Size Effects in Nanostructured Superconductors

A Thesis

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By

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Dedicated to my parents.....
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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.

This work was done under the guidance of Professor Pushan Ayyub, at Tata Institute of Fundamental Research, Mumbai.

Sangita Bose

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. Pushan Ayyub
Date:
Statement regarding 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. Pushan Ayyub. Most of the experiments have been conducted by me in TIFR. The results of the major portions of the work presented in this thesis have already been published in refereed journals.

Some of the work presented in this thesis was performed in collaboration with other researchers. The nanostructured Nb films were synthesized at Ohio State University by Prof. Rajarshi Banerjee and his students. The microstructural characterization of the nanostructured Nb and Pb films by transmission electron microscopy (TEM) was also done at the University of North Texas and Ohio State University by Prof. Rajarshi Banerjee and his students. Some of the low temperature work involving Point contact spectroscopy and susceptibility measurements were done in collaboration with Dr. Pratap Raychaudhuri of the Department of condensed matter physics and material science at TIFR. The microstructural characterization by scanning electron microscope (SEM) of the Pb-Ag nanocomposite films was carried out by Dr. Heinrich Jaksch at the Carl Zeiss SMT in Germany. The bi-phasic Pb-Sn nanoparticles dispersed in the Al matrix were synthesized by Victoria Bhattacharya under the guidance of Prof. Kamanio Chattopadhyay at the Indian Institute of Science, Bangalore. The structural characterization of these samples by TEM were also been done at IISC by her.
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I will also like to thank my collaborator, Prof. Rajarashi Banerjee, who had initially synthesized the nanostructured Nb films, which initiated my thesis work on nanostructured superconductors. I will also like to thank him for carrying out the transmission electron microscopy and electron energy loss spectroscopy on the Nb and Pb films which formed a very important part in understanding the microstructure of these samples. I have also gained a lot from the long discussions with him regarding various aspects of structural properties of nanostructured materials.

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Synopsis

This thesis deals with the experimental study of elemental superconductors at reduced dimensions. It is organized as follows. I will first introduce the topic of nanoscale-superconductivity in Chapter 1. I will discuss how length constraints influence the superconducting order parameter both in pure elemental superconductors and also the behavior of superconductors in proximity with normal metals or other superconductors with lower $T_c$. Thereafter in Chapter 2, I will describe the various experimental techniques used. This chapter includes the synthesis of nanostructured films, their morphological characterization and finally the methods employed to measure the different superconducting properties. In Chapter 3, I will present our studies of the size effects on the superconducting and the normal state properties of the intermediate coupling, type II superconductor, Nb. This will be followed by a similar study of the superconducting properties of a strong coupling superconductor, Pb, as a function of grain size in Chapter 4. Our results will elucidate the mechanism controlling $T_c$ in nano-superconductors. Finally, in Chapter 5, I will discuss our results on the study of the superconducting proximity effect in Pb-Ag nanocomposites and Pb-Sn bi-phasic nanoparticles embedded in an Al matrix. Our results show that the theory of superconducting proximity effect formulated for bilayers and multilayers can be modified to explain the observed changes in $T_c$ in these random, 3D systems. A brief description of the contents of each chapter is given below.

1. Introduction

It is important to know the ground state properties of a superconductor when its effective dimensions become less than the characteristic length scales, such as the penetration depth ($\lambda_L$) and coherence length ($\xi_0$). There are many studies of superconducting systems at reduced dimensions, such as thin films (2D), nanowires (1D) and granular materials (0D). In homogenous, atomically flat superconducting thin films grown by quench condensation one observes a gradual decrease in $T_c$ with decreasing thickness (below ~10nm), which has been attributed to the decrease of the amplitude ($\Psi_0$) of the superconducting wave function ($\Psi = \Psi_0 e^{i\phi}$, $\phi$ being the phase of the superconducting wave function). In inhomogeneous, quench condensed, granular thin films, no decrease in $T_c$ is observed but a superconductor-to-insulator transition occurs at a critical thickness. In the insulating state of these films the individual grains remain superconducting while the macroscopic superconductivity of the
film is destroyed because of phase de-coherence between the individual grains. In superconducting 1D nanowires, though $T_c$ does not change much when the diameter is below the coherence length, superconducting and thermal fluctuations cause novel phenomena like phase slip centers which give finite resistance at temperatures below $T_c$. In zero-dimensional superconductors too, superconductivity is known to persist at dimensions lower than $\xi_0$ and $\lambda_L$. In fact, Anderson had predicted in 1959 that there is a third length scale that controls the superconducting order parameter in nano-superconductors. According to the Anderson criterion, there will be complete destabilization of superconductivity for grain sizes at which the energy level spacing (arising from quantum size effects in small particles) becomes equal to the superconducting energy gap, $\Delta(0)$. This criterion has since been experimentally verified in many elemental superconductors. However, the mechanism controlling the variation of the superconducting $T_c$ with grain size has remained debatable. In weak coupling Type I superconductors like Al, Sn and In, an increase in $T_c$ has been observed while no change (or a small decrease) in $T_c$ has been observed in the strong coupling Pb. There are two alternative mechanisms to explain the variation of the superconducting transition temperature in finite size superconductors.

According to the first mechanism, the changes in $T_c$ occur due to surface effects caused by a reduction in the phonon frequencies (phonon softening) arising from the larger surface to volume ratio in nanoparticles. This leads to an increase in the electron-phonon coupling constant ($\lambda$), thereby increasing the $T_c$. The second mechanism for the size dependence of $T_c$ is related to quantum size effects arising from the quantization of the electronic wave vector ($k$). With decreasing grain size, there is a discretization of the energy levels, which has been shown to decrease the effective density of states. According to the BCS relation, this would result in a decrease in $T_c$ with decreasing grain size. However, it should be noted that this mechanism will cause a proportionate effect on $T_c$ and $\Delta(0)$ and will therefore not change the electron-phonon coupling strength ($\lambda$).

Thus, a complete understanding of the mechanism influencing $T_c$ in nano-superconductors requires one to determine the size dependence of the coupling constant ($\lambda$). It should be noted that the superconducting properties like $T_c$, $\Delta(0)$ and the critical fields ($H_C$) are interrelated parameters. Hence, the understanding of superconductivity at reduced length scales cannot be complete without a detailed study of each of these properties with reducing grain size. With this in mind, we carried out a systematic study of the superconducting properties such as $T_c$, $\Delta(0)$ and $H_C$ as a function of grain size in two types of elemental
superconductors: Nb and Pb, which have different coupling strengths ($\lambda$). The coupling strength is characterized by the quantity $2\Delta(0)/k_B T_c$, which ranges from 3.1 in weak coupling superconductors (Al, Sn, etc.) to 4.4 in strong coupling ones like Pb. For Nb: $2\Delta(0)/k_B T_c \sim 3.8$, making it an intermediate coupling, Type II superconductor.

Superconducting proximity effect in nanocomposites and nano-grains embedded in a normal metal or superconducting matrix forms yet another interesting problem in nano-superconductivity. The theory of superconducting proximity effect was established for bilayers and multi-layers way back in 1960.\(^5\) According to this theory, when a superconductor is in close proximity with a normal metal or another superconductor with a lower $T_c$, then the superconducting wave function may penetrate across the interface into the normal metal and a pair-breaking effect on the Cooper pairs is felt in the superconducting side. This phenomenon is observed when the thickness of the normal metal and the superconductor are both less than their respective coherence lengths ($\xi_{N,S} = [\hbar D_{N,S}/2\pi k_B T]^{1/2}$). Here, $D_{N,S}$ are the diffusivities of the normal/superconducting layers respectively. This is known as the “Cooper Limit”.\(^6\)

The coherence length of most elemental superconductors ranges between few tens of nm to a few hundred nm. Hence, very thin films are needed to study this phenomenon which makes the synthesis complicated. We aimed to probe the effect of length constraints in all three dimensions in nanocomposites and random mixture of nanograins of superconductors and normal metals. Is the theory of superconducting proximity effect for 2D films valid in such cases? If it is, then which is the relevant parameter that determines the $T_c$ in such random mixtures? With this in mind, we carried out a study of superconducting proximity effect in two different types of 3D random mixture systems. We have studied the $T_c$ of both these systems in the framework of the superconducting proximity effect (SPE) as valid for bilayers and multilayers.

2. Experimental Details

In this section I will discuss the experimental techniques used for the synthesis of the nanocrystalline films and bulk samples used in this study, the various structural characterization tools and the techniques for measuring the superconducting $T_c$, the normal state transport properties, the critical fields ($H_{c2}$) and the energy gap ($\Delta(0)$) of the superconducting samples.
2.1 Synthesis
High pressure DC magnetron sputtering was used to synthesize the metallic nanocrystalline thin films. Relatively high sputtering pressures (100-400mtorr) and low substrate temperatures (80-300K) aid the formation of small grains. In general, process parameters such as the sputtering gas pressure, the substrate temperature, the sputtering power and the deposition time control the particle size in the nanocrystalline films.

2.2 Characterization
The samples were characterized by x-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), electron energy loss spectroscopy (EELS) and energy dispersive x-ray absorption (EDAX). The grain size was determined from x-ray line profile analysis (correcting for the instrumental broadening and contribution from the Kα2 line) using the XFIT and WINFIT programs. The grain size was also independently determined from TEM, which matched quite closely with that obtained from XRD. The morphology, chemical analysis and chemical composition were determined from HRTEM, EELS and EDAX.

2.3 Superconducting and Normal state properties
Different techniques like DC and AC magnetization, AC susceptibility, DC transport (sometimes in presence of magnetic field), point contact spectroscopy and planar tunneling spectroscopy were used to measure the superconducting properties like Tc, Hc and Δ(0). The normal state property has been determined by DC transport. I will briefly describe each technique.

2.3.1 DC Magnetization: DC magnetization was measured in a commercial MPMS SQUID magnetometer and a commercial Oxford vibrating sample magnetometer (VSM). In SQUID the lowest temperature and the highest field attainable are 1.8K and 7T respectively. In the VSM the lowest temperature and the highest field are 1.6K and 12T respectively.

2.3.2 DC Transport: This was done using the standard 4 probe method in a custom built set up where the lowest temperature and the highest field attainable are 2K and 8T respectively.

2.3.3 AC susceptibility: This was done in a home built set up where the measurement probe consisted of two planar coils between which the sample is sandwiched. When the sample is in its normal state, the secondary coil detects a signal induced from the primary coil. However, as soon as the sample becomes superconducting, all flux lines get shielded by the sample, which is in the Meissner state. Hence, a sharp drop in signal is observed at the superconducting transition. Though it cannot give the absolute value of the magnetization, it
is a powerful method to detect a superconducting transition, especially in thin films (where the volume of the sample is very small). It should be noted that in conventional AC susceptibility, the signal is proportional to the volume of the sample and hence provides weak signals for thin films. The planar coil technique was used to measure $T_c$ and $H_c$ of the superconducting films.

2.3.4 Point Contact spectroscopy: The Point Contact Andreev Reflection (PCAR) technique was used to measure the superconducting energy gap of the Nb films. It was also done in a custom built set up where a fine tip of a normal metal (Pt-Ir) was brought in contact with the superconducting sample at low temperatures and the differential conductance of the junction was measured vs. the bias voltage by the standard AC modulation technique. An electron incident at a normal metal superconductor interface with energy less than the superconducting energy gap gets reflected back as a hole, transmitting a Cooper pair in the process. This causes a doubling of conductance at energies below the superconducting energy gap. To get energy resolved information, the contact needs to be in the ballistic regime (contact diameter should be less than the mean free path of the electrons). This was obtained by changing the pressure on the contact and analyzing the spectra obtained for each contact.

2.3.5 Planar tunnel junctions: This was fabricated to measure the superconducting energy gap of the Pb films. As Pb is a very soft metal, establishing a ballistic contact for point contact measurements was difficult. The tunnel junction device was prepared in the following way. A longitudinal strip of Al was sputtered at the center of a glass slide (substrate) using an appropriate mask. Subsequently the film was exposed to air for 15-20 min. so that surface oxidation takes place. Cross strips of Pb (using proper masks) were then sputtered on this forming the tunnel junction device. For small particles of Pb, an overlayer of Si (~40nm) was deposited in situ over the Pb film to prevent oxidation. The so formed junction area was $0.1 \times 0.2 \text{ cm}^2$.

3. Size effects on the normal and superconducting properties in the intermediate coupling Type II superconductor: Nb

3.1 Synthesis and Structural Properties: The nanostructured Nb films were synthesized by high pressure magnetron sputtering, in which the process parameters like power, inert gas pressure, substrate temperature and time of deposition were controlled to vary the grain size in the 5-60nm range. The nanostructured Nb films are textured along the [110] direction. The strain corrected grain size ($d_{XRD}$) was determined from x-ray line profile analysis. The upper
limit to the width of the size distribution was also obtained from the XFIT software and found to be ~20%. The grain size independently obtained from TEM matched quite closely with that from XRD. Careful HRTEM studies show that there is an increase in the grain boundary width with decreasing \( d_{\text{XRD}} \), which was used to understand certain properties of the Nb films. HRTEM and EELS data obtained from the grains and the grain boundary region of the films show that the grain boundary region for films with \( d_{\text{XRD}} < 20 \) nm consist of an amorphous Nb-O phase. Thus, the nanostructured Nb films consist of superconducting grains separated by insulating grain boundaries and behave as a random dispersion of weakly connected Josephson junctions. This was further verified by electrical transport measurements.

Nb shows a lattice expansion (~6%) as \( d_{\text{XRD}} \) decreases from 60 to 5nm (Fig. 1). We have tried to understand this on the basis of a linear elasticity model. According to this model, the excess free volume of the grain boundaries produces an internal stress field within the grains, which causes the lattice expansion. We tried to fit our lattice expansion data with equations obtained for a polycrystalline model consisting of square crystallites with orthogonal set of grain boundaries. Interestingly, we found that the experimental curve cannot be simulated using a single grain boundary width (\( \delta \)). However, if we use a grain size dependent grain boundary width of the form: 

\[
\delta = 0.48 + 1.86 \exp(-0.14d_{\text{XRD}}),
\]

we can simulate the experimental curve very closely (see Fig. 1, inset). A broadening of the grain boundaries with decreasing size is corroborated by HRTEM. Bright field TEM images of the large grain samples show that the Nb grains are closely packed with very sharp interfaces while samples with \( d_{\text{XRD}} < 20 \) nm show the presence of thicker grain boundaries. The 5nm sample shows a grain boundary width as large as ~1nm. We will show later that the dependence of \( \delta \) on \( d_{\text{XRD}} \) influences the normal state transport.

### 3.2 Superconducting and normal state properties

#### 3.2.1 Mechanism for size-dependence of the transition temperature (\( T_c \)):

The \( T_c \) of the nano Nb films was measured by both dc magnetizations using a SQUID magnetometer and dc electrical transport. There is no change in \( T_c \) from its bulk value ~9.4K, down to a size of 28nm. Between 28nm to 8nm, there is a decrease in \( T_c \) from 9.4 to 4.7K (see Fig. 2) and
below 8nm the films become non-superconducting, which is consistent with the Anderson criterion. The $T_c$ values obtained from magnetization and transport are in close agreement.

In order to understand the decrease in $T_c$ with $d_{\text{XRD}}$, we measured $\Delta(0)$ for samples with different grain size by using Point Contact Andreev Reflection (PCAR) spectroscopy. The point contacts on nano-Nb films were made with a mechanically cut Pt-Ir tip. The value of $\Delta(0)$ was determined by fitting the PCAR spectra with the Blonder-Tinkham-Klapwijk theory. We observe a direct correlation between $T_c$ and $\Delta(0)$ (Fig. 3) with a slope of $2\Delta(0)/k_B T_c \sim 3.6$, which clearly indicates that Nb remains in the intermediate coupling limit down to the smallest size. This is also confirmed by the observed temperature variation of $\Delta(0)$ which can be fitted well (for all sizes) with the behavior expected from the weak coupling BCS theory.

The two mechanisms generally used to explain the change in $T_c$ are based on (a) phonon softening and (b) the changes in the electronic density of states (DOS). Phonon softening is the possible reason for the observed increase in $T_c$ in the weak coupling Type 1 superconductors like Al, Sn, In etc. This mechanism would lead to an increase in $2\Delta(0)/k_B T_c$ with decreasing size. To investigate the changes in DOS due to quantization of the electronic wave vector, the BCS equation is solved invoking the discretization of the energy levels. This shows that there is a depression in $T_c$ through the decrease in DOS at the Fermi level, $N(0)$. $\Delta(0)/T_c$ would remain constant with size as this mechanism has an equal effect on both $T_c$ and $\Delta(0)$. The linear relation between $\Delta(0)$ and $T_c$ seen in our films strongly indicate that the changes in the electronic density of states play a dominant role in nano-Nb while the effect of phonon softening is negligible.

3.2.2 Size dependence of the upper critical field ($H_{C2}$): In order to see if the suggested decrease in the DOS with decrease in $d_{\text{XRD}}$ in nano Nb is consistent with other superconducting properties, we carried out the measurements of the upper critical field ($H_{C2}$) and the irreversibility fields ($H_{irr}$). These were determined from a magneto-transport measurement using the standard four probe method. $H_{C2}$ was taken to be the field at which $2\Delta(0)/k_B T_c \sim 3.6$
the resistance dropped to 90% of the normal state resistance ($R_N$), while $H_{irr}$ was taken as the field at which the resistance dropped to 0.1$R_N$. $H_{irr}$ was independently determined using the planar coil AC susceptometer. The value was taken as the field at which the imaginary part of susceptibility showed a dip. $H_{irr}$ observed from both methods matched quite closely. The critical fields were measured with the nano Nb films both parallel and perpendicular to the external magnetic field. No orientation dependence was visible, showing that the Nb films essentially behave as 3D nanostructured films. The H-T phase diagrams were plotted to get the extrapolated $H_{C2}(0)$ values. Interestingly, nano Nb films show a large increase (2.3 times) in $H_{C2}$ and $H_{irr}$ as the grain size is reduced from 60 to 20nm (Fig. 4). We expect a decrease in $\xi_{GL}(0)$ with decreasing $L_{eff}$ (smaller grain size), which would result in increased $H_{C2}$. However, below 20nm, we observe a decrease in $H_{C2}$. From the WHH theory\textsuperscript{14} $H_{C2}$ is related to the normal state resistivity, $\rho_N$, through the expression
\[
H_{C2}(0) = 0.69T_c \frac{4 e \rho_c}{\pi} N(0) \rho_c \quad \text{where } N(0) \text{ is the DOS at Fermi level. Thus as long as there is no appreciable change in N(0) and } T_c, \text{ } H_{C2} \text{ should increase with increasing } \rho_N. \text{ As shown in the previous section, the } T_c \text{ decreases drastically below 20nm due to a decrease in N(0), though } \rho_N \text{ increases monotonically. Hence, below 20nm, the increase in } \rho_N \text{ is offset by the decrease in N(0), which explains the non-monotonic behaviour of } H_{C2} \text{ with grain size in nanostructured Nb.}
\]

3.2.3 Size induced metal-insulator transition in nanostructured Nb: The effect of inter and intra granular transport: Since the normal state properties are intricately related to the superconducting properties (e.g. $\rho_N$ and $H_{C2}$), we will here describe the normal state transport properties of nano-Nb.\textsuperscript{15} The temperature variation of resistivity for the films with grain size ($d_{\text{XRD}}$) between 5-60nm is shown in Fig. 5. (The scale to the left is for samples with $d_{\text{XRD}} \geq 8$nm while the right is for $d_{\text{XRD}} < 8$nm). There is a metal to insulator transition at the grain size of 8nm. The resistivity of the films with $d_{\text{XRD}} < 8$nm shows a weak activated behaviour (as in a semiconductor). These films are non-superconducting consistent with the Anderson criterion. To understand the origin of the negative temperature coefficient of resistance (TCR) we attempted to fit the $\sigma$–$T$ curves ($d_{\text{XRD}} < 8$ nm) with an activated transport behaviour. Since fitting with a single exponential was not satisfactory, we used the empirical trial function: $\sigma = \sigma_0 + A \exp(-E_{g1}/k_B T ) + B \exp(-E_{g2}/k_B T )$, where $\sigma = \rho^{-1}$. The activation
energies \( (E_{g}) \) and the proportionality constants A and B are used as best-fit parameters. The fit of the data to this equation produced satisfactory results for all the samples, (see the solid curves in Fig. 6) down to the lowest temperature (4.2 K). The physical basis for the two activation energies \( (E_{g1} \) and \( E_{g2} \)) is as follows. Both \( E_{g1} \) and \( E_{g2} \) increase monotonically with decrease in size. Since the lower energy \( E_{g1} \) obtained from the fit matches with the calculated Kubo gaps, we can associate \( E_{g1} \) with the discretization of the energy levels in small particles that arises purely from intra-granular transport. However, this manifests itself at very low temperatures and is not responsible for the insulating nature close to room temperature. The HRTEM of the films with smaller grains indicate that the grains are separated by a thicker insulating grain boundary compared to the larger grain samples (\( d_{XRD} > 8\text{nm} \)). Thus, with decreasing size, a potential barrier opens at the grain boundary which has to be overcome by the electrons. This inter-granular transport dominates at high temperatures and is responsible for \( E_{g2} \). Thus, our results show that both inter and intra-granular transport in nano Nb with \( d_{XRD} < 8\text{nm} \) are responsible for the size induced metal-insulator transition. It is also interesting to note that at 7nm, the \( E_{g2} \) is of the order of the superconducting energy gap of Nb (~1.5meV). Since, at this particle size, Nb becomes non-superconducting, this validates the Anderson’s criterion for the destruction of superconductivity with decreasing particle size.

4. Size effects on the superconducting properties in the strong coupling Type I superconductor: Pb

4.1. Synthesis and structural properties: The nanostructured Pb films were synthesized by high pressure DC magnetron sputtering. As Pb is highly prone to oxidation, we put an overlayer of Si, approximately 40nm thick on the Pb films in situ. This protected the films from oxidation over many days. The nanostructured Pb films were characterized by XRD,
TEM and EDAX. The grain size, determined from an x-ray line profile analysis, varied between 5-60nm. The thickness of the films was between 200-400 nm.

