4-8 we plot the histograms of $h$ for

![Histograms of coherence peak height $h$ for sample with $T_c$ = 11.9K, 6.4K, 3.5K, 2.9K, 2.1K and 1.65K. The plots show that with increasing disorder coherence peaks are suppressed and the distribution becomes wider.](image)
six samples with increasing disorder. From the plots we observe the distinct trend that the coherence peak heights continuously decreases with increasing disorder. For quantitative analysis we define the normalized local order parameter as,

\[ S_i = \frac{h_i}{\text{Max}[h]} \]  

(4.3)

Figure 4-9(a) shows the order parameter \(S\) distribution (OPD) for four samples with \(T_c = 1.65\text{K}, 2.9\text{K} \text{ and } 3.5\text{K} \text{ and } 6.4\text{K}\). We observe that for the sample with \(T_c = 6.4\text{K}\) OPD peaks around \(S = 0.4\). With increasing disorder this weight gradually shifts towards zero and also the OPD gets broadened. Similar distributions are obtained in the numerical simulations\textsuperscript{14} within both fermionic and bosonic models of disordered superconductor mapped onto directed polymer in finite dimension. It has also been shown in Ref [14] that by defining the new scaling variable given by logarithm of OP normalized to its variance, rescaled OPD for various disorder levels fall onto the single universal distribution. To see the similar relevance we introduce the new scaling variable,

\[ R_S = \frac{\ln S - \ln S_{typ}}{\sigma_S} \]  

(4.4)

where \(S_{typ} = \exp(\ln S)\) and \(\sigma_S^2 = \ln^2 S - \ln S^2\). When plotted the probability distribution for rescaled OP \(R_S\) (Figure 4-9(b)) we see that rescaled OPD for all the samples collapse onto a single curve showing universality of the OPD. The OPD is also

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**Figure 4-9.** (a) Order parameter distribution for four samples with \(T_c = 6.4\text{K}, 3.5\text{K}, 2.9\text{K}, 1.65\text{K}\). (b) The same data as in panel (a) plotted in terms of the rescaled variable \(R_S\). The solid line corresponds to the Tracy-Widom distribution.
in good agreement with Tracy-Widom (TW) distribution whose relevance is recently discussed in connection with directed polymer physics in finite dimensions\textsuperscript{15,16} although it deviates slightly for high values of $R_S$. Agreement between theory and experiments also confirms our correct identification of the local OP.

### 4.8 Temperature evolution of the inhomogeneous superconducting state in disordered NbN

This section focusses on temperature evolution of domain structure that is seen at the lowest temperature as the system is driven across $T_c$ into pseudogap state. At high temperatures coherence peaks get diffused due to thermal broadening and the $h$-maps can no longer be used as a reliable measure of the OP distribution. This problem is however overcome by tracking the ZBC value in the tunneling spectra to trace the

![Figure 4-10.](image)

Figure 4-10. (a)-(c) shows colormap of spatial evolution of $h$ for three samples, (d)-(f) show the corresponding colormap of ZBC ($G_N(V=0)$) and (g)-(i) show corresponding 2D histogram of $h$ and ZBC. Weak anticorrelation between $h$ maps and ZBC maps can be seen from the two maps and it is further evident from 2D histograms as we see the dense line with negative slope. The values of $T_c$ corresponding to each row for panels (a)-(i) are given on the left side of the figure.
temperature evolution of domains based on our observation of weak anticorrelation between $h$ maps and ZBC maps at lowest temperature as discussed below.

Figure 4-10(d-f) shows the surface plot of ZBC ($G_N(0)$) value (we will call it as ZBC maps here onward) for the three samples shown along with $h$-maps (Figure 4-10(a-c)). The domain patterns observed in $h$-maps can also be seen in ZBC maps. The ZBC maps show an inverse correlation with the $h$-maps: Regions where the superconducting OP is large have a smaller ZBC than places where the OP is suppressed. The cross-correlation between the $h$-map and ZBC map can be computed through the cross-correlator defined as,

$$I = \frac{1}{n} \sum_{i,j} \frac{(h(i,j) - \langle h \rangle)(ZBC(i,j) - \langle ZBC \rangle)}{\sigma_h \sigma_{ZBC}}$$

where $n$ is the total number of pixels and $\sigma_{ZBC}$ is the standard deviations in the values of ZBC. A perfect correlation (anti-correlation) between the two images would correspond to $I = 1(-1)$. We obtain a cross correlation, $I \approx -0.3$ showing that the anti-correlation is weak. Thus ZBC is possibly not governed by the local OP alone. This is also apparent in the 2-dimensional histograms of $h$ and ZBC (Figure 4-10(g-i)) which show a large scatter over a negative slope.