4.2 Size dependence of Superconducting properties

4.2.1 Mechanism influencing small change in $T_c$ down to 7nm: The $T_c$ of the nano-Pb films as obtained from both DC transport and AC susceptibility matched quite closely. The $T_c$ showed a small decrease (~10%) from the bulk value of 7.25K as the grain size is reduced from 60nm to 7nm. Below 5nm, the films became non-superconducting, as predicted by the Anderson criterion [Fig. 7(a)]. The superconducting energy gap of the films was determined from tunneling spectroscopy after fabrication of tunnel junctions. The temperature dependence of the bulk Pb film ($d_{XRD} \sim 60$nm), shows a BCS like variation with $2\Delta(0)/k_B T_c \sim 4.4$. However, with decreasing grain size there is a deviation from the BCS theory [Fig. 7(b)] indicating that Pb goes to an even stronger coupling limit with reduction in grain size. This shows that there is considerable “phonon softening” in nano Pb. However, as discussed previously, this should lead to an increase in $T_c$ with decreasing grain size, which is contrary to our observation. Thus, our data indicate that the phonon softening effect is offset by some other effect. Pb being a strong coupling superconductor, the quantization of the phonon wave vector with decreasing grain size will make the low frequency cut off shift to higher frequencies. Moreover, the discretization of the energy levels and subsequent decrease in the electronic density of states could also offset the increase in $T_c$ due to increased electron-phonon coupling, giving almost no change in $T_c$ with reduction in grain size in Pb. Fenton et al. have shown that yet another factor can give the observed null effect in $T_c$. They have shown from a detailed analysis of the Eliashberg theory for fine particles of Pb that a null effect in $T_c$ accompanied by a small increase in $\Delta(0)$ can occur only if it is assumed that the electron-phonon coupling in the bulk is equal to that in the surface. More detailed theoretical work is needed for a better understanding of the situation.
4.2.2 Enhancement of $H_{C2}$ with decreasing particle size: Pb shows a monotonic increase in $H_{C2}$ with decreasing grain size [Fig. 8]. This observation is consistent with the WHH theory which predicts an increase in $H_{C2}$ with decreasing grain size (increasing $\rho_N$) as long as there is no change in $T_c$ and $N(0)$. In nano-Pb, there is a very small (~10%) change in $T_c$ as grain size is reduced from 60-7nm, unlike in the intermediate coupling superconductor, Nb. Hence, we observe a monotonic increase in $H_{C2}$ (~3.6 times) as grain size is reduced from 60-7nm.

5. Superconducting proximity effect in biphasic nanostructured systems

5.1 Superconducting / normal metal nanocomposites – Random distribution of Pb and Ag nanoparticles

5.1.1 Synthesis and characterization: Biphasic Pb-Ag nanocomposite films were synthesized by co-sputtering of Pb and Ag. The growth conditions were controlled to keep the grain size of both Pb and Ag less than the coherence length of Pb (80nm). The composition was varied by the synthesis conditions. The grain size was estimated from the x-ray line profile analysis and SEM. High resolution SEM shows local distribution of the Pb and Ag grains such that they indeed form a random nanocomposite. The elemental composition was obtained from EDX.

5.1.2 Results and discussions: There was a decrease in $T_c$ (measured by planar coil AC susceptibility) from the bulk value of 7.2K to 5.1K in the nanocomposite films as the atomic % of Pb changed from 100 to 63%. Films with < 20% of Pb were non-superconducting. To see if $T_c$ is dependent on the grain size of Pb, we grew films with approximately the same Pb (~85%) but with the grain size of Pb varying between 60-20nm. The $T_c$ was found to remain the same (~6.7K). Hence, it is the ratio of the volume fractions of the two components in the nanocomposites, and not the grain size that plays the dominant role in controlling $T_c$. The theory of proximity effect valid for bilayer systems has been modified by Sternfeld et al\textsuperscript{17} who have shown that the parameter influencing $T_c$ in random mixtures (with typical grain size $d<<\xi_{S,N}$) is the ratio of volume concentrations $P_S/P_N$ (rather than $t_S/t_N$) where $P_{S,N}$ is the fractional volume concentration and $t_{S,N}$ is the thicknesses of the superconductor and normal metal. Hence the equation of proximity effect for a strong coupling superconductor ($\lambda>1$) in contact with a normal metal assumes the modified form:
\[
\ln(1.45 T_c) = \frac{\lambda_S \ln \omega_{DS} + \lambda_N \ln \omega_{DN} \alpha(P_N / P_S)}{\lambda_S + \lambda_N \alpha(P_N / P_S)} - \frac{\lambda_S + 1 + (\lambda_N + 1) \alpha(P_N / P_S)}{\lambda_S - \mu^* - (\lambda_N - \mu^*) \alpha(P_N / P_S)}
\]

For a weak coupling superconductor (\(\lambda < 1\)) in contact with a normal metal, the modified equation is:

\[
\ln\left(\frac{T_c}{1.14 \Theta_D}\right) = -\frac{1 + \alpha(P_N / P_S)}{N_S(0)V}, \quad \text{where } \lambda \text{ is the electron-phonon coupling constant, } \mu^* \text{ is the repulsive Coulomb coupling constant, } \Theta_D \text{ the Debye temperature, } N(0) \text{ the density of states at the Fermi level, } V \text{ the attractive potential, and } \alpha \text{ the ratio of density of states of the N and S components.}
\]

We have calculated the \(T_c\) for the Pb-Ag nanocomposite using known parameters, under both the weak coupling and the strong coupling limits. Figure 9 shows the experimental points (solid circles), the theoretical curve from strong coupling theory (dashed line) and the curve obtained from the weak coupling theory (solid line). Clearly, there is a good match between the weak coupling theory and experiment. Hence, our results show that 3D random mixture of a S-N metal nanocomposite follow the de Gennes theory of proximity effect with \(P_S/P_N\) being the relevant parameter that controls \(T_c\). It also shows that Pb which is normally a strong coupling superconductor behaves as a weak coupling superconductor when randomly distributed with a metal with weak electron-phonon interaction.

**5.2 Biphasic superconducting nano grains (Pb-Sn) in bulk superconducting (Al) matrix**

**5.2.1 Synthesis and characterization:** A random dispersion of Pb-Sn composite biphasic particles (with 54 atomic % Pb) in an Al matrix was prepared by rapid melt quenching of the ternary Al-Pb-Sn melt. The melt phase separates during cooling, yielding nanodroplets of Pb-Sn binary melt. The size of the Pb-Sn composite particles varies between 5 and 300nm with the mode at 20nm. The distribution is markedly skewed and has a long tail at larger sizes. The volume-weighted mean size is \(\approx 100\) nm.

**5.2.2 Results and discussions:** The biphasic (Pb-Sn) particles nanodispersed in Al exhibited a \(T_c\) of \(-3.1\)K, which is much lower than the bulk \(T_c\) of either Pb (7.2K) or Sn (3.7K). Hence, proximity effect between Pb and Sn alone cannot explain the observed \(T_c\). We show that it is
essential to take account of the effect of the Al matrix in proximity with the composite to explain our observations.\textsuperscript{19}

We will first investigate how the proximity effect between Pb and Sn affects the $T_c$ of the system. For the Pb-Sn nanocomposite with 54 atomic % of Pb, we can find the volume per cent of each component within a single grain of a specific size and hence obtain the ratio of the thickness of each component within the grain assuming a cuboid geometry. TEM data indicates that this assumption is reasonable. Then, using the theory of proximity effect for strong coupling superconductors, $T_c$ is evaluated for the Pb-Sn nanocomposite as a function of the volume % of Pb. (Fig. 10). For 57% by volume of Pb, the $T_c$ is expected to be 6.16K, which is much higher than that experimentally obtained. Thus it is clear that the Al matrix ($T_c = 1.17$ K) must significantly influence the effective $T_c$ of the system.

We know that the total amount of Pb+Sn nanocomposite phase in the Al matrix is about 2% by volume. For all practical purposes, the Al matrix can therefore be taken to be of infinite extent with respect to the Pb+Sn composite grains of average size $\approx 20\,\text{nm}$. We can then compare the above situation to the case where a thin superconducting metal is in contact with a thick normal / superconducting metal (of lower $T_c$) and find out how proximity effect influences the effective $T_c$ of such a system.

Using Werthamer’s theory of proximity effect, we calculate the $T_c$ of the system as a function of the grain size of the biphasic nanodroplets. We have taken the $T_c$ of the Pb+Sn nanocomposite to be 6.16K, as obtained from our previous analysis. The Fermi velocity of the composite was taken as the weighted average of the Fermi velocities of Pb and Sn, and the mean free path is assumed to be limited by the grain size (i.e., $l_s \approx D_S$). The resulting plot of $T_c$ vs. grain size for the Pb+Sn nanocomposite dispersed in Al, is shown in Fig. 11. It is clear that the distribution in grain size (as is the case in our system) will result in a distribution in the $T_c$. However, the actual onset of superconductivity is expected to be governed by the larger particles since the volume average lies close to 100nm. We do find a
distribution in $T_c$, though the observed onset is slightly higher than that predicted from the theory. However, the prediction from proximity effect is quite satisfactory in view of the rather gross assumptions made in the estimation of the Fermi velocity and the mean free path. Thus, we have shown that the proximity of the Al matrix plays a major role in determining the $T_c$ of the biphasic nanocomposites of Pb+Sn dispersed in the Al matrix.

6. Conclusions

We have studied finite size effects on the superconducting properties of two well known elemental superconductors: Nb and Pb. Our results show that the variation of the $T_c$ in the two systems is quite different since the dominant mechanism controlling the size dependence is not the same. This has been elucidated by a careful experimental measurement of the size dependence of the superconducting energy gap in the two systems. The decrease in $T_c$ in Nb is attributed mainly to the changes in the density of states at the Fermi level with decreasing grain size. In Pb, on the other hand, there are strong competing effects from phonon softening (manifested by an increase in the coupling strength) and the decrease in the density of states. However, the variation of $H_{C2}$ with grain size in both these systems is consistent with the WHH theory. In both systems, there is a substantial increase in $H_{C2}$ with decreasing size.

Proximity effect studies on 3D random distributions of a superconductor and a normal metal (Pb-Ag nanocomposite and biphasic Pb-Sn nanoparticles in Al matrix) show that the superconducting proximity effect theory for bilayers is also valid in such nanodispersed systems, with the ratio of the volume fraction of the two components controlling the $T_c$. 
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4. **Size induced metal insulator transition in nanocrystalline thin films of Niobium: Intragrular and intergranular contributions**  

5. **Upper critical field in nanostructured Nb: Competing effects of the reduction in density of states and the mean free path**  

6. **Nanostructures and enhanced absorption in intense laser interaction with matter: effect of laser prepulses**  

7. **Sputter deposition of self-organized nanoclusters through porous anodic alumina templates**  
   Smita Gohil, Ramesh Chandra, Bhagyashree Chalke, **Sangita Bose** and Pushan Ayyub, J. Nanoscience and Nanotechnology, 7, 641 (2007)

8. **Nanoscale phase separation in amorphous immiscible copper-niobium alloy thin films**  

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10. **Fast ion beams from intense, femtosecond laser irradiated nanostructured surfaces**  
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J. Appl. Physics (submitted)

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(Manuscript under preparation)

Sangita Bose, Anantha Puthucode, Pushan Ayyub, and Rajarshi Banerjee  
(Manuscript under preparation)

Papers presented in Conferences:

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Sangita Bose, Rajarshi Banerjee, Parinda Vasa and Pushan Ayyub  
Poster presented at “National Seminar on Science & Technology of Nanomaterials, 2003, Kolkata”

2. Finite size effects in nanocrystalline thin films of Nb  
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Poster presented at “International Conference on Nanoscience and Technology, 2003, Kolkata”

3. Self Organized Hexagonally Ordered Nanopores Arrays in Anodized Alumina  
Chinmay Belthangady, Sangita Bose, Smita Gohil, Jayeeta Bhattacharya, Subhendu Kahaly, Pushan Ayyub and Arnab Bhattacharya  
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6. Size dependence of the $T_c$ and the superconducting energy gap in nanocrystalline thin films of Nb
   
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Chapter 1

Nanoscale Superconductivity

1.1 Fundamentals of superconductivity

1.1.1 Introduction

Superconductivity was discovered in 1911 by Kamerlingh Onnes\(^1\) when he observed that on cooling Mercury, the electrical resistivity vanished abruptly at 4.2K. This phenomenon of *perfect conductivity* below a temperature \(T_c\) - known as the superconducting transition temperature - is a characteristic feature for all superconductors. In addition, they also exhibit *perfect diamagnetism* below this temperature \(T_c\). This phenomenon, known as Meissner effect, was discovered by Meissner and Ochsenfeld in 1933.\(^2\) They discovered that, not only is the magnetic field excluded from the superconductor (as in a perfect conductor), it is expelled out when it is cooled below \(T_c\). In a magnetic field, screening currents are generated that flow through the surface of the superconductor and cancels the flux density within it. There is also a critical field, \(H_C\), beyond which flux can enter into the superconductor. \(H_C\) is related thermodynamically to the difference in free energy of the normal and superconducting states in zero field. Due to the phenomenon of perfect conductivity shown by superconductors, there is almost no loss of electrical energy when current is passed through it. However, there is a maximum current density - called the critical current density, \(J_C\) - above which it becomes a normal metal. \(J_C\) is a function of temperature and increases monotonically as \(T \rightarrow 0\) .

There are a large number of metals and alloys that show superconductivity with \(T_c\) ranging between few mK to few tens of K. A list of commonly known superconductors with their respective \(T_c\) and \(H_C\) is given in Table 1.1.\(^3\) MgB\(_2\) is a non-oxide superconductor with the highest \(T_c\) of 40K.\(^4\) In 1986, with Lanthanum Barium Copper Oxide being found to be a superconductor with \(T_c = 30\)K, a new path was paved for the discovery of high \(T_c\) oxide superconductors.\(^5\) Till date, the mercury-based oxide compounds under high pressure exhibit the highest \(T_c \approx 164\)K.\(^6\) However, efforts are on for the discovery of a room temperature superconductor which will be a major breakthrough in this area.

For decades, a fundamental understanding of this phenomenon eluded the scientists working in this area. Initially, a phenomenological model was proposed by the London
brothers, which could explain both perfect conductivity and the Meissner effect.\textsuperscript{7} Subsequently, in the early 1950, Ginzburg and Landau gave their phenomenological model which dealt mainly with the superconducting electrons and the spatial variation of the superconducting wave function.\textsuperscript{8} The GL theory was a macroscopic theory which was useful in understanding the unique electrodynamic properties of the superconductor. Finally, in 1957, Bardeen, Cooper and Schriefer put forward their epoch making microscopic theory that provided a complete and satisfactory picture of the classical superconductors.\textsuperscript{9} 

In the following sections, I will briefly describe the highlights of some of the theoretical work in superconductivity that is relevant to the rest of the thesis.

1.1.2 Characteristic length scales in a superconductor: penetration depth ($\lambda_L$) and coherence length ($\xi_0$)

*Penetration depth:* For a superconductor in an applied magnetic field, the screening currents which circulate to cancel the magnetic flux inside it must flow within a finite surface layer. Consequently, the flux density does not vanish abruptly to zero at the boundary of the superconductor. It penetrates up to a region in which the screening currents flow, and the width of this region is known as the penetration depth of the superconductor. This is illustrated in Fig. 1.1 where a semi-infinite slab of a superconductor is shown. If at a distance $x$ into the metal the flux density falls to a value $B(x)$, we can define the penetration depth $\lambda_L$ by

$$\int_{0}^{\infty} B(x)dx = \lambda_L B(0) \quad (1.1)$$

*Figure 1.1:* A schematic representation of the penetration depth ($\lambda_L$) across a normal metal superconductor interface.
Table 1.1: The transition temperature ($T_c$) and critical field ($H_C$) of elemental superconductors. $T_c$ is given in K and $H_C$ is given in Gauss. The elements shown by * forms stable superconductors only in the thin film form or under high pressures. (Ref: Kittel, Introduction to Solid State Physics, 7th Ed., Ch. 12)

<table>
<thead>
<tr>
<th>Superconductor</th>
<th>$\xi_0$(nm)</th>
<th>$\lambda_L$(nm)</th>
<th>$2\Delta/k_B T_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indium</td>
<td>260</td>
<td>42</td>
<td>3.6</td>
</tr>
<tr>
<td>Aluminium</td>
<td>1600</td>
<td>16</td>
<td>3.5</td>
</tr>
<tr>
<td>Tin</td>
<td>230</td>
<td>34</td>
<td>3.55</td>
</tr>
<tr>
<td>Lead</td>
<td>83</td>
<td>37</td>
<td>4.4</td>
</tr>
<tr>
<td>Niobium</td>
<td>38</td>
<td>39</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Table 1.2: Coherence length ($\xi_0$), Penetration depth ($\lambda_L$) and coupling strength ($2\Delta/k_B T_c$) for some elemental superconductors. (Ref: Kittel, Introduction to Solid State Physics, 7th Ed., Ch 12)
where, B(0) is the flux density at the surface of the metal. The concept of penetration depth also originated from the phenomenological Londons’ theory.

The London equations: The phenomena of perfect conductivity and perfect diamagnetism observed in superconductors were coupled theoretically by the London brothers in 1935. The two fundamental equations proposed by them are:

\[
E = \frac{\partial}{\partial t} (\Lambda J_s)
\]

(1.2(a))

\[
B = -c (\nabla \times (\Lambda J_s))
\]

(1.2(b))

Here, \(E\) is the electric field, \(B\) is the magnetic field, \(J_s\) is the current density and \(\Lambda = m/n_s e^2\) with \(n_s\) denoting the superelectron density, \(m\) is the electronic mass and \(e\) is the electronic charge.

Combining the Eq. 1.2(b) with the Maxwell’s equation: \(\nabla \times B = (4\pi / c)J\), one gets,

\[
\nabla^2 B = B / \lambda_L^2
\]

(1.3)

where, \(\lambda_L = mc^2/4\pi n_s e^2\). In one dimension, the above equation will give,

\[
B(x) = B(0) \exp(-x / \lambda_L)
\]

(1.4)

This implies that the magnetic field penetrates up to a length scale \(\lambda_L\) from the surface into the interior of the superconductor, giving the penetration depth, a fundamental length scale, from the Londons equations. The temperature dependence of \(\lambda_L\) can be expressed by the empirical equation:

\[
\lambda(T) = \lambda(0) \left[1 - \left(T / T_c\right)^4\right]^{1/2}
\]

(1.5)

The typical value of the penetration depth for most of the elemental superconductors ranges between 10-2000 nm. It is listed in Table 1.2 for some of the known superconductors.

Coherence length: This is the second fundamental length scale in a superconductor, and was introduced initially by Pippard.\(^\text{i}\)\(^\text{o}\) He argued that the superconducting wave function should have a characteristic dimension \(\xi_o\) which can be estimated from the uncertainty principle. He proposed that only the electrons with energy within \(k_B T_c\) of the Fermi energy play a role in superconductivity which sets in at \(T_c\). These electrons have a momentum range \(\Delta p \approx k_B T_c / v_F\), where, \(v_F\) is the Fermi velocity and \(k_B\) is the Boltzmann constant. Thus, it follows from the uncertainty relation that

\[
\xi_o = \frac{0.18h v_F}{k_B T_c}
\]

(1.6)

Here, \(\xi_o\) is the coherence length of the pure superconductor.
The concept of coherence length was also introduced from the Ginzburg Landau (GL) theory. In their formalism, the superconducting state is described by a complex order parameter $\psi$ which describes the density of the superelectrons ($|\psi|^2 = n_s$). If the change of free energy at the S-N transition is small, the free energy $F_s$ of the superconducting state close to the transition point can be written (using variational principle) as a series in $\psi$:

$$F_s = F_n + \int d^3 r \left\{ \alpha |\psi|^2 + \frac{\beta}{2} |\psi|^4 + \frac{1}{2m_s} \left( -i\hbar \nabla - e_s A / c \right) |\psi|^2 + \frac{\hbar^2}{8\pi} \right\}$$

(1.7)

Here $F_n$ is the free energy of the normal state and $\alpha, \beta$ are temperature dependent coefficients.

The GL equations can be derived from minimizing the free energy with respect to the order parameter $\psi$ and the vector potential $A$. In the absence of field, one of the GL equations can be written in 1 dimension as:

$$0 = \psi'' + \left( \beta - \frac{\hbar^2}{2m_s} \right) \psi + \alpha |\psi|^2$$

(1.8)

This introduces the coherence length, defined as:

$$\xi^2 = \frac{\hbar^2}{2m_s} |\alpha| \propto 1/(1 - T/T_c)$$

(1.9)

The physical meaning of $\xi$ is that it characterizes the length scale over which $\psi(r)$ can vary without any cost of free energy. This ranges between 10-100nm for most of the elemental superconductors as listed in Table 1.2.

It is shown from the GL theory that near $T_c$, $\xi(T)$ varies differently in the pure and dirty limit as

$$\xi(T) = 0.74 \frac{\xi_0}{(1 - T/T_c)^{1/2}} \quad \text{(pure)}$$

(1.10(a))

$$\xi(T) = 0.855 \frac{(\xi_0 l)^{1/2}}{(1 - T/T_c)^{1/2}} \quad \text{(dirty)}$$

(1.10(b))

The dirty limit implies $l << \xi_0$, where $l$ is the mean free path of the electrons.

1.1.3 Type I and type II superconductors

The ratio of the two characteristic lengths, known as the GL parameter, $\kappa = \lambda(T)/\xi(T)$, determines the response of a superconductor in a magnetic field. Depending on the value of $\kappa$, we can define two types of superconductors:

Type I $\rightarrow \kappa < 1/\sqrt{2}$

Type II $\rightarrow \kappa > 1/\sqrt{2}$

30
For a Type I superconductor, loss of superconductivity occurs continuously via a first order phase transition at the critical field, $B_c$. The typical phase diagram is shown in Fig. 1.2(a). For a Type II superconductor, it is energetically favorable to form a mixed state, i.e., both normal and superconducting regions co-exist above a lower critical field, $B_{c1}$ ($B_{c1} = \phi_0 / 2\pi\xi^2$, where $\phi_0 = 2.07 \times 10^{-15}$ is the flux quantum). A schematic of the mixed state is shown in Fig. 1.3. The normal regions in the mixed state are in the form of cylinders with their axis along the direction of the magnetic field. The radius of these cylinders is equal to the coherence length ($\xi$). Current vortices circulate around these normal cores to generate the flux within. The direction of this current is opposite to the main surface shielding current which makes the flux in the superconducting region zero. With increase in the magnetic field beyond $B_{c1}$, the distance between the normal cores decreases. At a field equal to the upper critical field $B_{c2}$ ($B_{c2} = \phi_0 / 2\pi\xi^2$), there is complete overlap of the normal cores, and the

Figure 1.2: Phase diagrams of (a) Type I (b) Type II superconductor

Figure 1.3: Schematic representation of the mixed state of a Type II superconductor. The yellow regions denote the normal cores with current vortices around them shown by black arrows. The normal cores are separated by superconducting regions.
superconductor goes over completely to the normal state. The typical phase diagram is shown in Fig. 1.2(b).

Most elemental superconductors such as Al, Sn, In, Pb etc are Type I superconductors. Nb is the only elemental superconductor which is Type II. However, most of the alloys and compounds are Type II superconductors.

1.1.4 BCS theory

In 1957 Bardeen, Cooper and Schrieffer proposed their celebrated electron-pairing theory of superconductivity, which explains completely this complex phenomenon for isotropic superconductors. The basis of this theory is that even a very weak attractive interaction between electrons, mediated by phonons, creates a bound pair of electrons (called the Cooper pair) occupying states with equal and opposite momentum and spin (i.e. $k^\uparrow$, -$k^\downarrow$). The formation of the bound states creates instability in the ground state of the Fermi sea of electrons and a gap ($\Delta(T)$) opens up at the Fermi level. The minimum energy $E_g$ required to break a Cooper pair to create two quasi-particle excitations is $E_g = 2\Delta(T)$. This is shown schematically in Fig. 1.4.

The formation of the Cooper pairs mediated by the phonons is illustrated in a simple cartoon in Fig. 1.5. An electron with momentum $k$ traveling through the lattice will polarize it, thereby creating a local positive charge. A second electron with momentum $-k$ traveling through this lattice will be attracted to the local positive charge, thereby, getting attracted to the first electron. This leads to the formation of the Cooper pairs. The expression for the energy gap $\Delta$ as calculated from the BCS theory is given by:

![Figure 1.4](image-url)  

**Figure 1.4:** Energy band diagram of a superconductor at $T < T_c$. It shows the formation of cooper pairs condensing into the BCS state with a gap ($\Delta$) opening at the Fermi level.
\[ \Delta = 2\hbar \omega_c e^{-1/N(0)V} \]  

(1.11)

Here, \( \omega_c \) is the Debye frequency, \( N(0) \) is the density of states at the Fermi energy and \( V \) is the attractive interaction potential. However, this equation is valid only for weak coupling superconductors with \( N(0)V < 1 \). The critical temperature \((T_c)\) is the temperature at which \( \Delta(T) \to 0 \) and the excitation spectrum becomes the same as that of the normal state. The expression for \( T_c \) is given by:

\[ k_B T_c = 1.14\hbar \omega_c e^{-1/N(0)V} \]  

(1.12)

**Figure 1.5:** Simple cartoon depicting the formation of a cooper pair between two electrons traveling with momentum \( \mathbf{k} \) and \(-\mathbf{k} \), mediated by the lattice.

Comparing the above two expressions, it can be seen that for a weak coupling superconductor: \( \frac{2\Delta(0)}{k_B T_c} \approx 3.5 \). Experimentally, the values of \( 2\Delta \) for different superconductors generally fall in the range from \( 3k_B T_c \) to \( 4.5k_B T_c \) (Table 1.2). The temperature variation of the gap can be computed numerically using:

\[ \frac{1}{N(0)V} = \int_0^{\hbar \omega_c} \frac{\tan \frac{1}{2} \beta (\xi^2 + \Delta^2)^{1/2}}{\left( \xi^2 + \Delta^2 \right)^{1/2}} d\xi \]  

(1.13)

Here \( \beta = 1/k_B T_c \) and \( \xi \) is the quasiparticle energy. For weak coupling superconductors, the reduced gap \( \Delta(T)/\Delta(0) \) is a universal function of the reduced temperature \( T/T_c \). This is shown in Fig. 1.6. Physically, \( \Delta \) is nearly constant until a significant number of quasiparticles are thermally excited. Near \( T_c \), \( \Delta(T) \) drops to zero as:

\[ \frac{\Delta(T)}{\Delta(0)} \approx 1.76 \left( 1 - \frac{T}{T_c} \right)^{1/2} \]  

(1.14)

---

* Quasiparticles are the elementary excitations of a superconductor which are created when a Cooper pair breaks. They are also known as the Bogoliubons.
This energy gap is the order parameter for the superconductor, with a phase factor given by $e^{i\phi}$. Hence, the order parameter is equal to $|\Delta|e^{i\phi}$.

Quasiparticle excitations above the BCS ground state are coherent superpositions of the electron and hole quasiparticles and are in one-to-one correspondence with excitations in the normal state. Adding one quasiparticle to the BCS ground state adds energy $E$ to the system given by:

$$E = \sqrt{\left(\frac{\hbar^2 k^2}{2m} - E_F\right)^2 + \Delta^2}$$

Where, $k$ is the quasiparticle momentum. Thus, a minimum energy $\Delta$ is required to add a quasiparticle to the system. The corresponding quasiparticle density of states (DOS) is represented by the function:
$$N(E) = N(0) \frac{|E|}{\sqrt{E^2 - \Delta^2}} \quad (\text{for} \ |E| > \Delta)$$  \hspace{1cm} (1.15)

$$= 0 \quad (\text{for} \ |E| < \Delta)$$

Where, $N(0)$ is the normal state DOS and $E$ is the energy of the quasiparticle. The DOS is plotted in Fig. 1.7.

### 1.1.5 Josephson Effect

Brian Josephson in 1962 discovered that if two superconducting metals were separated by a thin insulating barrier, such as an oxide layer 1 to 2 nm thick, it is possible for electron pairs to pass through the barrier without resistance.\textsuperscript{11} This is known as the dc Josephson Effect. The current flowing through the junction, called the Josephson supercurrent, is given by:

$$I_s = i_c \sin \Delta \phi$$  \hspace{1cm} (1.16)

Here, $\Delta \phi$ is the phase difference of the GL wave function across the junction and $i_c$ is the maximum supercurrent which the junction can support. Fig. 1.8(a) and (b) show a Josephson junction and the $I$-$V$ curve for such a junction.

He further predicted that if a voltage difference $V$ is maintained across the junction, the phase difference $\Delta \phi$ would evolve according to:

$$\frac{d(\Delta \phi)}{dt} = \frac{2eV}{\hbar}$$  \hspace{1cm} (1.17)

This is called the ac Josephson Effect, where the current is an alternating current of amplitude $I_c$ and frequency $v = \frac{2eV}{\hbar}$. Both these predictions have been confirmed by many experiments.

---

**Figure 1.8 (a)** Schematic of a Josephson junction showing two superconductors separated by a thin insulating layer. **(b)** The current-voltage characteristic of a single Josephson junction.
RCSJ model: The RCSJ model (resistively and capacitatively shunted junction) provides a complete description for a Josephson junction in the presence of finite voltages involving the ac Josephson effect. The model considers an ideal Josephson junction to be shunted by a resistance $R$ and a capacitance $C$, as shown in Fig. 1.9. The resistance $R$ causes the dissipation at finite voltages without affecting the lossless dc regime, while $C$ is the geometric shunting capacitance between the two electrodes. Within this model, the time dependence of the phase $\phi$ in the presence of an externally supplied bias current can be derived by equating the bias current $I$ to the total junction current from the three parallel channel as follows:

$$ I = I_{c0} \sin \phi + V/R + CdV/dt $$

(1.18)

Using Eq. 1.17, the above equation can be written as a second order differential equation as:

$$ d^2\phi/d\tau^2 + Q^{-1}d\phi/d\tau + \sin \phi = I/I_{c0} $$

(1.19)

Where $\tau = \omega_p t$, with the plasma frequency ($\omega_p$) of the junction given by:

$$ \omega_p = (2eI_{c0}/h)^{1/2} $$

(1.20)

The quality factor $Q$ is defined as:

$$ Q = \omega_p/RC $$

(1.21)

The damping parameter, $\beta = Q^2$.

A long time average of $\phi$ gives the voltage across the junction. Thus, Eq. 1.20, which resembles the equation of a damped harmonic oscillator, where $\phi$ is replaced by $\sin \phi$, predicts the $I$-$V$ characteristics of a single Josephson junction. The behaviour of the junction depends on the value of $C$. We consider the two limiting cases:

(a) Overdamped junctions (small $C$, $Q \ll 1$): In this case, Eq. 1.19 reduces to a first order differential equation given by:
\[
\frac{d\phi}{dt} = \frac{2eI_{c0}R}{h} \left( I - \sin \phi \right)
\]  

(1.22)

One can find the time average of the voltage by integrating this equation to find the time period \(T\) when \(\phi\) changes by \(2\pi\) and then using the relation \(2eV/h = 2\pi/T\). The result obtained is:

\[
V = R \left( I^2 - I_{c0}^2 \right)^{1/2}
\]  

(1.23)

This implies that \(V = 0\) for \(I < I_{c0}\) and follows the Ohm’s law \(V = IR\), for \(I > I_{c0}\).

(b) Underdamped junctions (large \(C, Q \gg 1\)): It can be shown that for such junctions the \(I-V\) curve becomes hysteretic. In the absence of thermally activated processes, when \(I\) increases from zero to \(I_{c0}\), \(V\) remains zero. At \(I_{c0}\), \(V\) jumps discontinuously to a finite voltage corresponding to a state where the phase \(\phi\) increases at the rate \(2eV/h\). When \(I\) is reduced below \(I_{c0}\), \(V\) does not drop back to zero until a “retrapping current” \(I_0 \sim 4I_{c0}/\pi Q\) is reached.

1.2 Overview of low dimensional elemental superconductors

Nanoscale superconductivity has been studied over the past three decades. It is important to know how the ground state properties change when one or more of the system dimensions are reduced below the characteristic length scales for a bulk superconductor: the coherence length \((\xi_0)\) and the London penetration depth \((\lambda_L)\). The superconducting properties for confined systems often show dramatic changes from those of the bulk. At much reduced dimensions, new phenomena not seen in bulk superconductors may also be observed. Nanoscale superconductivity has been studied in 2-dimensional thin films\(^{12,13,14,15}\), 1-dimensional nanowires\(^{16,17}\) and zero dimensional nanoparticles\(^{18,19,20}\).

1.2.1 Two dimensional Superconductors

Superconducting thin films have been grown by a variety of methods like evaporation\(^{21,22}\), sputtering\(^{23,24}\), MBE\(^{25}\), quench condensation\(^{12,13,14}\) etc. The properties observed often depend on the film morphology. For Al\(^{26}\) and Sn films grown by evaporation and sputtering, a non-monotonic variation of the superconducting transition temperature \((T_c)\) have been observed with decreasing film thickness. However, Pb\(^{27}\), Nb\(^{15,22}\) and In\(^{28}\) films show a monotonic decrease in \(T_c\) with decreasing film thickness. The suppression of \(T_c\) has been attributed to either localization effects or proximity effects. In the proximity effect model, it is assumed that a normal metal layer of conductive oxide is formed at the surface of the superconductor,
which is typical for many elemental superconductors. It was shown by Cooper\textsuperscript{29} and later by de Gennes\textsuperscript{30} that if the superconductor and the normal metal are in good electrical contact and their thicknesses are less than the phase coherence length ($\xi_0$), the $T_c$ of the system is reduced. This is because the pairing amplitude of the Cooper pairs ($F$) penetrates into the normal metal. Applying the boundary conditions at the interface, it can be seen that $F$ is suppressed at the surface.

There seems to be some agreement on the observations and the mechanism of the destruction of superconductivity for quench condensed films, though these films cannot be well characterized morphologically. Quench condensed films are formed by evaporating the metal on substrates kept at very low temperatures ($< 20$K). This may lead to the formation of two types of films. (1) Homogenous films are formed wherein a thin layer of Ge is used as an underlayer so that atomically flat films can be grown.\textsuperscript{27,31} (2) Inhomogenous films are grown on oxidized substrates. These consist of superconducting grains (of size ~100-200nm) which are Josephson coupled.\textsuperscript{32} In both these types of films, a superconductor to insulator transition is observed at a critical thickness. However, the homogenous films exhibit a decrease in both the $T_c$ and the superconducting energy gap ($\Delta$) with decreasing film thickness. This is believed to be due to amplitude fluctuations of the order parameter. The inhomogenous films exhibit a broadening of the superconducting transition. It has also been observed that the individual superconducting grains retain the bulk value of $T_c$ and $\Delta$ though the film becomes insulating. It is believed that the destruction in superconducting order in this type of film is due to the fluctuations of the phase of the order parameter. Recently, using improved synthesis and characterization methods, it has been possible to track the evolution of superconductivity in almost monolayer films. Several groups have seen an oscillatory variation of $T_c$ with the number of the monolayers of the film. This is because in this regime, the film thickness becomes comparable to the Fermi wavelength and hence quantum confinement starts predominating. With the formation of well defined quantum well states in the vertical direction, the density of states at the Fermi wavelength $N(0)$ varies inversely with the film thickness. Since, $N(0)$ oscillates with the number of monolayers, $T_c$ also shows an oscillatory behaviour with film thickness.
1.2.2 One dimensional Superconductors

The study of 1-dimensional superconducting nanowires has become popular since the past decade with the development of novel methods of growing and studying single nanowires. The $T_c$ in most of the elemental superconducting nanowires does not change as the wire diameter is reduced from 100 to 20nm.\cite{17,33} There are no reports on the evolution of superconducting properties below a wire diameter of 20nm. However, a distinctive feature seen in the transport measurements of these nanowires is the presence of resistive tails and finite resistances below the $T_c$. This has been explained on the basis of the occurrence of phase slip centers (PSC) in the nanowires which are caused due to thermodynamic fluctuations.\cite{34,35} According to the theory proposed by Ambegaokar\cite{36}, the current carrying state is metastable and hence a free energy barrier is associated with the transport of the Cooper pairs which needs to be overcome for the system to relax to one of the metastable states. This activation across the free energy barrier gives rise to the resistive tails and the finite resistance at temperatures below $T_c$. At much lower temperatures, thermal activation becomes impossible and the Cooper pairs tunnels between the two metastable states. Such thermodynamic fluctuations make the amplitude of the order parameter vanish locally and the phase changes by $2\pi$ across the metastable states. Hence, the weak points in the nanowires act as the PSC. Recently, from a classic experiment on a MoGe nanowire (grown by DNA templating), Berzyadin et al were able to show the quantum origin of the resistive tails at very low temperatures. They showed that when the resistance of the nanowire (diameter $\sim$ 40nm) is more than the quantum resistance ($R_Q \sim 25k\Omega$), the wires become insulating. Thus, the occurrence of resistive tails is the manifestation of the confinement of superconducting wave function which leads to the thermodynamic fluctuations.

1.2.3 Zero-dimensional Superconductors

Superconducting nanoparticles have been studied since the early sixties.\cite{18,19,20} In these systems, in addition to the two characteristic length scales of $\lambda_L$ and $\xi_o$, there is a third length scale which determines the critical size below which superconductivity fails to exist. This arises from the quantum size effects. The discrete energy level spectrum (due to quantum size effects) in nanoparticles has been experimentally observed for the first time in a classic experiment by Ralph et al. in 1995, where they could make tunneling measurements on individual Al particles of diameter $\sim$10nm.\cite{37} The relation of the energy level spacing with superconductivity was suggested empirically by Anderson\cite{38} in 1959 and is known as the
Anderson criterion. According to this criterion, when the discrete energy level spacing ($\delta$) in nanoparticles (see Fig. 1.10) becomes equal to the superconducting energy gap ($\Delta(0)$), superconductivity can no longer be sustained in the small particle. It is easy to understand the physical origin of this postulate. For small particles, when $\delta \sim \Delta(0)$, (where $\Delta(0)$ for most elemental superconductors $\sim 1$-2meV), the number of electrons present in the particle is of the order of a few thousands. Hence, the fraction of the total number of electrons lying close to the Fermi level is very small. Moreover, in a bulk superconductor, electrons present in the energy interval $\Delta$ from the Fermi level condense to form the BCS state, thereby opening up an energy gap $\sim \Delta$ at the Fermi level. However, for small particles, when $\Delta \sim \delta$, there are no available electrons within the energy interval $\Delta$ of the Fermi level to form the condensate state and hence the superconducting state cannot be stabilized. The critical particle size for the disappearance of superconductivity can be calculated from the Anderson criterion as follows. For a nanoparticle of diameter $D$, the energy level spacing (Kubo gap) is:

$$\delta = \frac{4\varepsilon_F}{3N}$$

(1.24)

where, $N$ is the total number of conduction electrons in the particle. If $\lambda_F$ is the Fermi wavelength, then $N = \left(\frac{D}{\lambda_F}\right)^3$

Therefore, $\delta = \frac{4\varepsilon_F \lambda_F^3}{3D^3}$

(1.25)

From Eq. 1.6 we can express $\Delta$ in terms of the clean limit coherence length:

$$\Delta = \frac{0.18 h \varepsilon_F}{\xi_0}$$

(1.26)
By applying the Anderson criterion, $\delta \sim \Delta$, we get the critical particle diameter for the disappearance of superconductivity, $D_c$ to be:

$$D_c \propto \xi_0^{1/3} \lambda_F^{2/3}$$

(1.27)

Since, the typical value of $\lambda_F$ is $\sim 1$-2nm and $\xi_0$ is $\sim 10$-100nm for most elemental superconductors, the critical particle diameter for the disappearance of superconductivity usually ranges between 4 to 6nm. The validity of the above criterion has been successfully tested experimentally for small particles of Al, Sn, Pb, In, etc. However, there are contradicting reports on the actual nature of evolution of the $T_c$ with decreasing particle size till the Anderson criterion is reached in the elemental superconductors studied so far. Most of the early studies were on metallic nanograins grown by evaporating the metal in controlled amounts of oxygen. It was believed that the oxygen precipitated in the form of oxides at the grain boundaries, thereby capping the small superconducting grains. Most elemental superconductors like Al, Sn, In, Ga, etc. showed an increase in $T_c$ with reduction in the particle size. However, Pb, a strong coupling superconductor showed no change in $T_c$. Subsequently, there were reports by other groups on Al and Sn nanoparticles which confirmed the increase in $T_c$ with reduction in size. Recently Reich et al were able to grow Pb nanoparticles using a nucleopore membrane, where the membrane diameter controlled the grain size. They observed no change in $T_c$ in Pb down to a particle size of 10nm though there was substantial drop in the Meissner signal. More recently, Li et al studied the superconducting properties as a function of particle size in In and Pb. While In showed a non-monotonic variation in $T_c$, Pb showed a sharp decrease in $T_c$ below 10nm. Thus, we see that the variation of $T_c$ with particle size does not appear to follow a general rule. Different factors have been discussed in the literature to understand the mechanisms influencing the evolution of $T_c$ with particle size. These include phonon softening, substrate effects, proximity effects, quantum size effects etc. However, it is now generally agreed that the size dependence of $T_c$ arises predominantly from two mechanisms: surface effects and quantum size effects.

**Surface effects:** This is important for small particles due to the increase in the ratio of the surface to volume atoms. The surface atoms have a lower coordination number than the atoms in the bulk of the particle. This makes the phonon frequency of the surface lower than that of the bulk. This phenomenon is called phonon softening. It has also been shown theoretically by Dickey and Paskin using molecular dynamic simulations that there are low frequency (softer) phonon modes present for fine particles. This makes the electrons...
interact strongly with the phonons, thereby increasing the electron-phonon coupling constant \((\lambda)\) with decreasing particle size. With an increase in the coupling constant, the weak coupling BCS equations for \(T_c\) are no longer valid. In the strong coupling limit, the expression for \(T_c\), worked out by McMillan\(^{45}\) is given by:

\[
T_c = \frac{\Theta_D}{1.45} \exp \left[\frac{-1.04(1 + \lambda)}{\lambda - \mu^* (1 + 0.62 \lambda)}\right]
\] (1.28)

Where, \(\Theta_D\) is the Debye temperature and \(\mu^*\) is the effective electron-electron repulsion term. McMillan also showed that the \(\lambda\) is approximately proportional to the inverse of the phonon frequency (called the McMillan average squared frequency), where, \(\langle \omega^2 \rangle_M = \langle \omega \rangle / \langle 1/\omega \rangle\). This implies that a decrease in the phonon frequency \(\langle \omega^2 \rangle_M\) should increase \(\lambda\). From McMillan’s equation it is also clear that surface effects may cause \(T_c\) to increase or decrease with decreasing particle size depending on how fast \(\lambda\) increases with respect to \(\mu^*\). Now with decreasing particle size, increasing disorder leads to an increase in the repulsive interaction between the electrons as screening effects decreases. Therefore, if \(\lambda\) increases faster than \(\mu^*\), \(T_c\) increases, else \(T_c\) decreases with decreasing particle size. However, experimentally, an increase in \(T_c\) has been reported for weak coupling superconductors like Al, Sn, Ga, In etc. Abeles et al have also measured the superconducting energy gap \((\Delta(0))\) for Al fine particles by tunneling and observed an increase in \(\lambda\) with decreasing particle size. Hence, the observed increase in \(T_c\) in these superconductors is believed to be due to phonon softening which is a manifestation of surface effects in small particles. However, in strong coupling superconductors like Pb this effect can be offset by an increase in the phonon frequency cut off arising from a quantization of the phonon wave vector, which effectively suppresses the \(T_c\) with decreasing particle size. Fenton and Leavens have worked out the entire Eliashberg theory for small particles (~ 5nm diameter) of Pb and shown that though \(T_c\) does not change appreciably, there is a significant increase in \(\Delta\), thus increasing the factor \(2\Delta/k_BT_c\).\(^{46}\) Hence, it should be noted that whenever surface effects dominate in small superconducting particles, any change in \(T_c\) will be accompanied by similar changes in \(2\Delta/k_BT_c\).

Quantum size effects (QSE): QSE is important in small particles due to the discretization of the energy levels arising from the quantization of the electronic wave vector which changes the density of states (DOS) at the Fermi level. Attempts to incorporate the discretization of the energy levels in the BCS equation to investigate the influence of QSE on \(T_c\) have lead to contradicting results. While Parmenter\(^{47}\) has shown that this would lead to an increase in \(T_c\), Strongin et al have predicted a decrease in \(T_c\) with decreasing particle size. Later, Fenton et
al argued that there was a serious flaw in Parmenter's argument, which assumed the Fermi level to lie on one of the energy levels, giving rise to an increase in $T_c$. Strongin et al. have correctly taken the Fermi level to lie in between the first occupied level and the first unoccupied level, causing an effective decrease in the DOS at the Fermi level, giving rise to a decrease in $T_c$ with decreasing size. According to Strongin et al., the expression for $T_c$ is given in terms of the energy level spacing $\delta$ by the following equation:

$$\ln\left(\frac{T_c}{T_{c0}}\right) = \frac{\pi}{2} \sum_{m \geq 0} \left( \frac{1}{2m+1} \right) \left[ \tanh\left( \frac{\pi}{2} \frac{(2m+1)2\pi T_c}{\delta} \right) - 1 \right]$$  \hspace{1cm} (1.29)

where, $T_{c0}$ is the superconducting transition temperature of the bulk superconductor. It can be seen from the above equation that since $\delta$ increases with decreasing particle size, $T_c$ reduces from the bulk value of $T_{c0}$. Also, it can be seen from the BCS relations (Eq. 1.11 and 1.12) that $T_c$ and $\Delta(0)$ show a similar dependence on $N(0)$ (the DOS) as follows:

$$T_c = 1.14\hbar\omega_D \exp\left[-\frac{1}{N(0)V}\right] \hspace{0.5cm} \text{and} \hspace{0.5cm} \Delta(0) = 2\hbar\omega_D \exp\left[-\frac{1}{N(0)V}\right]$$

where, $\omega_D$ is the Debye frequency and $V$ is the electron-phonon interaction potential. Hence, any variation in $T_c$ due to quantum size effects will cause a proportionate variation in $\Delta(0)$, so that the parameter $2\Delta(0)/k_BT_c$ should not change with decreasing particle size.