Using this weak anticorrelation we will now look into the temperature evolution of the domains that are formed at the lowest temperature as a function of temperature for the sample with $T_c \sim 2.9$ K. The bulk pseudogap temperature, $T^*$, was first determined for this sample by measuring the tunneling spectra at 64 points along a 200 nm line at ten different temperatures. Figure 4-11(a) shows the temperature evolution of the normalized tunneling spectra along with temperature variation of resistance. In principle $T^*$ is the temperature at which the normalized spectrum ZBC value is equal to conductance value at large bias in normalized spectra, i.e. $G_N(V = 0) \approx G_N(V \gg \Delta/e)$. Since this cross-over point is difficult to uniquely determine within the noise levels of our measurements, we use $G_N(V = 0)/G_N(V = 3.5mV) \sim 0.95$ as a working definition for the $T^*$. Using this definition we obtain $T^* \sim 7.2$ K for this sample.
Spectroscopic maps were subsequently acquired at 6 different temperatures over the same area as the one in Figure 4-10(e). Before acquiring the spectroscopic map we corrected for the small drift using the topographic image, such that the maps were taken over the same area at every temperature. Figure 4-11(b-g) show the ZBC maps as a function of temperature. Below $T_c$, the domain pattern does not show a significant change and for all points $G_N(V=0)/G_N(V = 3.5mV) < 1$ showing that a soft gap is present everywhere. As the sample is heated across $T_c$ Most of these domains continue to survive at 3.6K across the superconducting transition. Barring few isolated points...
the soft gap in the spectrum persist even at this temperature. At 6.9K, which is very close to $T^*$, most of the domains have merged in the noise background, but the remnant of few domains, originally associated with a region with high OP is still visible. Thus the inhomogeneous superconducting state observed at low temperature disappears at $T^*$.

Similar data as above is presented for the sample with $T_c = 3.5$K where we observe that some of the domains with large OP persists across the $T_c$ and very few all the way upto 5.3K (Figure 4-12.).

![Figure 4-12. Temperature evolution of the inhomogeneous superconducting state for the sample with $T_c = 3.5$K. (a) Temperature evolution of spatially averaged normalized tunneling spectra plotted in the form of intensity plot of $G_n(V)$ as a function of bias voltage and temperature. Resistance vs temperature (R-T) for the same sample is shown in white curve on the same plot. Pseudogap temperature $T^* \sim 7$ K is marked with the dotted black line on top of the plot. (b)-(g) Spatial variation of ZBC ($G_n(V=0)$) plotted in the form of intensity plot over the same area for six different temperatures.](image-url)
4.9 Discussion

We now discuss the implication of our results on the nature of the superconducting transition. In a clean conventional superconductor the superconducting transition, well described through BCS theory, is governed by a single energy scale, \( \Delta \), which represent the pairing energy of the Cooper pairs. Consequently, \( T_c \) is given by the temperature where \( \Delta \rightarrow 0 \). This is indeed the case for NbN thin films in the clean limit. On the other hand in the strong disorder limit, the persistence of the gap in the single particle energy spectrum in the pseudogap state and the insensitivity of \( \Delta \) on \( T_c \) conclusively establishes that \( \Delta \) is no longer the energy scale driving the superconducting transition. Indeed, the formation of an inhomogeneous superconducting state supports the notion that the superconducting state should be visualized as a disordered network of superconducting islands where global phase coherence is established below \( T_c \) through Josephson tunneling between superconducting islands. Consequently at \( T_c \), the phase coherence would get destroyed through thermal phase fluctuations between the superconducting domains, while coherent and incoherent Cooper pairs would continue to survive as evidenced from the persistence of the domain structure and the soft gap in the tunneling spectrum at temperatures above \( T_c \). Finally, at \( T^* \) we reach the energy scale set by the pairing energy \( \Delta \) where the domain structure and the soft gap disappears.

This picture is further supported by measurements of the superfluid phase stiffness \( (J) \) performed through low frequency penetration depth\(^{17}\) and high frequency complex conductivity \( (\sigma = \sigma'(\omega) - i\sigma''(\omega)) \)\(^{18}\) on similar NbN samples. Low frequency measurements reveal that in the same range of disorder where the pseudogap appears \( (T_c \leq 6K) \), \( J(T \rightarrow 0) \) becomes a lower energy scale compared to \( \Delta(0) \) (See Chapter 3 Figure 9). High frequency microwave measurements reveal that in the pseudogap regime the superfluid stiffness becomes strongly frequency dependent. While at low frequencies \( J (\propto \omega \sigma''(\omega)) \) becomes zero close to \( T_c \) showing that the global phase coherent state is destroyed, at higher frequencies \( J \) continues to remain finite up to a higher temperature (Figure 4-13), which coincides with \( T^* \) in the limit of very high frequencies. Since the probing length scale set by the electron diffusion length at microwave frequencies\(^{18}\) is of the same order as the size of the domains observed in STS, finite \( J \) at these frequencies implies that the phase stiffness continues to remains...
finite within the individual phase coherent domains. Similar results were also obtained from the microwave complex conductivity of strongly disordered InO$_x$ thin films$^{19}$.