Thus, we see that in order to understand the mechanism of the evolution of $T_c$ in nanostructured superconductors, one needs to study the evolution of the electron phonon coupling strength, $2\Delta(0)/k_BT_c$, with particle size. The parameter $2\Delta(0)/k_BT_c$ varies from 3.5 for weak coupling bulk superconductors such as Al, Sn, In, etc. to 4.5 for the strong coupling superconductor, Pb. Nb is an intermediate coupling superconductor with $2\Delta(0)/k_BT_c \sim 3.8$.

We have carried out detailed measurements of the important superconducting properties such as $T_c$, upper critical field ($H_{c2}$) and $\xi_o$ as a function of particle size in two typical, elemental nanostructured superconductors - Nb and Pb. Through a direct measurement of the superconducting energy gap $\Delta(0)$, we are able to understand the mechanism influencing the evolution of $T_c$ with particle size in both these systems. Since, the superconducting parameters are all interrelated; our studies also helped us to understand the evolution of $H_{c2}$ with particle size in these systems.
1.3 Superconducting proximity effect

The theory of superconducting proximity effect (SPE) had been developed for bilayers and multilayers way back in 1960.\(^4\) According to this theory, for a high transmission contact between a superconductor (S) and a normal metal (N) or another superconductor with a lower \(T_c\), some degree of phase coherence develops in the normal metal while there is a pair breaking effect in the superconductor at the length scale of the coherence length \(\xi_{N,S} = [\hbar D_{N,S}/2\pi k_B T]^{1/2}\), \(D_{N,S}\) are the diffusivities of the normal/superconducting layers respectively) of each material across the interface. This induces superconductivity in the normal metal and suppresses it in the superconductor. Applying the boundary conditions at the interface, it can be seen that the pairing amplitude \(F\) is suppressed at the surface, thereby changing the \(T_c\) of the S-N sandwich compared to that of the pure superconductor. This is shown schematically in Fig. 1.11. In the “Cooper limit” \((d_S<\xi_S\ and\ d_N<\xi_N)\), deGennes has worked out the following expression for the effective BCS pair interaction parameter:

\[
[N(0)V]_{eff} = \frac{N_S V^2 S d_S + N_N V^2 N d_N}{N_S d_S + N_N d_N} \tag{1.30}
\]

From this it is possible to calculate the effective transition temperature \((T_{cNS})\) using the weak coupling BCS relation:

\[
T_{cNS} = \frac{\Theta_D}{1.45} \exp \left[-\frac{1}{[N(0)V]_{eff}}\right] \tag{1.31}
\]

---

**Figure 1.11:** Schematic representation of superconducting proximity effect.
where $N_{S,N}$ is the DOS of the superconductor (normal metal) at the Fermi level, $\Theta_D$ is the Debye temperature and $V_{S,N}$ is the electron-phonon interaction potential in the superconductor (normal metal). The above expression has successfully explained the observed $T_c$ of multilayers of superconductors and normal metals with near perfect interfaces. However, modifications to the existing theory were later proposed, which includes a finite interfacial layer (of thickness $d_i$) between the superconductor and normal metal for each bilayer.\(^{49}\) In this case, the effective BCS coupling parameter is given by:

$$[N(0)V]_{eff} = \frac{N_S^2 V_S d_S + N_N^2 V_N d_N + N_i^2 V_i d_i}{N_S d_S + N_N d_N + N_i d_i}$$

(1.32)

It can be seen from the above equation that for negligible intermixing ($d_i = 0$) and for a constant $d_S/d_N$, $T_{cNS}$ is independent of $\Lambda = d_S + d_N$. However, for a thicker interfacial layer, the variation of $T_{cNS}$ with $\Lambda$ is stronger. The proximity effect theory has also been worked out by Werthamer\(^{50}\) for a thin superconductor in contact with a thick normal metal. In this case, the $T_{cNS}$ no longer depends on the thickness of the normal metal and can be evaluated from the simple relation:

$$d r_S = \frac{\pi}{2} (1-t)^{1/2} \cot^{-1} \left[ \left( \frac{2}{\pi} \right)(t^{-1} - 1)^{1/2} \right]$$

(1.33)

where the reduced variables $d r_S$ and $t$ are defined as,

$$d r_S = d_S \left( \frac{h v_{FS} I_S}{6 \pi k_B T_S} \right)^{-1/2} \quad \text{and} \quad t = T_{cNS} / T_S$$

(1.34)

Here, $T_S$ is the transition temperature of the pure superconductor, $v_{FS}$ is the Fermi velocity, $I_S$ is the mean free path of the electrons in the superconductor and $k_B$ is the Boltzmann constant.

The above discussion of SPE for thin superconductor and normal metal layers in contact with each other is valid for weak coupling superconductors ($\lambda < 1$) only. For strong coupling superconductors ($\lambda > 1$), the theory has been worked out by Silvert\(^{51}\) who modified the McMillan’s equation (Eq. 1.28). Within the “Cooper limit” ($d_{S,N} \ll \xi_{S,N}$) the $T_{cNS}$ of the strong coupling superconductor in contact with the normal metal is given by:

$$\ln T_{cNS} = \frac{\langle \lambda \rangle \ln \Theta}{\langle \lambda \rangle} - \frac{1}{\lambda^*} - \ln 1.14$$

(1.35)

where $\langle \lambda \rangle$ = mean electron phonon coupling strength, $\Theta = $ Debye temperature

$$\lambda^* = \frac{\langle \lambda \rangle - \mu^*}{1 + \langle \lambda \rangle} ; \mu^* \text{ is the Coulomb pseudo potential term}$$

45
Silvert has shown that for a strong coupling superconductor of thickness $d_S$ in contact with a normal metal or a superconductor of thickness $d_N$ with a lower $T_c$

$$\langle \lambda \rangle = \frac{(d_S N_S \lambda_S + d_N N_N \lambda_N)}{(d_S N_S + d_N N_N)} = \beta_S \lambda_S + \beta_N \lambda_N$$  \hspace{1cm} (1.36)

$$\langle \lambda \ln \Theta \rangle = \beta_S \lambda_S \ln \Theta_S + \beta_N \lambda_N \ln \Theta_N$$  \hspace{1cm} (1.37)

$$\beta_S = \frac{d_S N_S}{d_S N_S + d_N N_N} = 1 - \beta_N$$  \hspace{1cm} (1.38)

Here, $N_S$ and $N_N$ are the density of states at the Fermi level of the superconductor and the normal metal respectively from the free electron theory.

The above mentioned predictions have been tested in various limits in a large number of bilayer/multilayer systems. However, there are very few models and little experimental data on 3D composite systems, in which superconducting grains are randomly distributed in a normal matrix. Since the coherence length of most elemental superconductors ranges between few tens of nm to a few hundred nm, the study of SPE in bilayers and multilayers requires the synthesis of very thin films. Hence, we aimed to probe the effect of length constraints in thick nanocomposite films of superconductors and normal metals where their individual particle sizes are kept less than their respective coherence lengths. We aimed to understand if the theory of superconducting proximity effect for 2D films is also valid in such cases. If it is, then which are the relevant parameters that determine the $T_c$ in such random mixtures? With this in mind, we carried out a study of superconducting proximity effect in two different types of 3D random mixture systems. The first system consists of 3D nanocomposite films of randomly interdispersed Pb and Ag nanoparticles. Here, we have tried to understand the evolution of $T_c$ as a function of the ratio of the volume fractions of the two components. The second system consists of Pb/Sn biphasic nanoparticles randomly distributed in an Al matrix. Here, again we have invoked the modified theory of SPE to explain the observed $T_c$ of the system.

1.4 Organization of thesis

This thesis deals with the experimental study of elemental superconductors at reduced dimensions. It is organized as follows. In Chapter 1, I have introduced the topic of nanoscale-superconductivity. I have discussed how length constraints influence the superconducting order parameter both in pure elemental superconductors and also the behavior of
superconductors in proximity with normal metals or other superconductors with lower $T_c$.

Thereafter in Chapter 2, I will describe the various experimental techniques used. This chapter includes the synthesis of nanostructured films, their morphological characterization and finally the methods employed to measure the different superconducting properties. In Chapter 3, I will present our studies of the size effects on the superconducting and the normal state properties of the intermediate coupling, Type II superconductor, Nb. This will be followed in Chapter 4 by a similar study of the superconducting properties of a strong coupling superconductor, Pb, as a function of grain size. Our results will elucidate the mechanism controlling $T_c$ in nano-superconductors. Finally, in Chapter 5, I will discuss our results on the study of the superconducting proximity effect in Pb-Ag nanocomposites and Pb-Sn bi-phasic nanoparticles embedded in an Al matrix. Our results show that the theory of superconducting proximity effect formulated for bilayers and multilayers can be modified to explain the observed changes in $T_c$ in these random, nanostructured, 3-D systems.
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Chapter 2

Experimental details

In this chapter I will discuss the experimental techniques used for the synthesis of the nanocrystalline superconducting films used in the present study, the various structural characterization tools and the techniques for measuring the superconducting transition temperature ($T_c$), the normal state transport properties, the critical fields ($H_{c2}$) and the energy gap ($\Delta(0)$) of the superconducting samples.

2.1 Synthesis of nanocrystalline thin films

Magnetron sputtering is a popular technique used to deposit thin films of different materials. Through a suitable choice of process parameters, it is possible to apply this method for the deposition of nanocrystalline thin films.$^{1,2}$ While Fig. 2.1 shows a schematic, Fig. 2.2 shows the picture of the magnetron sputtering setup in our lab, which was used to deposit the nanocrystalline films. The material whose nanoparticles are to be synthesized forms the

![Figure 2.1: Schematic of a home-made magnetron sputtering system](image-url)
sputtering target and the material on which the film is deposited is called the substrate. A dc or rf voltage is applied across the target and the substrate which is kept at a common ground potential with respect to the rest of the sputtering chamber. Dc sputtering is used only for conducting targets while rf-sputtering can be used for both conducting and non-conducting targets. Sputtering is mostly done in the presence of an ultra pure inert gas. Substrate temperature is kept between room temperature and the boiling point of liquid nitrogen.

A magnetron sputter gun consists of a series of permanent magnets arranged in a circular geometry, providing a radial magnetic field parallel to the target surface. Plasma is created when secondary electrons produced by the collision of positive ions (stray ions present in the chamber) hit the target surface. Due to repeated collisions a cascade of electrons is generated which sputter out the target atoms by transferring its energy and momentum. The magnetic field from the magnetron sputter gun confines the plasma close to the target surface thereby giving maximum flux of the ejected target atoms perpendicular to the target surface.¹

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¹ Figure 2.2: The sputtering system used in our lab
The sputtering guns used in our setup (Atom Tech 320-O and Excel Instruments) are long (250mm) axial, planar magnetron sources with 50mm diameter target holder. For dc sputtering, we used a Glassman LV series power supply (0-600V, 0-1.7A), while a rf Plasma Products power supply (1KW at 13.6 MHz) with a MN-500 impedance matching network was used for rf sputtering. Suitable substrates such as Si wafer, quartz or glass slides were stuck on a copper plate with GE-varnish, providing good thermal conductivity at low temperatures.

The particle size of the deposited nanoparticles can be controlled by mainly adjusting the substrate temperature, inert gas pressure and applied power. We generally obtained smaller particle size for higher sputtering gas pressure. This is because with increasing pressure, as the gas density increases, the probability of sputtered atoms losing their kinetic energy to the gas atoms during collisions is larger and they are left with little energy when they deposit on the substrate. This helps in controlling the growth of particles by thermal diffusion. A similar effect is also achieved by lowering the substrate temperature or the applied power. Nanostructured films (average grain size ≈2–20nm) of most materials can be sputtered onto desired substrates by dc/rf sputtering at relatively high gas pressures (≈10–400 mTorr) and low substrate temperatures (77–300 K). For dc sputtering, the applied voltage was generally in the 200-400V range (corresponding to a current of ~300mA, depending on the target resistivity). For rf sputtering, the applied power was in the range of 25-80W.

The above method was used to synthesize nanostructured thin films of Nb and Pb and the nanocomposites of Pb-Ag. The process parameters used to synthesize them is discussed in later chapters. As the Pb films oxidized on exposure to air, we were required to deposit on it a non-conducting overlayer, in situ. Therefore, we modified the sputtering chamber where two magnetron guns were placed at 180° to each other in order to carry out sequential sputtering (see Fig. 2.2). The details of this are given in chapter 4.

### 2.2 Structural characterization

The structural characterization of the as-deposited films was carried out mainly by X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Electron Energy Loss Spectroscopy (EELS), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDX) and Atomic force microscopy (AFM). These techniques are explained briefly in the following subsections.
2.2.1 X-ray Diffraction (XRD)

XRD is one of the most important tools available for characterization of crystalline materials. Information about the different crystallographic phases present, unit cell parameters, presence of impurities etc. can be obtained from the analysis of the XRD pattern of a material. In case of polycrystalline materials, it gives information about the mean crystallite size and size distribution. We have extensively used XRD for characterization of the targets and the nanocrystalline films.

![Schematic of the beam path in an X-Ray Diffractometer](image)

Figure 2.3: Schematic of the beam path in an X-Ray Diffractometer

The occurrence of peaks in the x-rays diffracted from a periodic crystal is governed by the Bragg condition for constructive interference:

\[
2d \sin(\theta) = n\lambda
\]

where \(d\) is the spacing between two adjacent atomic planes belonging to the same family, \(\theta\) is the angle between the atomic plane and the incident x-rays, \(n\) is the order of diffraction, and \(\lambda\) is the wavelength of x-rays. We have used a Siemens D-500 diffractometer using CuK\(\alpha\) source typically at 30kV and 30mA. The diffraction pattern was obtained by rotating the crystal and the detector (\(\theta-2\theta\) geometry). A schematic diagram of the beam path in an x-ray diffractometer is shown in Fig. 2.3. The detector was a scintillation (Tl activated NaI crystal) coupled to a photomultiplier tube (PMT). Generally, the CuK\(\alpha\) line is also present in the incident beam and gives rise to its own diffraction pattern. For the structural analysis of the sample, contribution of this line was removed by Rachinger correction. This technique uses
the known wavelengths and intensity ratio of the two lines to separate the two diffraction patterns.

Theoretically, for an infinite crystal, the Bragg reflection peaks are delta functions. However for real crystals, peak broadening comes from the “instrumental width”, which is caused by the finite spectral width of the x-ray beam, its non-parallel nature, imperfect focusing, finite slit-widths etc. For smaller crystallite sizes (typically below 50nm), an additional broadening occurs. Due to the presence of only a few diffracting planes, in which the contributions from the planes having their angles slightly higher and lower than the Bragg angle \( \theta \) do not get completely cancelled by destructive interference.\(^6\) The size of the crystal can be estimated from the width of Bragg reflection and is given by the Scherrer formula:

\[
d_{XRD} = \frac{0.94 \lambda}{B \cos(\theta)}
\]

where \( d_{XRD} \) is the length of the crystal in the direction perpendicular to the reflecting planes, \( B \) is the integral width (IW) or full width at half maximum (FWHM) of the Bragg reflection in radians on the 20 scale. It is important to subtract the instrumental line width from the observed line width to get a correct estimate of broadening due to small particle size.

In addition to finite size effect of the crystals, x-ray line broadening can also occur from strain in the sample. The strain corrected particle sizes can be estimated from an x-ray line profile analysis using the Warren Averbach method.\(^7\) In this method, the x-ray line profile is fitted to a pseudo-Voigt function. By carrying out a Fourier transform and working in the reciprocal space, contributions from strain and particle size can be separated. We did this analysis using the XFIT and WINFIT softwares.

### 2.2.2 Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray spectroscopy (EDX)

The **SEM** is a type of electron microscope capable of producing high-resolution images of a sample surface.\(^8\) SEM images have a characteristic three-dimensional appearance and are useful for judging the surface structure of the sample.

In a typical SEM, electrons are thermionically emitted from an electron source (tungsten filament, lanthanum hexaboride (LaB\( _6 \)) cathode, field emission gun) and are accelerated towards an anode. The electron beam, which typically has an energy ranging from a few hundred eV to 50 keV, is focused by one or two condenser lenses into a beam with a very fine focal spot size of 1 nm to 5 nm. The beam passes through pairs of scanning
coils in the objective lens, which deflect the beam horizontally and vertically so that it scans in a raster fashion over a rectangular area of the sample surface. The electron beam transfers its energy to the specimen, thereby ejecting secondary (SE) and backscattered electrons (BSE). The interaction volume of the specimen varies from 100nm to 5µm from the surface depending on the accelerating voltage. A detector counts these electrons and sends the signals to an amplifier. The final image is built from the number of electrons emitted from each spot of the sample which gives a three dimensional appearance. A schematic of a typical SEM is shown in Fig. 2.4. In addition to the image of the surface of the specimen, the backscattered electrons can be used to give information of the chemical composition at the local scale. This is because backscattered electrons give contrast between areas with different chemical compositions, when the average atomic number of the various regions is different, since the

**Figure 2.4:** Schematic of a SEM
brightness of the BSE image tends to increase with the atomic number.

The spatial resolution of the SEM depends on the size of the electron spot and the size of the interaction volume. The spot size and the interaction volume are both very large compared to the distances between atoms, so the resolution of the SEM is not high enough to image down to the atomic scale. Depending on the instrument, the resolution can be between 1 nm and 20 nm.

The EDX analysis system is an integral part of the SEM and cannot operate on its own. It is a powerful tool to find the elemental composition of a particular area of the sample. It is used to detect impurity elements and the local homogeneity of the sample. The working principle is as follows. The primary electron beam on interacting with the sample knocks out electrons from the inner atomic shells of the different elements present in the sample. These vacancies are occupied by outer shell electrons which lose energy by emitting a characteristic x-ray. Since, the x-ray energy is unique to a particular element, detecting the x-rays provides information of the elements present in the sample. The EDX spectrum plots the intensity of the x-rays for each of the energies emitted. Analyzing this spectrum gives the atomic % and hence the stoichiometry of the different elements present in the sample.

2.2.3 Transmission Electron Microscope (TEM) and Electron Energy Loss spectroscopy (EELS)

TEM is used for morphological and compositional analysis of materials. The resolution obtained is of the order of 1Å which is much better than an SEM. The basic working principle is as follows. Electrons generated from an electron gun are accelerated upto voltages of 300kV, focused by a set of electromagnetic lenses onto an electron transparent sample. This requires the sample to be very thin; of the order of 5-10nm. The sample image can be magnified upto $10^6$ times to give atomic spatial resolution. The schematic of the imaging system used in a TEM is shown in Fig. 2.5. We can get both the sample image and the electron diffraction pattern of the sample. With the TEM we can do both bright field imaging and dark field imaging. The bright field images are formed by the transmitted light which illuminates the entire field of view. The dark field image on the other hand is formed by a selected portion of the diffracted light and hence shows grains of a particular orientation only. Hence, this is a powerful tool to obtain the grain size and its distribution of nanostructured materials and also to find the crystalline structure and composition of the material at the local scale.
Figure 2.5: Schematic of a TEM

EELS is often spoken to be complimentary to EDX. It is capable of measuring atomic composition, chemical bonding, valence and conduction band electronic properties, surface properties, and element-specific pair distance distribution functions. In contrast to EDX, it is most efficient for elements with low atomic number. Transmission EELS is the most popular today in which the kinetic energies are typically 100 to 300 keV and the incident electrons pass entirely through the material sample. The basic principle is as follows. A beam of electrons with known kinetic energies is made incident on the sample. Some of the electrons undergo inelastic scattering. Inelastic interactions include phonon excitations, inter and intra band transitions, plasmon excitations and inner shell ionizations. The electron energy loss is measured. The inner shell ionizations are particularly useful for detecting the elemental components of a material. Looking at a wide range of energy losses, one can determine the types of atoms, and the numbers of atoms of each type, being struck by the beam.
2.2.4 Atomic Force Microscope (AFM)

AFM is used to image the topography of samples with atomic resolution. It uses a physical probe like a sharp tip (diameter ~ few nm) at the end of a cantilever, while the sample is placed on a piezoelectric material (scanner). To move the piezoelectric scanner along the x and y direction, voltages are applied in the two directions. This makes the tip raster scan across the sample. A positive feedback loop is used to maintain a constant interaction force between the probe and the sample. A position-sensitive photodetector records the angle of reflection from a laser beam focused on the top of the cantilever. The position of the probe and the feedback signal are electronically recorded to produce a three dimensional map of the sample surface. A schematic is shown in Fig. 2.6. AFM works in two modes: (1) Contact mode (2) Tapping mode. In the contact mode, the force between the tip and the surface is kept constant during scanning by maintaining a constant deflection. In the tapping mode, the cantilever is oscillated at or close to its resonant frequency. The oscillation amplitude, phase and resonance frequency are modified by tip-sample interaction forces; these changes in oscillation with respect to the external reference oscillation provide information about the sample's topography.

Figure 2.6: Schematic of an AFM
Figure 2.7: Schematic of a SQUID magnetometer
2.3 Superconducting and Normal state properties

The superconducting and the normal state properties of the nanostructured films were measured by a number of techniques like dc magnetization using SQUID and VSM magnetometers, ac susceptibility, dc transport, tunneling and point contact spectroscopy.

2.3.1 DC Magnetization

2.3.1 (a) Superconducting Quantum Interference Device (SQUID) magnetometer: This is the most sensitive instrument to measure the magnetic property of a sample. We have used the Quantum Design MPMS SQUID magnetometer.\textsuperscript{11} It measures the change in the magnetic flux density produced by the sample as it moves through superconducting pick up coils, placed at the center of a superconducting magnet. The schematic of the set-up is shown in Fig. 2.7. The sample is mounted in a plastic straw (with negligible magnetic moment) which is held at the end of the sample rod. The rod is inserted in the sample space in a liquid He Dewar, at the end of which there is a stepper motor used to position the sample at the center of the pick up coils. The pick up coils are made of Nb wire, wound in four coils configured as a second-order gradiometer, as shown in Fig. 2.8(a). In this configuration, the top and bottom coils are single turn wound clockwise and the centre coil is two turns wound anticlockwise.

![Figure 2.8(a): Configuration of a second order gradiometer superconducting detection coil](image)

(b) SQUID response of a diamagnetic sample from a second order gradiometer detection coil

This is used to reduce noise in the detection circuit caused due to fluctuations in the magnetic field of the superconducting magnet. A spatial dependence of an ideal signal for a diamagnetic sample (a point magnetic dipole) for a second-order gradiometer is shown in Fig. 2.8(b). To obtain a similar SQUID profile the sample should be smaller than the detection
coils (~2-3mm). The sample can move over a length of (~2-6cm) along the axis of the magnet. As the sample moves through the coils, it induces a current in the pickup coils at each position of the sample. Since, the coils are superconducting, the total flux $\Phi$ through them is quantized. These pickup coils are connected to the input of a SQUID loop, located in a magnetic shield. The main element of the SQUID is a superconducting loop with two Josephson junctions. The impedance of the SQUID is a periodic function of the magnetic flux threading it. Any modulation of the applied bias current along with a lock-in detector is used to measure the impedance. Hence, it acts as an efficient current to voltage converter. Thus, the variations in the current in the detection coils produce corresponding variations in the SQUID voltage which is proportional to the magnetic moment of the sample. Finally, there are computer routines which fit the SQUID profile (as shown in Fig. 2.8(b)) and extract the magnetic moment of the sample from the SQUID output.

The MPMS SQUID magnetometer allows measurements at temperatures between 1.8-300K and magnetic fields up to 7T.

(b) Vibrating Sample Magnetometer (VSM): The basis of the VSM is to measure the rate of change of magnetic flux due to the mechanical vibration of the magnetized sample which produces an induced emf in a detection coil system. The sample, placed in a uniform dc magnetic field provided by the superconducting magnet (placed in a liquid He Dewar), is
made to oscillate sinusoidally with small fixed amplitude (~1.5mm). The induced voltage is
given by:
\[\varepsilon = -\partial \phi / \partial t = -\partial \phi / \partial z \times \partial z / \partial t,\]
where \(z = z_o + \cos(\omega t)\), \(\omega\) is the frequency of vibration
(55Hz). The sample is taken to be a magnetic dipole.

We have used an Oxford Instruments VSM, where the temperature can be varied
between 1.6K-300K and a magnetic field upto 12T can be applied. A schematic of the set-up
is shown in Fig. 2.9. The sample is positioned at the center of the detection coils by a stepper
motor fixed at the end of the sample rod. This position is such that the response from the
dipole moment is maximum.

2.3.2 High frequency ac Susceptibility
This was custom built to measure the superconducting transitions of thin films. The film or
the sample is sandwiched between two planar coils of 110 turns each. A sinusoidal voltage of
high frequency (15kHz) is applied to the primary coil. A voltage proportional to the
frequency is induced in the secondary coil which is detected by lock-in detectors. A
schematic of the planar coil geometry is shown in Fig. 2.10. When the sample becomes
superconducting at \(T_c\), it shields the magnetic flux of the primary coil. Hence, there is a sharp
drop in the voltage of the secondary coil (signal). This gives the superconducting transition
temperature \((T_c)\) of the sample. When the signal from the secondary coil is recorded while
sweeping the magnetic field, a sudden increase in signal at a particular field denotes the
critical field \((H_C)\) of the sample, the field at which the sample becomes normal.

![Figure 2.10: Schematic of AC susceptibility set-up](image-url)
It is important to point out that though this method does not give the absolute value of the magnetization, it is an extremely sensitive technique to measure the superconducting transition, especially of thin films. In conventional susceptometers the signal is proportional to the volume of the sample and is not very efficient for the measurement of thin film where the volume is very low. However, in this geometry, the signal is proportional to the area of the sample making it ideal for the measurement of thin films.

2.3.3 DC transport

Measurement of the resistivity of a sample by the conventional four probe method is one of the most popular techniques of characterizing samples in solid state physics. Four silver paint or In-Ag solder contacts are made with thin copper wires on the sample. Current is passed from a constant current source by the outer two wires and the voltage is measured by a nanovoltmeter using the two central wires. The four probe method isolates the current and voltage contacts. As long as the sample and contact resistance is less than the resistance of the voltmeter, the contact resistances does not affect the resistance of the sample as the voltage leads do not draw any appreciable current. The insert for carrying out maneto-resistance measurements (dc transport in the presence of a magnetic field) and the zero field resistivity measurements of the superconducting films used in the present study was fabricated in house. It is shown in Fig. 2.11.

![Figure 2.11: The resistivity insert fabricated by us. Inset shows a close up of the insert head](image-url)
2.3.4 Tunneling spectroscopy with planar tunnel junctions

This is a very useful technique to measure the superconducting energy gap ($\Delta(T)$) of a sample. It was first demonstrated successfully by Giaever in 1960.\textsuperscript{12} It is based on the principle of single particle tunneling of electrons between a superconductor (S) and a normal metal (N) (or another superconductor (S)) when separated by a very thin (5-10nm) insulating layer (I). In the present work we have carried out measurements with planar tunnel junctions made by a superconductor (Pb films) and a normal metal (Al) separated by a thin insulating layer (the native oxide layer of Al).

**Experimental technique:** Planar tunnel junctions between superconductors and normal metals can be prepared in large number of ways. The choice of the insulator and the normal metal is specific to the superconducting material. For conventional superconductors, Al is the commonly used bottom electrode which can be grown by evaporation, sputtering etc. It is known to form a surface oxide layer (of thickness ~ 5-10nm) easily when exposed to air. The top electrode is deposited in a cross geometry on the Al and is formed by the superconductor whose superconducting energy gap is to be measured. However, this cannot be used for the high $T_c$ superconductors. To date, the most reliable method of tunnel junction fabrication on high-temperature superconductors has been by evaporation of Pb counter electrodes directly on the superconductor surface. A chemical interaction between the materials forms a good insulating tunnel barrier. Greene et al have shown that an organic layer (alkylamines) forms a very good insulating layer for the case of YBCO based tunnel junctions and gives reproducible tunneling characteristics.\textsuperscript{13} Freshly cut In pressed on a superconducting material

![Planar view of tunnel junction device](image)

![Cross-sectional view](image)

**Figure 2.12:** Schematic of planar tunnel junction
is also known to give reliable tunnel junction characteristics (both for conventional and high $T_c$ superconductors).

The planar tunnel junctions between nanostructured Pb films and Al have been fabricated in the conventional way as done by Giaever. A strip of Al (~200nm thick and 1mm wide) was deposited by sputtering at the center of a properly cleaned glass slide using a stainless steel (SS) mask. It was exposed to air for 15-20 minutes for the native surface oxide layer to grow. Thereafter, Pb was deposited by dc sputtering in the form of cross-strips, again using SS masks. The thickness of Pb film was ~200nm and the width of the strip was 2mm. Contact pads of Au were deposited to make the current and voltage leads across the junction by evaporation. Schematic of the planar and cross-sectional view is shown in Fig. 2.12. Four probe measurements were performed to measure the I-V characteristic of each tunnel junction. Each device had 2 tunnel junctions to increase the statistics of measurements. The typical junction area was $1 \times 2$ mm$^2$. Reducing the junction area using thinner masks made by lithographic techniques helps in improving the success rate of the tunnel junctions.

**Principle:** For a superconductor-insulator-normal metal (S-I-N) junction, the tunneling current is given by:

$$I \propto |T|^2 N_N(0) \int_{-\infty}^{\infty} N_S(E)[f(E - eV) - f(E)]dE$$

Here, $|T|$ denotes the matrix elements of the transmittivity between the normal metal and superconductor and depends on the insulating barrier in between, $N_N(0)$ is the density of states (DOS) of the normal metal which can be taken as constant, $N_S(E)$ is the DOS of the superconductor and $f(E)$ is the Fermi distribution function. The DOS of the superconductors satisfies the condition:

**Figure 2.13** (a) I-V characteristics of a tunnel junction at $T = 4.2K$, (b) Differential conductance of the same junction at $T = 4.2K$
\[
N_s(E) = \frac{E + i\Gamma}{\sqrt{(E + i\Gamma)^2 - \Delta^2}} \quad \text{for } E > \Delta
\]
\[
= 0 \quad \text{otherwise}
\]

Here, \(\Gamma\) is the broadening parameter arising from the finite lifetime of the quasiparticles \((\tau = 1/\Gamma)\).

The I-V characteristic of an S-I-N junction at finite temperatures is shown in Fig. 2.13(a). Differentiating this curve gives the differential conductance \((G(V))\), which needs to be normalized with respect to the normal state conductance \((G_N)\) to give the normalized differential conductance \((G(V)/G_N)\) of the junction. The plot of \(G(V)/G_N\) as a function of the bias voltage is shown in Fig. 2.13(b). Fitting this curve using Eq. 2.3, with \(\Delta\) and \(\Gamma\) as the fitting parameters at the known temperature \((T)\), gives the unknown parameter, \(\Delta(T)\).

### 2.3.5 Point Contact Andreev Reflection Spectroscopy (PCAR)

Point contact spectroscopy (PCS) has become popular over the past few decades and is used extensively to extract energy, momentum and spin resolved information about the Fermi surface for superconductors and ferromagnets.\(^\text{15}\) In this work, PCAR which is a special form of PCS has been used to measure the superconducting energy gap \((\Delta(T))\) of the nanostructured Nb films. I will describe in detail the experimental details and the principle of finding \(\Delta(T)\) (energy resolved information) from these measurements.

![Figure 2.14 (a) Schematic of the needle-anvil technique to establish a point contact (b) Electrochemically etched gold tip used for point contact spectroscopy](image)

**Experimental technique:** To measure \(\Delta(T)\) by PCAR, a very sharp tip of a normal metal is brought in contact with the superconductor whose gap is to be measured. To get any energy resolved information, the contact requires to be in the ballistic regime i.e. the contact diameter \((a)\) should be much smaller than the mean free path of the electrons \((l)\). This can be
done either by needle-anvil technique (Fig. 2.14(a)) using a differential screw arrangement\textsuperscript{b,16} or a piezoelectric bi-morph\textsuperscript{c,17} or by lithographic methods.\textsuperscript{18} Different methods are employed to make fine tips depending on the material of the tip. Metals such as copper, silver, platinum, platinum-iridium etc can be made by mechanically cutting the wires of the said material whereas metals like gold is prepared by electrochemical etching. The starting diameter of the wire is usually 100-300 microns. After processing, the tip diameter is reduced to a few tens of nanometer (as shown in Fig. 2.14(b)) However, the final contact diameter is controlled by the pressure on the tip. We have used the differential screw arrangement to control the pressure on the tip. The schematic of the point-contact insert head and the actual head used in the experiments have been shown in Fig. 2.15. In the differential screw arrangement, you have a

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{schematic.png}
\caption{(a) Schematic of a differential screw arrangement (b) Picture of the point-contact head used in our experiments}
\end{figure}

differential screw with \textasciitilde 100 threads per inch rotated by a stepper motor from outside the cryostat. Some set-ups also have a peizo tube below the screw which is used to fine tune the pressure.

\textsuperscript{b} In a differential screw arrangement, the tip is mounted at the end of a differential screw (in which rotational motion is translated into vertical motion) which enables the tip to move closer/away from the sample placed below it.

\textsuperscript{c} In this method, a piezoelectric bi-morph (converter of electric input to mechanical motion), is used and the tip is mounted on one of the bi-morphs while the sample is placed on the other bi-morph piece. The tip moves closer/away from the sample by applying voltages on the piezoelectric bimorph piece which holds the tip.
contact. Ideally, the conventional PCAR spectrum shows two peaks at $\frac{\Delta}{e}$ and $-\frac{\Delta}{e}$ respectively, and beyond the superconducting gap voltage no structure apart from the smooth decay of the density of states is expected (Fig. 2.16). However, large zero bias conductance peaks (Fig. 2.17(a)) or anomalous dip structures (shown by arrows in Fig. 2.17(b)) at bias voltages beyond the superconducting energy gap in the PCAR spectra are sometimes observed, which helps to ascertain if the contact is in the ballistic regime. To understand the origin of the dip structures, one needs to look at the different regimes of transport at a point contact between two metals. Electrical transport through a metallic point contact can be divided in different regimes based on the ratio of the diameter ($a$) and the mean free path ($l$) of the electron. They are as follows:

**Ballistic regime:** In the ballistic regime the contact diameter is smaller than the elastic ($l_e$) or inelastic ($l_i$) mean free path. In this regime electron does not undergo any elastic or inelastic scattering while passing through the point contact and the conductance is represented by the sum of individual quantized conduction channels each with a conductance, $G_0 = \frac{2e^2}{h}$. In a ballistic contact statistically, the electron freely accelerates in the area of the contact without undergoing any scattering. The resistance of a ballistic contact between two metals in their normal state is thus independent of the bulk resistivity of the material and is given by

$$R_s = \frac{2h}{e^2(a k_F)^2},$$

where $k_F$ is the Fermi momentum.

**Thermal regime:** The other extreme limit of a point contact is when $a >> l_e, l_m$. In this regime the electronic transport through the contact is dominated through scattering in the point contact region and the point contact resistance is proportional to the bulk resistivity of the metal. Since the electron dissipates its energy in the point contact region, Joule heating causes substantial increase of the temperature at the point contact. The resistance of a point contact in the thermal regime is given by the Maxwell resistance

$$R_M = \frac{\rho}{2a}.$$ 

No spectroscopic information can be obtained from a point contact in the thermal regime.

When the point contact is not in either of these two extreme regimes, the expression for the contact resistance gets modified due to the scattering of the electrons between conduction channels. The contact resistance ($R_d$) in the intermediate regime was derived by Wexler as $R_d = R_s + \Gamma(l/a) R_M$, where $\Gamma(l/a)$ is a slowly varying function in the range 0.6-1. Since $R_S$ varies as $1/a^2$ and $R_M$ varies as $1/a$, $R_S$ dominates in this expression when $a$ is
**Figure 2.16:** A typical PCAR spectra obtained for a Nb film at $T = 4.2$ K. The circles denote the experimental data while the solid line indicates the fit using the BTK theory.

**Figure 2.17** (a): PCAR spectra showing zero bias conductance peak for a point contact between a Nb film ($d_{XRD} \sim 11$ nm) and a Pt-Ir tip (b) PCAR spectra showing conductance dips at voltage biases greater than the superconducting energy gap ($\sim 1.5$ meV) for a point contact between a Nb film ($d_{XRD} \sim 11$ nm) and a Cu tip. The different spectra (shown by different color lines) are obtained for different contacts with different contact resistances ($R_d$)
small and the contact is in the ballistic regime. When $a$ is large $R_M$ dominates and the contact is in the thermal regime. If the contact is not in the ballistic regime both $R_M$ and $R_S$ are important and the contact resistance is dramatically affected when the superconducting transition takes place and $\Gamma(T_{\text{eff}})$ becomes zero. In the I-V characteristic this transition causes a sharp change in the slope at the voltage corresponding to the critical current of the superconductor. Consequently, the dip structures appear in the normalized differential conductance versus voltage (PCAR) spectrum. For very high relative contribution from $R_M$, there is a large enhancement in the zero bias conductance.

To establish a ballistic point contact, the method followed is as follows. The first contact is made such that it punctures the thin surface oxide layer present on the surface of most of the samples. Thereafter, the ballistic contact is achieved by slightly withdrawing the tip thereby decreasing the contact area (increasing the contact resistance, $R_d$). For each contact, a spectrum is recorded which helps us to identify a ballistic contact. On establishing a ballistic contact (with typical contact resistance $\sim 1$-$100 \Omega$), the measurement is done by the standard ac modulation technique with phase sensitive detection. The measurement is done in the four probe geometry. A dc voltage ($V_{dc}$) is modulated by a small ac voltage ($V_{ac} \cos(\omega t)$, $V_{ac} \sim 10\%$ of $V_{dc}$). A voltage to current converter (shown in Fig. 2.18(b)) converts the voltage to current $(I + i \cos(\omega t))$ which is passed through the tip-sample. The output voltage of the point contact can be expressed in a Taylor series;

$$V(I + i \cos(\omega t)) = V(I) + \frac{dV}{di}i \cos(\omega t) + \frac{1}{4} \frac{d^2V}{di^2}i^2(1 + \cos(2\omega t)) + \ldotsd$$

The first harmonic of the signal measured by a lock-in amplifier (locked in at the input frequency $\omega$) is proportional to the differential conduction $(dI/dV)$ of the junction (for small $i$). The schematic of the experimental set-up is given in the Fig. 2.18(a). The differential conductance of the junction is measured as a function of the bias voltage. The PCAR spectra is generally depicted by the normalized conductance $(G(V)/G_N)$ vs the bias voltage $(V)$ (Fig. 2.16). Since PCAR depends on the surface of the sample, hence to interpret the results correctly a large number of contacts need to be made and analyzed.
**Figure 2.18 (a):** Schematic of the experimental set up for Point contact spectroscopy  
**Figure 2.18 (b):** Electronic circuit of the V-I converter

**Principle:** The principle of PCAR is based on Andreev reflection which describes ballistic transport between normal metals and superconductors. When an electron is incident at the normal metal-superconductor interface with an energy $E_1 > \Delta$, it crosses over into the available states in the superconductor (as shown in Fig. 2.19). However, when an electron is incident at the interface with an energy $E_2 < \Delta$, it gets reflected back as a hole in the opposite spin band and a Cooper pair propagates in the superconductor. This phenomenon is known as Andreev reflection$^{23}$ and forms the basis PCAR spectroscopy. This process gives rise to an enhancement in the conductance of a N/S junction at bias voltages below the superconducting energy gap voltage, $\Delta/e$. PCAR is modeled by the theory proposed by Blonder, Tinkham and
Klapwijk in 1980. They solved the Bogolubov-de Gennes equations with the appropriate boundary conditions for N-S ballistic point contact. Within the BTK model, an interfacial barrier is accounted for by a delta function potential barrier, $V(x) = V_0 \delta(x)$. This barrier is often expressed in terms of the dimensionless parameter $Z = \frac{V_0}{\hbar v_F}$, where $v_F$ is the geometric mean of the Fermi velocities in the superconductor and the normal metal. This barrier arises either from a physical oxide barrier present at the interface or due the Fermi velocity mismatch of the two metals.

$$Z = \frac{2\pi V_0}{\hbar v_F}$$

![Figure 2.19: Schematic diagram showing Andreev reflection between a normal metal and a superconductor](image)

The essence of Andreev reflection lies in the fact that unlike normal metals, the elementary excitations in a superconductor are not electrons and holes but complex objects consisting of a combination of electrons and holes, called Bogoliubons. Bogoliubons are a natural outcome of the solution of the BCS Hamiltonian. In a normal metal an electron and a hole (propagating in the x-direction) are represented as $\begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{ikx}$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix} e^{-ikx}$ respectively. Similarly, in a superconductor the elementary excitations are the electron-like and hole-like Bogoliubons, represented as $\begin{pmatrix} u \\ v \end{pmatrix} e^{iqx}$ and $\begin{pmatrix} u \\ v \end{pmatrix} e^{-iqx}$ respectively, where
$u^2 = 1 - v^2 = \frac{1}{2} \left[ 1 + \frac{(E^2 - \Delta^2)}{E^2} \right]$, and $E$ is the energy of the quasiparticle with respect to the Fermi energy. For energies $E \gg \Delta$, $u \to 1$ and $v \to 0$; thus for energies much larger than $\Delta$ the elementary excitations in a superconductor becomes identical to those in a normal metal.

Thus based on the principle of Andreev reflection, the total wave function in the normal metal ($\Psi_N$) and superconductor ($\Psi_S$) is given by:

$$\Psi_N = \begin{pmatrix} \frac{1}{0} \varepsilon^{ikx} + d(0) \varepsilon^{ikx} + b(1) e^{-ikx} \end{pmatrix}$$

where, $a$ and $b$ are the probability of Andreev and normal reflection respectively

$$\Psi_S = c\left( \begin{array}{c} u \\ v \end{array} \right) e^{iqx} + d\left( \begin{array}{c} v \\ u \end{array} \right) e^{-iqx}$$

The values of $a, b, c$ and $d$ can be obtained from the boundary conditions

$$\Psi_S(x = 0) = \Psi_N(x = 0) \quad \text{and} \quad \Psi_S'(x = 0) - \Psi_N'(x = 0) = \frac{2mV_0}{\hbar^2} \Psi_N(x = 0),$$

where $m$ is the electronic mass.

The current versus voltage characteristics of a ballistic N/S point contact is given by:

$$I(V) \propto N(0)v_F \int_{-\infty}^{\infty} [f(E - eV, T) - f(E, T)] [1 + A(E) - B(E)] dE \quad (2.5)$$

Where $f(E)$ is the Fermi-Dirac distribution function, $N(0)$ is the density of states at Fermi level and $v_F$ is the Fermi velocity of the normal metal. Here $A(E) = a^*a$ and $B(E) = b^*b$. The expressions of $A(E)$ and $B(E)$ as calculated from the BTK theory is given as follows:

<table>
<thead>
<tr>
<th>Co-efficient</th>
<th>$E &lt; \Delta$</th>
<th>$E &gt; \Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A(E)$</td>
<td>$\frac{(\Delta/E)^2}{1 - \varepsilon(1 + 2Z^2)^2}$</td>
<td>$\frac{(uv)^2}{\gamma^2}$</td>
</tr>
<tr>
<td>$B(E)$</td>
<td>$1 - A(E)$</td>
<td>$\frac{[u^2 - v^2]Z^2(1 + Z^2)}{\gamma^2}$</td>
</tr>
</tbody>
</table>

Here, $\gamma^2 = \left[ (u^2 - v^2)Z^2 + u^2 \right]^2$ and $\varepsilon = \frac{E^2 - \Delta^2}{E^2}$.

In some cases, it may be necessary to introduce a broadening parameter ($\Gamma = 1/\tau$) which accounts for a broadening of the BCS DOS due to the finite lifetime of the quasiparticle.
modifies the Bogolubov-de Gennes equation, thereby giving modified expressions for \( A(E) \) and \( B(E) \) in terms of \( \Gamma \).\(^{25}\)

The PCAR spectrum is analyzed within the framework of the BTK formalism using Eq. 2.5 with \( \Delta(T) \), \( Z \) and \( \Gamma(T) \) as the three fitting parameters. Thus, fitting the experimental PCAR spectrum with the theoretical model given by the BTK theory, the unknown superconducting energy gap (\( \Delta(T) \)) can be evaluated at a particular temperature, \( T \).