### 4.10 Summary

We have demonstrated the emergence of an inhomogeneous superconducting state, consisting of domains made of phase coherent and incoherent Cooper pairs in homogeneously disordered NbN thin films. The domains are observed both in the local variation of coherence peak heights as well as in the ZBC which show a weak inverse correlation with respect to each other. The origin of a finite ZBC at low temperatures as well as this inverse correlation is not understood at present and should form the basis for future theoretical investigations close to the SIT. However, the persistence of these domains above $T_c$ and subsequent disappearance only close to $T^*$ provide a real space perspective on the nature of the superconducting transition, which is expected to happen through thermal phase fluctuations between the phase coherent domains, even when the pairing interaction remains finite. However, an understanding of the explicit
connection between this inhomogeneous state and percolative transport for the current above and below $T_c$ is currently incomplete\textsuperscript{20,21,22}, and its formulation would further enrich our understanding of the superconducting transition in strongly disordered superconductors.

We finally present the evolution of various energy scales as a function of disorder for NbN in the form of phase diagram\textsuperscript{23} in Figure 4-14. Superfluid stiffness $J$ was measured using two coil mutual inductance technique and converted to temperature scale using $J/k_B$. $T_c^{BCS}$ is obtained using the BCS relation,

$$T_c^{BCS} = \frac{\Delta(0)}{1.76k_B}$$  \hspace{1cm} (4.6)

![Figure 4-14](attachment:image.png)

Figure 4-14. Phase diagram of for strongly disordered NbN showing various temperature scales as a function of $k_F l$. $T_c$ is obtained transport measurement. $T^*$ is pseudogap temperature, $J/k_B$ is the superfluid stiffness converted into temperature scale. $T_c^{BCS}$ is obtained from BCS relation for superconducting transition temperature and ground state energy gap $\Delta(0)$.

where $\Delta(0)$ is ground state superconducting energy gap obtained by fitting tunneling spectra using DOS given by equ. (4.1). It is instructive to note that in the range of disorder where pseudogap appears, $T_c^{BCS}$ is close to $T^*$ as expected from BCS
theory. In the same range of disorder $J/k_B$ is smaller than $T_{c}^{\text{BCS}}$ showing that the superconducting transition is governed by phase fluctuations. Our conclusion is that energy scale determining $T^*$ is $\Delta(0)$ whereas the energy scale determining $T_c$ minimum of either of $\Delta(0)$ and $J$.

4.11 References


Chapter 4. Emergence of inhomogeneity …


Chapter 4. Emergence of inhomogeneity …


Chapter 5

Summary and Future Directions

In this thesis we have explored the role of disorder on the superconducting properties of NbN, which is a conventional s-wave superconductor. The study was mainly carried out through the scanning tunneling microscopy and spectroscopy measurements with its unsurpassed power to probe the local superconducting order parameter.

The results of all our investigations over past six years, including transport and \( \lambda \) measurements, has been summarized in the following phase diagram where all the energies are converted into temperatures and plotted as a function of disorder.

![Figure 5-15. Phase diagram of NbN showing various energy scales converted into temperatures and plotted as a function of \( k_F l \).](image-url)
Chapter 5. Summary and Future directions

The critical temperature $T_c$ represented by black circles\(^1\) decreases with increasing disorder and becomes zero at $k_F l \sim 1$. Thus the zero resistance state is seen in the half dome, shaded with grey colour and bounded by $T_c$ line. The superfluid stiffness, $J/k_B$, is represented by red line\(^2,3\), decreases very rapidly with increasing disorder. $T_c^{BCS}$ is the expected transition temperature calculated using the BCS relation\(^4\)

$$\Delta(0) = 1.76 k_B T_c^{BCS}.$$ 

In the intermediate disorder regime ($k_F l > 2.7$), $J/k_B > T_c^{BCS}$ and therefore the transition in this regime is governed by vanishing of the energy gap as described by BCS theory. We indeed see in the tunnelling spectra that the gap vanishes exactly where the resistance appear and the spectra can be fitted with the BCS density of states for all the temperatures.

In the strong disorder regime ($k_F l \leq 2.7$), $J/k_B \leq T_c^{BCS}$ and the formation of pseudogap state, together indicates that here the superconductivity is suppressed through phase fluctuations while the pairing remain finite all the way upto the temperature $T^*$. This scenario is further confirmed through the close resemblance of $T_c^{BCS}$ with the $T^*$.

For the strong disorder regime we proposed that the coherence peak height represents a measure of the local order parameter (OP) and showed that it has universal distribution irrespective of disorder strength. With this OP we observed the emergence of inhomogeneous domains with large OP separated by regions of small OP. This emergent inhomogeneity is seen over the length scale of few tens of nanometer while the structural disorder is uniformly distributed over the atomic scale. We have also demonstrated that these inhomogeneous domains that are formed at the lowest temperature evolve smoothly with temperature across $T_c$ and persists all the way upto $T^*$.

For $k_F l < 1$, MR data indicated the superconducting correlations persisting upto the temperatures close to $T^*$ (Magenta circles), therefore it would be interesting to explore this regime using STS to see whether the gap in the tunnelling spectra is also seen\(^5\).

Finally it will be interesting to study spatially resolved STS measurements in presence of magnetic field at various levels of disorder which will help us explore the
recent propositions on formation of superconducting island on the insulating side of the SIT. This would ultimately help us understand better the nature of disordered driven SIT.

References