In summary, in this chapter I have described in detail all the experimental tools used to synthesize, characterize and measure the superconducting properties of the nanostructured superconducting samples which have been studied in this thesis.
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Chapter 3

Size dependence of the Superconducting and the Normal State Properties in the Intermediate Coupling Type II Superconductor: Niobium

3.1 Introduction

Bulk Nb is a Type II superconductor with an intermediate electron-phonon coupling strength with $2\Delta/k_B T_c \sim 3.8$. The superconducting parameters like the superconducting transition temperature ($T_c$), the coherence length ($\xi_0$), the penetration depth ($\lambda_L$), the superconducting energy gap ($\Delta(0)$), the upper and lower critical fields in the clean limit ($H_{C1}(0)$ and $H_{C2}(0)$) for bulk Nb is shown in Table 3.1. As discussed in Section 1.2.3, the superconducting properties are affected by both surface effects and quantum size effects for zero dimensional superconductors. While the surface effects increase the parameter $2\Delta/k_B T_c$ with decreasing particle size, quantum size effects do not change it. It is important to note that Nb is an interesting system to study size effects. This can be understood as follows. With a reduction in particle size, if surface effects dominate, the nano-superconductor would go over to the strong coupling limit where the weak coupling BCS relations are no longer valid. However, if quantum size effects dominate, there will be no change in $2\Delta(0)/k_B T_c$ with reduction in particle size, keeping it in the intermediate coupling limit. Hence, a change in $2\Delta(0)/k_B T_c$ will help us in identifying the mechanism influencing $T_c$ in small particles of Nb. This becomes difficult for the weak coupling superconductors since a small change in the electron-phonon coupling strength with reduction in particle size will still keep it in the weak coupling limit and it becomes difficult to dissociate the two effects from each other. Only a

<table>
<thead>
<tr>
<th>$T_c$ (K)</th>
<th>$\Delta(0)$ (meV)</th>
<th>$2\Delta(0)/k_B T_c$</th>
<th>$\xi_0$ (nm)</th>
<th>$\lambda_L$ (nm)</th>
<th>$H_{C1}$ (clean limit) (Oe)</th>
<th>$H_{C2}$ (clean limit) (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.4</td>
<td>1.5</td>
<td>3.8</td>
<td>39</td>
<td>40</td>
<td>1700</td>
<td>4000</td>
</tr>
</tbody>
</table>

Table 3.1: Superconducting parameters of bulk Nb

$2\Delta/k_B T_c$ with decreasing particle size, quantum size effects do not change it. It is important to note that Nb is an interesting system to study size effects. This can be understood as follows. With a reduction in particle size, if surface effects dominate, the nano-superconductor would go over to the strong coupling limit where the weak coupling BCS relations are no longer valid. However, if quantum size effects dominate, there will be no change in $2\Delta(0)/k_B T_c$ with reduction in particle size, keeping it in the intermediate coupling limit. Hence, a change in $2\Delta(0)/k_B T_c$ will help us in identifying the mechanism influencing $T_c$ in small particles of Nb. This becomes difficult for the weak coupling superconductors since a small change in the electron-phonon coupling strength with reduction in particle size will still keep it in the weak coupling limit and it becomes difficult to dissociate the two effects from each other. Only a
pronounced and large change in the coupling strength will help identify the mechanism influencing $T_c$ in these systems which may always not be present. Hence, it is important to make a detailed study of the size effects of the superconducting properties in this intermediate coupling superconductor to understand which is the dominant mechanism influencing their properties.

Hihara et al. recently grew Nb clusters with mean diameter of 6.3nm by plasma-gas-condensation. They observed that these Nb clusters were non-superconducting down to a temperature of 2K, consistent with the Anderson criterion. However, the evolution of superconducting properties till the Anderson criterion is reached has not been studied in detail as a function of decreasing particle size in Nb. We made a detailed study of the evolution of superconducting properties of sputter deposited nanostructured Nb films. Since all the superconducting properties like $T_c$, $\Delta(0)$ and $H_{C2}$ are interrelated quantities, a complete study of each of these properties is important to understand the evolution of superconductivity with decrease in particle size. Also the normal state properties such as the room temperature resistivity influence some of the superconducting properties and hence are required to be studied in relation to the superconducting properties. In this Chapter, I will discuss the study of the superconducting and the normal state properties of nanostructured Nb with the reduction in particle size. In Section 3.2, I will describe the synthesis and the structural characterization of the nano-Nb films. These films show very interesting changes as a function of decreasing particle size such as lattice expansion, decrease in $T_c$ and $\Delta(0)$, non-monotonic variation of $H_{C2}$ and a metal-insulator transition. Section 3.3 deals with the study of the lattice expansion in these films while Section 3.4 deals with the study of the superconducting properties ($T_c$, $\Delta(0)$, $H_{C2}$) and the normal state properties as a function of particle size of these nanostructured Nb films. Our results will elucidate the mechanism influencing the evolution of superconducting properties and the origin of the size induced metal-insulator transition in nanostructured Nb.

3.2 Synthesis and Structural properties

The nanostructured Nb films have been deposited using high-pressure magnetron sputtering. The sputter deposition was carried out in a custom-built UHV chamber with a base pressure prior to sputtering $\sim 5 \times 10^{-8}$ Torr. The target used for the sputter deposition was a commercially purchased elemental Nb target of 99.99% purity. All depositions were carried out on oxidized Si substrates which had a thick (~200 nm) thermally grown amorphous oxide
on the surface. The pressure of Ar gas in the chamber during sputtering was systematically altered to vary the particle size. Ar gas pressure was varied from 3 to 100 mTorr. Prior to introduction into the sputtering chamber, the Ar gas was purified by passing it through a gettering furnace consisting of a Ti sponge maintained at a temperature of 1073 K to remove any trace amounts of oxygen in the gas. In most cases the power was kept at 200W, though some depositions were also done at 25W. The substrate was kept at room temperature barring

<table>
<thead>
<tr>
<th>DC power (W)</th>
<th>Gas pressure (mTorr)</th>
<th>Substrate temperature</th>
<th>Deposition time (h)</th>
<th>d\textsubscript{XRD} (nm)</th>
<th>Lattice parameter (nm)</th>
<th>Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>3</td>
<td>500\textdegree C</td>
<td>3</td>
<td>60.4±10</td>
<td>0.3302</td>
<td>0.26%</td>
</tr>
<tr>
<td>200</td>
<td>3</td>
<td>400\textdegree C</td>
<td>3</td>
<td>43.0±8</td>
<td>0.3302</td>
<td>0.27%</td>
</tr>
<tr>
<td>200</td>
<td>3</td>
<td>400\textdegree C</td>
<td>2</td>
<td>28.2±5.2</td>
<td>0.3316</td>
<td>0.35%</td>
</tr>
<tr>
<td>200</td>
<td>50</td>
<td>RT</td>
<td>4</td>
<td>19.2±3.1</td>
<td>0.3317</td>
<td>0.35%</td>
</tr>
<tr>
<td>200</td>
<td>3</td>
<td>RT</td>
<td>1</td>
<td>18.2±3.0</td>
<td>0.3329</td>
<td>0.49%</td>
</tr>
<tr>
<td>200</td>
<td>10</td>
<td>RT</td>
<td>1</td>
<td>17.6±3.0</td>
<td>0.3339</td>
<td>0.53%</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>RT</td>
<td>3</td>
<td>10.7±1.8</td>
<td>0.3343</td>
<td>0.71%</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>RT</td>
<td>4</td>
<td>8.2±1.4</td>
<td>0.3411</td>
<td>0.75%</td>
</tr>
<tr>
<td>100</td>
<td>10</td>
<td>RT</td>
<td>1.5</td>
<td>7.0±1</td>
<td>0.3491</td>
<td>0.83%</td>
</tr>
<tr>
<td>200</td>
<td>50</td>
<td>RT</td>
<td>1</td>
<td>6.0±1.1</td>
<td>0.3437</td>
<td>0.86%</td>
</tr>
<tr>
<td>25</td>
<td>10</td>
<td>RT</td>
<td>2</td>
<td>5.0±1</td>
<td>0.3513</td>
<td>0.86%</td>
</tr>
</tbody>
</table>

*Table 3.2: Synthesis (dc sputtering) conditions and corresponding structural parameters for the nanostructured Nb films with different average crystallographic size (d\textsubscript{XRD}). The spread in d\textsubscript{XRD} has been obtained from x-ray diffraction line shape analysis. (RT = room temperature)*

two bulk films which were deposited at higher substrate temperatures (~400-500\textdegree C). Most of the films were grown for 1 hour duration. However, for a few thicker films (~1-2\textmu m), the deposition time was 3-4 hours. The synthesis conditions along with the corresponding particle sizes (d\textsubscript{XRD}) and lattice parameters are given in Table 3.2. The as-deposited Nb films have been characterized using X-Ray Diffraction (XRD) and Transmission Electron
Microscopy (TEM).\textsuperscript{5} The XRD studies were carried out in a Siemens D500 diffractometer using \( \text{CuK}\alpha \) as the incident radiation, while the TEM studies were carried out in a FEI/Philips CM200 electron microscope operating at 200 kV. The electron diffraction studies have been carried out using a camera length of 700 mm in the TEM. The bright field and dark field TEM images for the largest and smallest particle size Nb films have been shown in Fig. 3.1(a-d). Sharp interfaces are visible between the particles for the larger particle size film (grown at 10mtorr and at a substrate temperature \( \sim 500^\circ\text{C} \)), from the TEM bright field image (Fig. 3.1(a)). This shows that the particles are closely packed together which are stacked up to form a three dimensional nanostructured film. However, there are distinct grain boundaries visible for the film (grown at 100mtorr and at room temperature) with smaller particle size (Fig. 3.1(c)). Similarly, samples with intermediate particle size have intermediate grain boundary widths. This reveals that there is a particle size dependent grain boundary width in the nano-Nb films. It will be shown in the subsequent section that this is further corroborated from the analysis of the particle size dependence of the lattice parameter in these films. This will also help us to understand the normal state transport properties in these films and will be discussed in Section 3.4.3. Representative XRD pattern of the Nb films with the largest \( (d_{\text{XRD}} = 60\text{nm}) \) and smallest \( (d_{\text{XRD}} = 5\text{nm}) \) particle size is shown in Fig. 3.2. No impurity peak was obtained. The crystal structure for the Nb films (from x-ray) could be matched to the BCC phase down to the smallest particle size of 5nm. This is however different from the observation on nanocrystalline Nb grown by ball milling by Chattopadhyay \textit{et al}. In those films they have reported a BCC to FCC phase transformation below a critical particle size of 10nm. This phase transformation may be attributed to a high degree of strain present in ball milled samples. It could also be due to the influence of contaminants. This suggests that high pressure sputtering introduces much less strain in the films. XRD pattern showing the primary visible peak (indexed as the [110] peak corresponding to the BCC phase) of the nanostructured Nb films has been shown in Fig. 3.3. This shows that as-grown Nb films are textured. However, such texturing has also been reported in Nb films grown by other deposition methods on different substrates.\textsuperscript{6} The particle size was estimated from an x-ray line profile analysis (done with XFIT software) which corrected for the strain in the films using the Warren Averbach method.\textsuperscript{7} The average particle size (will be referred by \( d_{\text{XRD}} \)) in the different films was between 60-5nm which matched quite well with those obtained from the TEM image analysis. The upper limit of the width of particle size distribution estimated
**Figure 3.1 (a) and (c):** Bright Field TEM images for films with $d_{XRD} = 60$ and 5nm respectively, (b) and (d): Dark Field images for the films with $d_{XRD} = 60$ and 5nm respectively

**Figure 3.4:** HRTEM image of the film with $d_{XRD} = 5$nm
Figure 3.2: XRD pattern of the films with (a) $d_{XRD} = 60\text{nm}$ and (b) $d_{XRD} = 5\text{nm}$

Figure 3.3: XRD pattern of the Nb films with different particle sizes showing the BCC Nb [110] peak.
from both TEM and x-ray line profile analysis, was about 20%. Furthermore, to understand the nature of the grain boundaries, high resolution TEM (HRTEM) and electron energy loss spectroscopy (EELS) were recorded from within the particles and from the grain boundary region of the films. The HRTEM image of the film with $d_{XRD} = 5\text{nm}$ is shown in Fig. 3.4. This shows two particles of ~5nm diameter separated by an amorphous grain boundary region of width $> 1\text{nm}$. The nature of the inter-granular region (IGR) was probed in further detail using EELS. Fig. 3.5 shows the EELS spectra recorded from the following regions: (i) interior of a 18 nm particle (top curve), (ii) IGR of 18 nm particle (second from top), (iii) interior of a 5 nm particle (third), and (iv) IGR of 5 nm particle (bottom). The inset of Fig. 3.5 shows the standard EELS spectrum for Nb$_2$O$_5$ from the EELS atlas. The EELS spectra shown here correspond to the low energy loss region ($< 100 \text{ eV}$). The first strong peak in each spectrum is the zero loss peak (from electrons that do not interact with the specimen). The second and third peaks are plasmon peaks due to electrons that interact with the free electrons in the material, and indicate the free-electron density in the system. It is difficult to do a quantitative analysis due to the presence of two plasmon peaks in the low-loss spectra, but a qualitative analysis is possible. The EELS spectra from the particle interiors of both the 18 nm and 5 nm particles are similar and appear substantially different from the Nb$_2$O$_5$
standard spectrum. In contrast, the spectra for the IGR of both samples are quite similar to that of Nb$_2$O$_5$ (Fig. 3.5(b)). Thus the inter-granular regions in the nano-Nb samples appears to be made up of an amorphous phase rich in niobium and oxygen, possibly in the form of an amorphous niobium oxide. We can therefore describe the microstructure of the nano-Nb system in terms of isolated crystalline particles of BCC Nb in a structurally disordered matrix. Thus, these films behave as a random array of weakly connected Josephson junctions. This has further been verified by electrical transport measurements. The equation representing the I-V characteristics of a single Josephson junction under the framework of the resistively and capacitively shunted junction (RCSJ) model is given by equations:

$$d^2\phi/d\tau^2 + Q^{-1}d\phi/d\tau + \sin\phi = I/I_{c0}$$

(3.1)

Where, $I_{c0}$ is the maximum supercurrent, $\tau = \omega_p\tau$, with the plasma frequency ($\omega_p$) of the junction given by:

$$\omega_p = (2eI_{c0}/hC)^{1/2}$$

(3.2)

The quality factor $Q$ is defined as:

$$Q = \omega_p RC$$

(3.3)

As has been pointed out in Section 1.15, for an underdamped junction ($Q>>1$), the above equations predicts a hysteresis in the I-V characteristics of a single Josephson junction. However, it has been shown by computer simulations that a random array of Josephson junctions with a distribution in the junction parameters, is also likely to show a hysteresis in the I-V measurements. This has been confirmed by experiments on granular films prepared

![Figure 3.6: I-V characteristics of Bi granular films on sapphire [Ref: Phys. Rev. B, 66, 144512 (2002)]](image)
by quench condensation. Fig. 3.6 shows the hysteresis obtained in the I-V characteristics for a granular Bi film, showing that granular films form a Josephson junction array. We made similar measurements for the nanostructured Nb films (shown in Fig. 3.7). The bulk Nb film with the largest particle size of 60nm does not show any hysteresis. However, all the nanostructured films with lower particle sizes \( d_{XRD} < 20\text{nm} \) show a pronounced hysteresis in the I-V characteristics below \( T_c \) showing that the nano-Nb films form a random network of weakly connected Josephson junctions. Thus, the superconducting wave function is confined within a single Nb particle and we are justified in ascribing particle size effects in these systems.

![Image of I-V characteristics](image)

Figure 3.7: I-V characteristics of the nanostructured Nb films with different average sizes \( d_{XRD} \) at \( T = 5.1\text{K} \). The corresponding values of \( T_c \) is also included.

### 3.3 Lattice expansion in Nanostructured Nb films

From Fig. 3.3, it can be seen that in addition to the increasing line width, there is also a systematic shift of the [110] peak to smaller \( 2\theta \) values with increasing pressure of Ar. Such a shift indicates an increase in the interplanar spacing of BCC [110] planes. This suggests a systematic lattice expansion in nanocrystalline Nb with reduction in particle size. The XRD results were corroborated by electron diffraction results. Selected area electron diffraction patterns from the four nanocrystalline Nb films are shown in Figs. 3.8(a-d). The lattice parameter of the BCC phase is again found to increase with increase in the pressure of sputtering gas or decrease in the particle size. The values of the lattice parameter measured
Figure 3.8(a)-(d): Electron diffraction for the nanostructured Nb films with different particle sizes ($d_{XRD}$).
from electron diffraction studies were in agreement with those measured from the [110] peak shift in the XRD pattern. These data indicate that Nb undergoes a 6% increase in the lattice parameter as the particle size is reduced from 60 to 5nm. (Fig. 3.9(a)). This is contrary to what is observed in most metals which usually show a lattice contraction with reduction in particle size.\textsuperscript{10} However, the fact that Nb shows a size-induced expansion in the lattice was also reported by Chattopadhyay et al in nanocrystalline samples prepared by ball milling.\textsuperscript{11,12} The negative stress of the grain boundaries estimated in this report for a 6nm crystallite was about 6GPa which is equivalent to a ~5% lattice expansion.

The increase in lattice parameter with decreasing particle size appears to exhibit a smooth, monotonic, nonlinear trend. No phase transformation from BCC to FCC is observed in the nanocrystalline Nb films studied by us, contrary to the report in the ball-milled nanocrystalline Nb (which shows a BCC to FCC transformation for particle sizes below 10nm). This suggests a possible influence of contaminants as well as the high degrees of strain introduced at very high strain rates during ball-milling in the earlier study. In comparison, the nanocrystalline Nb thin films deposited by high pressure magnetron sputtering are expected to have a relatively lower degree of strain.

The observed lattice expansion is indicative of a negative stress field arising from the grain boundaries. It has been shown in the literature that vacancy-like defects give rise to an excess free volume ($\Delta V$) for the atoms in the grain boundaries, which can cause a negative stress field on the particles and lead to a lattice expansion.\textsuperscript{13} The lattice expansion in nanocrystalline materials has been modeled on the basis of a linear elasticity theory according

![Figure 3.9(a): Variation of lattice parameter (a) with particle size ($d_{XRD}$), (b) Variation of grain boundary width ($\Delta d$) with particle size ($d_{XRD}$). The open circles denote $\Delta d$ obtained from Eq 3.4 and 3.5 and the solid line is the exponential fit (Eq. 3.6)](image-url)
to which the displacement of an atom from its equilibrium position is proportional to $1/x^2$ where $x$ is the distance of the atoms to the center of the defects in the grain boundaries. According to this theory, the lattice expansion is given by:

$$\Delta r/r = r/r_0 = \frac{1}{2d_{XRD}} \frac{\Delta d (\Delta d + 2a_0)}{\Delta d + a_0} \left(\sqrt{\Delta V + 1} - 1\right)$$

(3.4)

Where, $r_0 =$ lattice parameter of the perfect (bulk) crystallite, $a_0 =$ nearest neighbour interatomic distance for the perfect lattice, $d_{XRD} =$ crystallite size, $\Delta d =$ width of the grain boundary.

To find the excess free volume ($\Delta V$) associated with the atoms of the grain boundary, Chattopadhyay et al assumed a system of spherical particles with an orthogonal set of grain boundaries (as shown in Fig. 3.10). The atoms at the grain boundaries enjoy an extra degree of freedom i.e. migration along the grain boundary plane. Hence, the excess free volume associated with these atoms is confined along a plane parallel to the grain boundary plane. $\Delta V$ is given by the fractional excess area occupied by the atoms in the grain boundary plane situated at a distance of $(d_{XRD} + \Delta d/2)$ distance from the grain. Therefore, $\Delta V$ is given by:

$$\Delta V = \left[\left(d_{XRD} + \Delta d/2\right)^2 - d_{XRD}^2\right]/d_{XRD}^2$$

(3.5)
In most prior calculations of the excess free volume, the width of the grain boundary has been assumed to be a constant ($\Delta d = 0.5$ nm), independent of the particle size. The predicted values of the normalized lattice expansion for nanocrystalline Nb, calculated using Eq. 3.4 and 3.5 with $\Delta d = 0.5$nm, were found to be different from the experimentally measured values of lattice expansion for the different particle sizes. While the experimental values are in good agreement with the predicted values, with $\Delta d = 0.5$ nm for the particle sizes greater than 20 nm ($d_{XRD} > 20$nm), the experimental values exceed the predictions for smaller particle sizes if $\Delta d$ is kept fixed at 0.5nm. We therefore varied $\Delta d$ between 0.5nm and 1.4 nm and calculated the normalized lattice expansion ($\Delta a/a_o$) as a function of particle size. We observed that the experimental data point for $d_{XRD} = 10$nm lay on the curve generated with a grain boundary width of 0.9nm, while the data point for $d_{XRD} = 5$nm lay on the curve generated with $\Delta d = 1.4$nm. These results appear to indicate that as the particle size decreases, the grain boundary width ($\Delta d$) increases. Fig. 3.9(b) plots the obtained grain boundary widths ($\Delta d$) for different particle sizes ($d_{XRD}$). We could fit this to an empirical exponential function, of the form:

$$\Delta d = 0.48 + 1.86\exp(-0.14d_{XRD})$$  \hspace{1cm} (3.6)

The increase of the grain boundary width with the reduction in particle size was also observed experimentally from the bright field and HRTEM images of the nanostructured Nb films (Fig. 3.1(a)&(c) and Fig. 3.4). We will show later (Section 3.4.3) that the dependence of $\Delta d$ on $d_{XRD}$ significantly influences the normal state transport for films with $d_{XRD} < 8$nm.

### 3.4 Superconducting and normal state properties

#### 3.4.1 Mechanism for size-dependence of the transition temperature ($T_c$)

The superconducting transition temperature ($T_c$) was determined from both dc magnetization measurements obtained from both SQUID magnetometer and a VSM, as well as dc transport done in a custom built, home made apparatus. The criteria used to determine $T_c$ were as follows. In magnetization measurements (Fig. 3.11(a)) $T_c$ was taken as the temperature of the onset of the Meissner transition. From transport measurements (Fig. 3.11(b)) it was taken as the temperature at which the resistance deviated from zero. As shown by Fig. 3.11, the $T_c$ obtained from both these methods matched quite closely. This shows that though the poorly conducting grain boundaries leads to localization of the electronic wave functions within the particles, it does not lead to any change in the $T_c$. Otherwise, the $T_c$ obtained from transport would be expected to be different from that obtained from magnetization.
The normal state resistance (at any temperature above $T_c$) showed a monotonic increase with decreasing particle size, which is presumably due to the increase in the grain boundary scattering that results from the increased grain boundary with decreasing particle size. The variation of $T_c$ with particle size is shown in Fig. 3.12. We can see that the $T_c$ is equal to 9.4K (bulk Nb $T_c$) for films with $d_{XRD} \geq 20$nm. Below 20nm, $T_c$ decreases from 9.4K to 4.7K as the particle size is reduced from 20 to 8nm. Below 8nm, the Anderson criterion is reached (that is the energy level spacing, $\delta$ (Kubo gap) arising from the discretization of the energy levels is comparable to the superconducting energy gap $\Delta(0)$ of Nb) and the films become non-superconducting. More precisely these samples show no superconducting transition down to 1.6K.

Extraneous factors affecting the $T_c$ of the nanostructured Nb films can be ruled out as argued below. We have already indicated that since the $T_c$ measured from both magnetization and transport is the same, the non-conducting intergranular region or the presence of Josephson junctions does not appear to affect the $T_c$ of the system. The observed lattice expansion would cause an increase in the amplitude and a reduction in the frequency of the ionic vibrations. This would lead to an increase in the electron phonon coupling constant ($\lambda$) which is contrary to our observations (reduction in $T_c$). Clearly, the lattice distortion is not responsible for the decrease in $T_c$. Also the hysteresis obtained in the I-V characteristics

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**Figure 3.11 (a):** Temperature variation of susceptibility ($\chi$) from magnetization measurements, (b) Temperature variation of resistivity ($\rho$) from transport measurements for the nanostructured Nb films with different particle sizes ($d_{XRD}$)
(Fig. 3.7) in the nano-Nb films below a particle size of 20nm show that these films form a random network of weakly connected Josephson junctions and the electronic wave function is confined within a single grain. Thus, it seems that the observed decrease in $T_c$ is mainly induced by particle size. We now proceed to find out whether surface effects or quantum size effects, have the more dominant effect on the $T_c$. To address this question, we are required to measure the superconducting energy gap ($\Delta$) of the nanostructured Nb films, so that we can find out the evolution of the electron-phonon coupling strength ($\lambda$) with particle size.

The superconducting energy gap was measured by the method of Point Contact Andreev Reflection spectroscopy (PCAR). As explained in detail in Section 2.3.5, in this method we bring a sharp tip (which in our case was a Pt-Ir tip) in contact with the superconducting Nb film. We did a four probe measurement to measure the differential conductance ($G(V) \sim dI/dV$) of the junction as a function of the bias voltage ($V$) by the ac modulation technique (given in Section 2.3.5). In this technique, a dc voltage ($V_{dc}$) is modulated by a small ac signal ($V_{ac} \cos(\omega t)$). A voltage to current converter converts the voltage to current ($I + i \cos(\omega t)$) which is passed across the tip-sample junction. The ac signal of the output voltage of the junction is detected by a lock in amplifier (locked in at the input frequency $\omega$) while the dc signal ($V$) is detected by a multimeter. The output voltage of the point contact can be expressed in a Taylor series expansion. For small $i$, the first harmonic signal of the lock-in amplifier gives the differential voltage ($dV$) of the junction. Similarly the

![Figure 3.12: Variation of $T_c$ with particle size $d_{XRD}$. The triangles are from magnetization measurement and the circles are from transport measurements.](image-url)
Figure 3.13: PCAR spectra showing differential resistance ($R_d$) vs bias voltage for contacts between a nanostructured Nb film ($d_{XRD} = 18\text{nm}$) and Pt-Ir tip when:

(a) Contact formed on more than 2 grains, 
(b) Contact formed on 2 grains, 
(c) Contact formed on a single grain

One important point about the PCAR measurements on nanoparticles is that in addition to the contact being in the ballistic regime (i.e. $a << l$), it is also necessary that the contact be established on a single particle. (The details of establishing and identifying ballistic contacts has been extensively been worked out by Sheet et al.$^{17}$) Sometimes, when the contact is on more than one particle, due to a small distribution in the particle size ($\sim 20\%$), there is also a distribution in the energy gap ($\Delta$) and the PCAR spectra shows double or multi-gap features (Figs. 3.13(a)-(b)). Though each of the contacts is in the ballistic regime, these spectra cannot be analyzed under the BTK formalism (which assumes a contact...
between a single superconductor with a well defined superconducting energy gap and a normal metal) to obtain the average superconducting energy gap ($\Delta$). Whenever we obtained these types of spectra, we had to change the pressure of the contact (by slightly withdrawing the tip) so that the contact is established on a single particle. A contact on a single particle gave the typical single gap feature in the PCAR spectra (Fig. 3.13(c)) and we analyzed only these kinds of spectra for obtaining $\Delta$. The PCAR spectra for the nanostructured Nb films are shown in Fig. 3.14, taken at the lowest achievable temperature in the system of around 2K. The open circles denote the experimental data, while the solid lines are the theoretical fits using the BTK theory. A summary of the fit parameters used to fit the PCAR spectra for the four films is given in the Appendix 3.1.

![Figure 3.14: PCAR spectra for Nb samples with different average particle size ($d_{XRD}$). The open circles show the conductance data (normalized to the conductance in the normal state) while the solid line is the fit to the BTK theory. The values of the gap ($\Delta(T)$) obtained from the fits at the particular temperature ($T$) is displayed for each spectrum.](image)

To find the effect of the distribution of particle size (~20% about the average) on the superconducting energy gap ($\Delta(0)$), a large number of point contacts need to be made for each sample. This has been done by slightly withdrawing or engaging the tip which changes the contact resistance (thereby changing the contact area slightly). Spectra obtained from
Figure 3.15: (a) and (b): PCAR spectra obtained for two different contacts for the film with $d_{XRD} = 60\text{nm}$ and $T_c = 9.4\text{K}$. (c) and (d): PCAR spectra obtained for two different contacts for the film with $d_{XRD} = 17\text{nm}$ and $T_c = 7.2\text{K}$. (e) and (f): PCAR spectra obtained for two different contacts for the film with $d_{XRD} = 11\text{nm}$ and $T_c = 5.9\text{K}$. In each spectrum, the data points are shown by open circles while the solid lines are the fits obtained from the BTK theory. The fitting parameters $\Delta(T)$, $z$, $\Gamma(T)$ are shown for each spectra recorded at the particular temperature ($T$).
different contacts give a slightly different gap value as contacts are established on grains with slightly different gaps. This can be seen from the spectra obtained for each sample for different contacts. (Fig. 3.15). Analyzing spectra for different contacts give the error bar on the energy gap value (~5%).

Before proceeding to interpret the data, I would like to comment on the origin of the broadening parameter ($\Gamma$) and barrier parameter ($Z$) for the nanostructured samples. As was pointed out in Section 2.3.5, $\Gamma$ originates from the finite lifetime ($\tau = 1/\Gamma$) of the quasiparticles. However, for nanoparticles having a finite size distribution, $\Gamma$ can also be affected by the distribution of the superconducting energy gap. It has been shown through computer simulations by Raychaudhuri et al in a different context (for a multiband superconductor YNi$_2$B$_2$C), that $\Gamma$ can arise from the distribution in $\Delta^{18}$. We believe that this is the possible origin for a finite $\Gamma$ obtained in the fits of our data on nanostructured Nb films.

Also, the measured gap ($\Delta$) reflects the average of the different gaps on different particles. While $\Gamma$ varies depending on the local distribution around the particle being probed, $\Delta$ remains constant within the error bar (obtained from taking large number of readings on each of the nanostructured Nb films). Another important point is that the non-conducting grain boundary just contributes to the barrier layer which is taken care in the model as the barrier parameter ($Z$) used to fit the spectra. Thus, tunneling through a non-conducting layer would not change the energy gap ($\Delta$) measured by point contact spectroscopy.

![Figure 3.16: Variation of $\Delta(0)$ with $T_c$](image)

In the graph, $\Delta(0)$ is plotted against $T_c$ with a linear relationship to $2\Delta(0)/kT_c = 3.6$, where $k$ is the Boltzmann constant.
Figure 3.17: PCAR spectra at different temperatures for Nb films with (a) \( d_{XRD} = 60\text{nm} \), and (b) \( d_{XRD} = 11\text{nm} \)

Figure 3.18: Temperature variation of the superconducting energy gap (\( \Delta(T) \)) for the Nb films with particle sizes: (a) \( d_{XRD} = 60\text{nm} \) and (b) \( d_{XRD} = 11\text{nm} \). The experimental data points are shown by open circles and the solid line is obtained from the BCS theory.
From Fig. 3.14, it can be clearly seen that the superconducting energy gap decreases with particle size. Fig. 3.16 shows the plot of $\Delta(0)$ as a function of $T_c$ and we observe a direct correlation between the two with a slope of $2\Delta(0)/k_B T_c = 3.6$, which clearly indicates that Nb remains in the intermediate coupling limit down to the smallest particle size. For a given contact we recorded the PCAR spectra for different temperatures. Analyzing these spectra gave the temperature variation of $\Delta$. The PCAR spectra acquired at different temperatures for the largest (~60nm) and the smallest (~11nm) particle size has been shown in Fig. 3.17. The experimental data are shown by open circles while the solid lines are fits using the BTK theory. The temperature variation of the gap (Fig. 3.18) shows that Nb continues to behave as a BCS superconductor down to the smallest particle size of 11nm.

As pointed out in Section 1.2.3, the two mechanisms generally used to explain the size induced changes in $T_c$ are based on (a) surface effects and (b) quantum size effects.\textsuperscript{19} Surface effects leading to phonon softening\textsuperscript{20,21} is the dominant reason for the observed increase in $T_c$ in the weak coupling Type I superconductors like Al,\textsuperscript{22} Sn,\textsuperscript{23} In\textsuperscript{24} etc. This mechanism would lead to an increase in $2\Delta(0)/k_B T_c$ with decreasing size. However, if quantum size effect are dominant, $2\Delta(0)/k_B T_c$ would remain constant with size as this mechanism has an equal effect on both $T_c$ and $\Delta(0)$. Furthermore, it has been shown by Strongin et al that the discretization of the energy levels leads to a depression in $T_c$ through a decrease in the density of states (DOS) at the Fermi level, $N(0)$\textsuperscript{25}. Since we observe NO change in the parameter $2\Delta/k_B T_c$ with particle size in our films, there is a strong indication that the electron phonon coupling ($\lambda$) does not change with particle size. This proves that the quantum size effects dominate over phonon softening in controlling the $T_c$ of the nanostructured Nb films. Quantum size effects decrease the electronic density of states at the Fermi level (due to discretization of the electronic wave vector) thereby reducing the $T_c$ with decreasing particle size till the Anderson criterion is reached and superconductivity is destabilized altogether.

### 3.4.2 Size dependence of the upper critical field ($H_{C2}$)

As of now, there are only a few reports of the size dependence of the critical fields in superconductors, and these are mostly on Type-I elemental superconductors such as Al and Pb.\textsuperscript{26} There are reports of an enhancement in $H_{C2}$ of up to 60% in nanocrystalline Al with a particle size of 4nm. However, there are very few studies of the upper critical field ($H_{C2}$) in granular Type-II superconductors, though this is probably the property of utmost interest.
from the point of view of applications. Recent studies on nanocrystalline PbMo$_6$S$_8$ report an increase in $H_{C2}(0)$ by almost 100% with a decrease in the particle size.$^{27}$ A similar enhancement in the low-temperature critical field has been observed in K$_3$C$_{60}$ powder and has been attributed to granularity as well as on intrinsic mechanisms such as strong electron-phonon coupling.$^{28}$ Note that in none of these systems there is a size-induced decrease in $T_c$ in the relevant size regime as observed in nanostructured Nb films with $d_{XRD} < 20$nm. Hence, in order to see if the suggested decrease in the DOS which decreases $T_c$ with decrease in $d_{XRD}$ in nano Nb is consistent with other superconducting properties, we carried out the measurements of the upper critical field ($H_{C2}$) and the irreversibility fields ($H_{irr}$). Also, since some of the parameters like $T_c$, $\Delta$, critical fields, penetration depth ($\lambda_L$) and coherence length ($\xi_0$) of a superconductor are interrelated, a complete understanding of finite size effects in a superconductor can only be obtained when the evolution of each parameter is studied in detail.

The upper critical field ($H_{C2}$)$^d$ and the irreversibility field ($H_{irr}$)$^e$ were determined from the magneto-transport measurement using the standard four probe method.$^{29}$ The isothermal R vs H curves for the films with particle sizes 28 and 11 nm are shown in Fig. 3.19(a)-(b). In these measurements, the film was kept parallel to the magnetic field. $H_{C2}$ was taken to be the field at which the resistance dropped to 90% of the normal state resistance ($R_N$), while $H_{irr}$ was taken as the field at which the resistance dropped to 0.1$R_N$. For a Type II superconductor, in its mixed states, at this field the Lorentz force ($F = J \times H_{irr}$) overcomes the pinning force ($F_p$) and the flux lines pinned to impurities start moving. This causes dissipation and hence a finite resistance appears. Hence, we identify $H_{irr}$ from the transport measurements as the field where the resistance just starts increasing from zero. $H_{irr}$ was independently determined using the planar coil ac susceptometer. The measurement was carried out at 15kHz with an applied ac field of less than 1 Oe. An external superconducting magnet was used to superpose a dc field for the isothermal $\chi$–$H$ runs. The value of $H_{irr}$ from the susceptibility measurements was taken as the field at which the imaginary part of susceptibility showed a dip. It is known that the field at which the dissipation peak in the ac susceptibility ($\chi''$) occurs can be related to the field corresponding to the 10% of the normal

---

$^d$ For a Type II superconductor, it corresponds to the field at which the superconductor becomes completely normal (with complete penetration of flux lines within it).

$^e$ For a Type II superconductor, this corresponds to the field below which the magnetization becomes irreversible so that flux gets trapped within it. From the Bean’s critical state model it can be shown that this is associated with a finite critical current density ($J_c$) (which makes the Type II superconductors technologically important).
Figure 3.19: Magnetoresistance data \((R \text{ vs } H)\) for nanostructured Nb films with (a) \(d_{\text{XRD}} = 28\text{nm}\) (b) \(d_{\text{XRD}} = 11\text{nm}\). Different curves refer to \(R \text{ vs. } H\) data recorded at different temperatures as indicated.

Figure 3.20: AC susceptibility data for the Nb film with \(d_{\text{XRD}} = 17\text{nm}\) at different temperatures showing
(a) Variation of the real part of susceptibility \((\chi)\) with magnetic field \((H)\)
(b) Variation of the imaginary part of susceptibility \((\chi)\) with field \((H)\)
state resistance obtained from magneto-resistive measurements.\textsuperscript{30} Hence, it is expected that the $H_{\text{irr}}$ measured from both these measurements should match closely. For an accurate

determination of $H_{\text{irr}}$ at temperatures close to $T_c$ (where the values of $H_{\text{irr}}$ are low), a dual magnet power supply was used to correct for the remanence of the superconducting magnet. Shown in Fig. 3.20(a)-(b), are the isothermal plots of the real part of susceptibility ($\chi'$) vs $H$ and the imaginary part ($\chi''$) vs $H$ for the film with $d_{\text{XRD}} = 17$nm. $H$-$T$ phase diagrams were plotted to get the extrapolated $H_{C2}(0)$ values. Fig. 3.21(a-d) shows such phase diagrams for four nano-Nb samples with particle sizes of 45nm, 19nm, 17nm and 11nm respectively. The irreversibility line (obtained from both magnetoresistance and ac susceptibility data) has also been plotted for the same samples in parallel and perpendicular orientations. As expected for conventional, low-$T_c$ superconductors, the irreversibility line lies quite close to the $H_{C2}$-$T$ curve. It is also clear that the values of $H_{\text{irr}}$ determined from ac susceptibility and

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.21}
\caption{Variation of $H_{C2}$ and $H_{\text{irr}}$ with temperature ($T$) for the four nano-Nb films with (a) $d_{\text{XRD}}$ = 45nm, (b) $d_{\text{XRD}}$ = 19nm, (c) $d_{\text{XRD}}$ = 17nm, and (d) $d_{\text{XRD}}$ = 11nm respectively. The solid and open circles denote $H_{C2}$ with the samples in parallel and perpendicular orientation, upright and inverted triangles denote $H_{\text{irr}}$ in parallel and perpendicular orientations, respectively, all determined from transport measurements. The stars denote $H_{\text{irr}}$ obtained from ac susceptibility measurements.}
\end{figure}
Table 3.3. Grain size dependence of various superconducting and normal-state properties of nanocrystalline Nb. RRR is the residual resistivity ratio.

<table>
<thead>
<tr>
<th>d_{XRD} (nm)</th>
<th>T_c (K)</th>
<th>RRR (300K/10K)</th>
<th>H_{C2}(0) (T)</th>
<th>(dH_{C2}/dT)_{T_c} (T/K)</th>
<th>ξ_{GL}(0) (nm)</th>
<th>ρ(μohmcm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>9.4</td>
<td>8.4</td>
<td>2.8</td>
<td>0.3</td>
<td>10.8</td>
<td>7.1</td>
</tr>
<tr>
<td>45</td>
<td>9.4</td>
<td>6.4</td>
<td>2.8</td>
<td>0.3</td>
<td>10.8</td>
<td>43.2</td>
</tr>
<tr>
<td>28</td>
<td>9.2</td>
<td>4.2</td>
<td>3.4</td>
<td>0.35</td>
<td>9.8</td>
<td>199.3</td>
</tr>
<tr>
<td>19</td>
<td>7.8</td>
<td>2.3</td>
<td>6.6</td>
<td>0.85</td>
<td>7.03</td>
<td>200.2</td>
</tr>
<tr>
<td>17</td>
<td>7.2</td>
<td>1.88</td>
<td>5.1</td>
<td>0.70</td>
<td>8.03</td>
<td>213.4</td>
</tr>
<tr>
<td>11</td>
<td>5.9</td>
<td>1.49</td>
<td>5.1</td>
<td>0.84</td>
<td>8.06</td>
<td>240.44</td>
</tr>
</tbody>
</table>

magnetoresistance match quite closely. Further, the values of H_{irr} and H_{C2} change very little with the orientation of the film with respect to the external magnetic field. We should not, in fact, expect any orientation dependence of the critical fields, since the nanocrystalline films are about 0.5μm thick and hence essentially behave as bulk systems with insignificant orientation dependence.

We observe from Fig. 3.21 that the critical field (H_{C2}) varies linearly with temperature for the samples with particle sizes < 20nm, as expected for granular superconductors. A detailed microstructural characterization by TEM and transport measurements had earlier shown that the nano-Nb films in this size regime behave as granular superconductors with the crystalline particles separated by relatively narrow intergranular regions consisting of an insulating Nb-O phase.\(^5,14\) Hence, the films form a network of weakly-connected Josephson junctions. For Type-II superconductors, H_{C2} is related to ξ_{GL} as:

\[
H_{C2}(T) = \frac{\varphi_0}{2\pi[\xi_{GL}(T)]^2}
\]

where \(\varphi_0\) is the flux quantum. The intrinsic coherence length is given by:

\[
\xi_0 = \frac{0.18hν_F}{k_B T_c}
\]

where, \(ν_F\) is the Fermi velocity. Now, in the dirty limit \((l_{eff} << ξ_0)\), ξ_{GL}(0) has the following temperature dependence near T_c:

\[
ξ_{GL}(0) = ξ_0 \left(1 + \frac{T}{T_c}ight)^{-1}
\]
\[ \xi_{GL}(T) = 0.85 \left( \frac{\xi_{0}^2 \mu_{0} I_{\text{eff}}}{1 - T / T_C} \right)^{1/2} \]  \hspace{1cm} (3.9)

For granular superconductors in the dirty limit, \( H_{C_2} \) would therefore vary linearly with temperature near \( T_c \) given by:

\[ H_{C_2} \approx \frac{\phi_0}{2\pi \xi_{0}^2 \mu_{0} I_{\text{eff}}} \left( 1 - T / T_c \right) \]

\( H_{C_2}(0) \) was determined from the \( H-T \) phase diagrams by extrapolating the curves to zero temperature. The variation of \( H_{C_2}(0) \) with particle size is shown in Fig. 3.22. \( H_{C_2} \) increases from 2.8T for the film with the largest particle size (~60nm) that shows the bulk \( T_c \) (9.4K) to 6.6T for the film with a particle size ~19nm with \( T_c = 7.8K \). However, for the films with particle size below 19nm, \( H_{C_2} \) decreases till it reaches a value of 5.1T for the smallest sized superconducting sample \( (d_{\text{xRD}} = 11nm) \). Thus, \( H_{C_2} \) exhibits a non-monotonic size dependence in nanostructured Nb. The particle size dependence of \( \xi_{GL}(0) \) was obtained by substituting the observed values of \( H_{C_2} \) in Eq. 3.7. Expectedly, \( \xi_{GL}(0) \) also shows a non-monotonic dependence with particle size. As a consistency check we made an independent determination of \( \xi_{GL}(0) \) using the following relation obtained from the GL theory: \(^{31}\)

\[ \xi_{GL}(0) = \left[ \frac{\phi_0}{2\pi T_c \left( \frac{dH_{C_2}}{dT} \right) T_c} \right]^{1/2} \]  \hspace{1cm} (3.10)

\[ \text{Figure 3.22: Variation of } H_{C_2} \text{ with grain size } (d_{\text{xRD}}) \text{ for the nano-Nb films. Note the break in monotonicity around 20nm.} \]
Figure 3.23: Grain size dependence of the Ginzburg-Landau coherence length, $\xi_{GL}(0)$ calculated from $H_{C2}$ (using Eq. 3.7) and also measured from the slope of the $H_{C2}$-$T$ curve (using Eq. 3.10).

The variation of $\xi_{GL}(0)$ with particle size obtained from both these methods is shown in Fig. 3.23 and it is clear that they agree within experimental error. Table 3.3 shows the coherence length ($\xi_{GL}(0)$) for the six samples with different particle sizes ($d_{XRD}$) and their $T_c$ and $H_{C2}$. Note that (see Table 3.3) the Ginzburg-Landau coherence length for the largest particle sample ($d_{XRD} = 60$nm) still shows a much reduced value (10.8nm) than that of bulk Nb (41±3nm). This is because our ‘bulk’ samples are also in the dirty limit with very low residual resistivity ratio ($\rho_{300K}/\rho_{10K}$), which corresponds to mean free paths of the order of a few nanometers.

The increase in $H_{C2}$ by ≈ 2.3 times in the intermediate size regime (from 60nm down to 20 nm) can therefore be correlated with the size-dependent decrease in $\xi_{GL}(0)$. It is expected that with reducing particle size and a consequent increase in grain boundary scattering, the mean free path ($l_{ef}$) should monotonically decrease and hence also the coherence length. However this factor alone should lead to a monotonic enhancement of $H_{C2}(0)$ with decreasing particle size, (see Eq. 3.7-3.9) which is contrary to our observations. Thus, our results emphasize the fact that the size dependence of the coherence length is not determined by the mean free path alone.

To understand if the coherence length ($\xi_{GL}(0)$) is related to any other parameter, we need to look at the expression of the intrinsic coherence length ($\xi_0$) more closely (Eq. 3.8).
Now, the Fermi velocity \(v_F\) is inversely proportional to the density of states at the Fermi level \(N(0)\). Thus, \(\xi_0 \propto 1/T_c N(0)\). Therefore,

\[
\xi_{GL}(0) \propto \left[ \frac{l_{\text{eff}}}{T_c N(0)} \right]^{1/2} \tag{3.11}
\]

Also, from the free electron theory, \(l_{\text{eff}} \propto \frac{1}{\rho_N}\), where, \(\rho_N\) denotes the normal state resistivity.

Hence, from Eqs. 3.7 and 3.11 we can see that:

\[
H_{C_2}(0) \propto \rho_N T_c N(0) \tag{3.12}
\]

It is clear from Eq. 3.12 that the critical fields can be increased with increasing \(\rho_N\) (decreasing particle size) as long as there is no decrease in the product of \(T_c\) and \(N(0)\). Werthamer-Helfand-Hohenberg used the above arguments to derive the expression for \(H_{C_2}(0)\) in the dirty limit \((l_{\text{eff}} << \xi_0)\). It is given by:

\[
H_{C_2}(0) = 0.69T_c \frac{4eck_B}{\pi} N(0)\rho_N \tag{3.13}
\]

From independent measurements of the \(T_c\) and the superconducting energy gap \(\Delta(0)\) in the lower size regime (<20nm), we have earlier shown that both \(T_c\) and \(\Delta(0)\) decrease proportionately with particle size. Thus Nb remains in the weak coupling limit with \(2\Delta(0)/k_B T_c \approx 3.6\), down to the smallest particle size of 11nm. The decrease in \(T_c\) for sizes <20nm can therefore be attributed to a change in the electronic density of states \((N(0))\) near the Fermi energy due to a size-induced discretization of the energy levels (Kubo gap). Note that quantum size effects may cause a decrease in the \(T_c\) even for sizes (10-20nm in this case) for which the Kubo gap is still smaller than the superconducting energy gap. This is due to the decrease in the effective density of states at the Fermi level, \(N(0)\). The Fermi level lies in between the highest filled and the lowest unfilled electronic states. Therefore, when the spacing between adjacent levels is larger than the typical broadening of each level, there will be a decrease in the effective density of states at the Fermi level. It is clear from Eq. 3.13 that a decrease in \(N(0)\) accompanied by a decrease in \(T_c\) at sufficiently small sizes would give rise to a concomitant decrease in \(H_{C_2}\), overriding the effect of decreasing mean free path. This results in the observed non-monotonic behavior of \(H_{C_2}\).

We point out that the monotonic increase in \(H_{C_2}\) observed in earlier studies of granular superconductors were on systems such as Al and Pb, which either show an increase in \(T_c\) (in Al) or no change (in Pb)\(^{26}\). Hence, in such systems, the reduction in the mean free path with decreasing particle size plays the most dominant role in controlling the critical
field. Interestingly, even a non-monotonic behavior of $H_{C2}$ has been observed earlier – not in nanocrystals – but in ultrathin films (< 10nm thick) of Nb. Both $H_{C2∥}$ and $H_{C2⊥}$ (measured in fields parallel and perpendicular to the film plane, respectively) showed a non-monotonic dependence on film thickness. As might be expected in the light of the present study, those Nb films also exhibited a reduction in $T_c$ with film thickness.

Another system which shows a similar non-monotonic behavior of $H_{C2}$ however does not belong to the class of low dimensional superconductors. This is the Al doped MgB$_2$ system (both in bulk and thin film form)\textsuperscript{33} where the $H_{C2}$ initially increases with Al doping and then decreases at higher doping levels. Al-doping is equivalent to an increase in the disorder in the system and leads to a reduction in the $T_c$. In such systems too, one observes a decrease in the superconducting energy gap and hence the effect is attributed to a decrease in the superconducting order parameter. It is useful to point out that MgB$_2$ is a multiple band superconductor where interband scattering plays a vital role in determining the properties. Hence, it should not be directly related to Nb, which is a single band conventional s-wave superconductor.

Summarizing, we observe a non-monotonic variation in $H_{C2}(0)$ with particle size in nanostructured Nb films due to competing effects of the decrease in the mean free paths ($l_{eff}$) with decrease in particle size ($d_{XRD}$), and the decrease in the superconducting transition temperature ($T_c$) caused by an effective decrease in the density of states ($N(0)$) at the Fermi level.

### 3.4.3 Normal state properties; Size induced metal-insulator transition in nanostructured Nb: The effect of inter and intra granular transport

Since the normal state properties are closely related to the superconducting properties (e.g. $\rho_N$ and $H_{c2}$), we have also studied the normal state transport properties of the nanostructured Nb films. In Section 3.4.1, we saw that the nanostructured Nb films with $d_{XRD} > 8$nm are metallic and superconducting with a measurable $T_c$ decreasing with particle size. We have also seen that the films with $d_{XRD} < 8$nm were non-superconducting, consistent with the Anderson criterion. However, when we measured the resistivity of these latter class of films with $d_{XRD} < 8$nm by the conventional four probe technique, from room temperature down to 2K, we observed that these films show a weakly insulating behaviour with a negative temperature coefficient of resistance ($\alpha = 1/\rho)(dp/dt)$, i.e. the resistivity increased with decrease in temperature. Interestingly, the film with $d_{XRD} = 8$nm, showed an almost
temperature independent resistivity clearly separating the metallic films with a positive temperature coefficient of resistance \((d_{XRD} > 8 \text{nm})\) from the films showing an activated behaviour \((d_{XRD} < 8 \text{nm})\). Thus, the nanostructured Nb films show a clear size-induced metal insulator transition at a particle size of 8nm. The temperature variation of resistivity for the films with particle size \((d_{XRD})\) between 5-60nm is shown in Fig. 3.24. (The scale to the left is for samples with \(d_{XRD} \geq 8 \text{nm}\) while the right is for \(d_{XRD} < 8 \text{nm}\)). We also notice that while the room temperature resistivity, \(\rho_{300} = 7 \mu \Omega \text{cm}\), for the sample with \(d_{XRD} = 60 \text{nm}\) is comparable to that of bulk Nb, there is three orders of magnitude increase in \(\rho_{300}\) to 14m\(\Omega\)cm for the sample with \(d_{XRD} = 5 \text{nm}\). Thus, based on their transport properties, we can categorize the nanostructured Nb films into three different size regimes. Nano-Nb films with \(d_{XRD} > 28 \text{nm}\) behave like bulk, metallic Nb with a positive TCR between \(T_c\) and 300K. Samples with 28nm \(\geq d_{XRD} \geq 11 \text{nm}\) also show a metallic behavior with a positive TCR. However, in this regime,

![Figure 3.24](image.png)

**Figure 3.24:** Temperature dependence of the resistivity for nanostructured Nb films with different grain sizes \((d_{XRD})\). The scale on the left refers to the metallic films with \(d_{XRD} \geq 8 \text{nm}\) while the scale to the right is for the insulating films with \(d_{XRD} < 8 \text{nm}\)

the grain boundary acts as an insulating barrier, as observed from the presence of hysteresis in the critical current in the superconducting state (discussed in Section 3.4.1). However, the barrier is not very strong enabling the electrons to tunnel through them and showing a metallic behaviour. Also, in this regime, we observe a 6 fold increase in \(\rho_N\) as the particle size is reduced from 28 to 11nm (Fig. 3.24). This can be explained by the following intuitive argument. A reduction in the particle size by a factor of three would lead to (i) a three-fold increase in the fraction of grain boundaries (per unit volume) that are expected to act as
scattering centers (since the surface/volume ratio $\propto (1/\text{particle size})$), and (ii) a three-fold decrease in the mean free path, provided it is limited by the particle size alone. This should lead to a nine-fold increase in the resistivity. However, if the mean free path is not purely particle-size limited and decreases less slowly than the particle size, we would expect to see a somewhat smaller increase in the room temperature resistivity. Thus, the observed six-fold increase in $\rho_{300}$ appears reasonable. Finally, films with particles $d_{\text{XRD}} < 8\text{nm}$ show a weakly insulating behavior with negative TCR, while the film with $d_{\text{XRD}} = 8\text{nm}$ shows an almost temperature-independent resistivity. We now show that the insulating barrier present at the grain boundary (large barrier for $d_{\text{XRD}} < 8\text{nm}$) is the likely cause for activated behaviour in transport for these films.

We attempted to analyze and understand the metal-insulator transition observed in the electrical transport data (Fig. 3.24) in the following manner. Considering quantum size effects (QSE) alone, we should expect a metal-insulator transition to occur when the Kubo gap, $\delta \sim 4\varepsilon_F/3N$, ($N =$ number of conduction electrons at the Fermi energy, $\varepsilon_F$) becomes comparable to $k_B T$ ($k_B$ is the Boltzmann's constant, $1.38 \times 10^{-23}$). The QSE-driven metal-insulator transition is expected at $\sim 35\text{K}$ for $5\text{nm}$ sized Nb nanoparticles, and at $\sim 15\text{K}$ for $7\text{nm}$ particles. [For $d_{\text{XRD}} = 5\text{nm}$, $\delta = 2.9 \text{meV}$ (Table 3.4), Therefore, $T = (\delta / k_B) \times 1.6 \times 10^{-19} \sim 35\text{K}$] However, we observe the onset of the insulating behavior at a much higher temperature in samples with $d_{\text{XRD}} < 8\text{nm}$. Qin et al. have also seen a negative TCR in nano-Ag for particle sizes $< 9\text{nm}$ and a density of $\sim 45$-$50\%$, but attribute their observation to a high density of microscopic vacancy-like defects at the grain boundaries.

To understand the origin of the negative TCR and the high metal-insulator transition temperature in nano-Nb, we attempted to fit the $\sigma$-$T$ curves ($d_{\text{XRD}} \leq 7\text{nm}$) with an activated transport behavior. We used the following three types of empirical trial functions:

$$\sigma = A \exp \left( -E_g / k_B T \right)$$ (3.14)

$$\sigma = \sigma_0 + A \exp \left( -E_g / k_B T \right)$$ (3.15)

$$\sigma = \sigma_0 + A \exp \left( -E_{g1} / k_B T \right) + B \exp \left( -E_{g2} / k_B T \right)$$ (3.16)

where $\sigma = \rho^{-1}$. The activation energies ($E_g$) and the proportionality constants $A$ and $B$ were used as best fit parameters. The first one, which corresponds to a simple activation barrier with a single gap, clearly does not fit our data. The best fit of Eq. 3.15, which contains a temperature-independent contribution ($\sigma_0$) in addition to the activated behavior, to the $\sigma$-$T$ data for the $5\text{nm}$ Nb sample is shown by the dashed curve in Fig. 3.25(a). The corresponding
deviation from the data is shown by the dashed curve in Fig. 3.25(b). Obviously, the fit is unsatisfactory in the lower temperature region. However, an attempt to fit the data to Eq. 3.16 which contains two activation energies, $E_{g1}$ and $E_{g2}$ (in addition to the temperature-independent contribution), produced much more satisfactory results, as shown by the solid curve in Fig. 3.25(a). A comparison of the deviation of the $\sigma$ vs $1/k_BT$ data points from the single and double exponential fits for the 5nm sample (Fig. 3.25(b)) clearly indicates that the fit to the double exponential is significantly better, particularly at low temperatures. Fig. 3.25(c) shows the double exponential fits to the transport data for all the three insulating samples. The fit is good down to the lowest temperature (4.2K). The high temperature downturn in samples with $d_{XRD} = 6$ and 7nm comes from the temperature region in which the samples exhibit metallic behavior. We now show that the double exponential character of the conductivity has a convincing physical basis.

What is the physical origin of the two activation energies ($E_{g1}$ and $E_{g2}$) associated with the transport behavior of the insulating phase of nanostructured Nb? The values of $\sigma_0$, $E_{g1}$ and $E_{g2}$ obtained from the double exponential fits and the calculated Kubo gaps ($\delta$) for the three samples with the smallest particle sizes are listed in Table 3.4. Both the characteristic energies ($E_{g1}$ and $E_{g2}$) decrease monotonically with increasing particle size. From a comparison of their respective magnitudes and size dependences, we identify the lower of the two activation energies ($E_{g1}$) with the Kubo gap arising from the discretization of the
energy levels. The small discrepancy can probably be attributed to electron correlation effects. A physical estimation of this gap is important as it provides the energy scale for the validity of the Anderson criterion for low-dimensional superconductors. This is because for low dimensional superconductors, when the Kubo gap arising from the discretization of the energy levels becomes equal to the superconducting energy gap, superconductivity is destabilized. It is worth noting that $E_{gl}$ for the film with $d_{XRD} = 7$nm is 1.3meV (as obtained from the fits) is comparable to the superconducting energy gap ($\Delta(0)$) for bulk Nb $\sim$ 1.5meV. Hence, our normal state resistivity data independently suggest that $d_{XRD} = 7$nm should be the critical particle size at which the Anderson criterion is satisfied and indeed below this particle size we do not observe any superconductivity in the nano Nb films. Hence, $E_{gl}$ originates from the intra-granular transport, i.e. transport across the Kubo gap. However, the manifestation of the Kubo gap would only be appreciable at low temperatures, and is certainly not responsible for the insulating behavior (upturn in $\rho$-$T$) observed close to room temperature.

While we have argued that the smaller of the two activation energies has a purely intra-granular, quantum mechanical origin, the larger one ($E_{g2}$) appears to be related to inter-granular electronic transport. This can be clearly seen by comparing the characteristic temperatures $T_i = E_{g2}/k_B$ obtained from $E_{g2}$ for the three insulating samples (see Table 3.4) with the inflexion temperatures in the resistivity data. The higher of the two activation

<table>
<thead>
<tr>
<th>$d_{XRD}$ (nm)</th>
<th>$\Delta d$ (nm)</th>
<th>$E_{g1}$ (meV)</th>
<th>$E_{g2}$ (meV)</th>
<th>$\delta$ (meV)</th>
<th>Calculated</th>
<th>$T_i = E_{g2}/k_B$ (K)</th>
<th>$\sigma_0$ ($\Omega m)^{-1}$</th>
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</table>

Table 3.4: Activation energies ($E_{g1}$ and $E_{g2}$) calculated from the transport data for nanostructured Nb samples with three different particle sizes ($d_{XRD}$). The corresponding grain boundary widths ($\Delta d$) have been calculated from x-ray diffraction data using a procedure explained in the text. The theoretical values of the Kubo gap ($\delta$) and the experimental value of the metal-insulator transition temperature ($T_i$) are also tabulated.
energies \( (E_{g2}) \) is therefore associated with the metal-insulator transition in the smaller-sized nanostructured samples \( (d_{XRD} < 8\text{nm}) \). We now show that \( E_{g2} \) (whose value lies in the 16–31 meV range) appears to originate from the potential barrier at the grain boundaries that needs to be overcome for inter-grain conduction to occur. Since the 5nm particle has a grain boundary width, \( \Delta d > 1\text{nm} \) (see the HRTEM images in Fig. 3.4), while large-grained samples are known to have atomically sharp boundaries, it is clear that \( \Delta d \) is inversely related to the particle size in this system. This results in a size-dependent potential barrier that leads to the activated conduction at room temperature. Such a model also agrees with the explanation given by Qin et al. for the negative TCR in nanocrystalline Ag. A larger \( \Delta d \) implies an increase in the vacancy-like defects that tend to make the sample comparatively insulating.

Due to some degree of variability in the particle size as well as the grain boundary

![Figure 3.26](image_url)

**Figure 3.26:** Variation of the higher barrier energy \( (E_{g2}) \) with the grain boundary width. The critical width of the grain boundary where the gap just opens up is indicated by \( \Delta d_c \).
linear relation between the upper barrier energy \( (E_{g2}) \) and \( \Delta d \) (Fig. 3.26), an extrapolation of which suggests that the value of \( \Delta d \) corresponding to zero barrier energy is \( \approx 1.0 \text{nm} \). (Note that ‘zero barrier energy’ corresponds to relatively large sized particles with sharp enough grain boundaries such that it exhibits metallic properties.) The particle size corresponding to this value \( (\approx 1 \text{nm}) \) \( \Delta d \) is \( \approx 9 \text{nm} \), which is in excellent agreement with the experimentally observed critical particle size at which the metal-insulator transition is seen to occur \( (8 \text{nm}) \).

Assuming the grain boundary structure to be largely amorphous with an ordered first coordination shell, a partially ordered second coordination shell, and disordered higher shells (as suggested by recent EXAFS data), we would expect the energy gap at the grain boundary to open up for a boundary width \( \approx \) second coordination shell. The interatomic distance in Nb is 0.286 nm, and therefore the second and third coordination shells correspond to a spacing of \( \approx 0.57 \text{ nm} \) and \( \approx 0.86 \text{ nm} \) from the outermost fully ordered layer of the crystalline nanoparticle. The grain boundary is expected to be partially ordered if it is limited to the second coordination shells of adjacent particles leading to a boundary width of \( \approx 1.14 \text{ nm} \). If the boundary width is larger, we can expect the inter-granular region to be structurally disordered. Thus, an energy gap in the electrical transport should open when \( \Delta d \geq 1.14 \text{ nm} \), which is in very good agreement with the experimentally determined, limiting value of \( \Delta d \) of about 1 nm.

Note also that as according to our empirical best fit function, \( T \to 0, \sigma \to \sigma_0 \), a constant value. A physical interpretation of the temperature-independent component of conductivity \( (\sigma_0) \) is less straightforward than \( E_{g1} \) and \( E_{g2} \). The finite conductivity at zero temperature suggests the existence of an additional transport channel for which the electrons do not experience either of the above two activation barriers. This could originate from two sources: (i) The shape and the size distribution of the particles size is likely to introduce a significant number of mid-gap states within the Kubo gap, and (ii) we also may have a distribution of grain boundary widths, with a small fraction of the grain boundaries which are much more strongly connected than the rest. An electron passing across a percolating channel of strongly connected grain boundaries would essentially undergo metallic transport and not experience the potential barrier \( E_{g2} \). These electrons would therefore give rise to a finite conductivity even at the lowest temperatures. In this context, we point out that the resistivity of structurally disordered (amorphous) metals and alloys remains finite as \( T \to 0 \) unlike true insulators.
Transport in granular systems such as Au/SiO$_2$, W/Al$_2$O$_3$, Ni/SiO$_2$, in which there are metallic nanoparticles (< 4nm) in an insulating matrix, has been studied for a long time. In many of these systems, the resistivity data have been fitted to the relation: 

$$\sigma = \sigma_0 \exp\left[\frac{-1}{4} \left(\frac{T}{T_0}\right)^{1/4}\right]$$

obtained from Mott’s variable range-hopping (VRH) model, and 

$$\sigma = \sigma_0 \exp\left[\frac{-1}{2} \left(\frac{T}{T_0}\right)^{1/2}\right]$$

taking electron correlations into account. However, our data cannot be fitted to the (VRH) model (with or without electron correlations). To show this, we have plotted the log of the conductivity against $T^{-1/4}$ and $T^{-1/2}$ as shown in Figs 3.27(a)&(b) respectively. The fitting clearly shows that the conductivity is proportional to neither $T^{-1/4}$ nor $T^{-1/2}$ over the entire temperature range of 4.2-300K. According to a recent study, freshly prepared nanostructured Cu does show VRH behavior, while nanoparticles with appreciably oxidized grain boundaries show an activated behavior. Since the inter-granular region in our films is known to be partially oxidized, we not observe VRH-type behavior. We also point out that many previous reports on the metal-insulator transition showing a $T^{-1/2}$ dependence of the conductivity actually dealt with two-dimensional films (usually quench-condensed), in which the surface resistance dictates the transition. Our films are relatively thick (~0.5µm) and consist of stacks of weakly connected nanoparticles. These are essentially three-dimensional nanostructures, in which the volume resistivity (and not the surface resistance) is the relevant parameter.

^1 In the VRH model, transport of electrons is through hopping across localized electronic states in disordered systems.
It is therefore clear that the existing models based on variable range hopping conduction, that have been used to explain transport in granular or nanostructured systems do not fit our data. The model proposed by us is based on a size-dependent grain boundary width and not only describes our experimental results adequately, but is also quantitatively consistent with our data on size-dependent lattice expansion. The TEM data also supports our notion of smaller particle-sized samples having wider grain boundaries.

Summarizing, we have observed a size induced metal insulator transition in nanostructured Nb. Our transport data indicate that the conductivity is associated with two distinct activation energies, originating from quite different physical phenomena. While the larger activation energy is related to hopping across poorly conducting grain boundaries, the smaller one originates from the Kubo gap due to discretization of the energy levels in small particles. The effect of the smaller gap is also manifested in the observed disappearance of superconductivity, consistent with Anderson’s prediction. The critical particle size ($d_{XRD}$) at which an insulating energy gap opens up is $\approx 8$nm and corresponding grain boundary width is $\approx 1.1$nm. These values, obtained from our model, match our observations very well.

### 3.5 Conclusions

Nanostructured Nb films have been prepared by high pressure dc magnetron sputtering with particle size ranging between 5 and 60nm. We observed a 6% increase in the cubic lattice parameter as the particle size is reduced from 60 to 5nm. This has been modeled using linear elasticity theory which can simulate the lattice parameter vs particle size data using a size dependent grain boundary width. Thus, the nanostructured Nb films show an increase in the grain boundary width with decrease in particle size. Due to the presence of an insulating grain boundary (characterized by HRTEM and EELS spectroscopy) these films form a random network of Josephson junctions. This was independently verified from electrical measurements, as indicated by a hysteresis in the I-V characteristics of the films with particle sizes less than 20nm.

Nb shows a 50% decrease in the superconducting transition temperature ($T_c$) as particle size is reduced from 60 to 8nm. From a direct measurement of the superconducting energy gap ($\Delta$) by point contact Andreev reflection Spectroscopy, we have observed a direct correlation of $\Delta$ and $T_c$, with $2\Delta/k_B T_c \sim 3.6$ for the Nb film with smallest particle size ($d_{XRD} = 11$nm). From the temperature variation of $\Delta$ we have further seen that Nb follows the BCS behavior down to the smallest particle size. From our results we conclude that quantum size
effects arising from the discretization of the energy levels decreases the electronic density of states at the Fermi level, which decreases $T_c$ with reduction in particle size in nanostructured Nb.

Nanostructured Nb films also show a 2.3 times enhancement of the upper critical field ($H_{C2}$) as the particle size is reduced from 60 to 19nm. However, below 19nm, $H_{C2}$ decreases with particle size. We have shown that the increase in $H_{C2}$ down to a particle size of 19nm is mainly due the decrease in the coherence length. However, below 19nm, quantum size effects start dominating, which decreases the density of states, $N(0)$ at the Fermi level and hence also decreases $T_c$. This decrease in $T_c$ and $N(0)$ overrides the effect of the reduction in coherence length below the particle size of 19nm, and thereby decreases $H_{C2}$. Hence, we conclude that the competing effects of the decrease in coherence length and $N(0)$ cause the non-monotonic variation of $H_{C2}$ with particle size in nanostructured Nb.

A study of the normal state transport properties indicates that nanostructured Nb undergoes a size induced metal to insulator transition. Films with particle sizes greater than 8nm are metallic and superconducting while the films with particle size below 8nm show a weakly activated behavior. Fitting the conductivity vs temperature plots of the films with particle sizes below 8nm to an activated behavior with two exponential terms, we obtain two activation energies ($E_{g1}$ and $E_{g2}$). From the magnitudes and the size dependences of the two activation energies we conclude that the lower activation energy ($E_{g1}$) arises from the discretization of the energy level and is equivalent to the Kubo gap ($\delta$). This accounts for the intra-granular transport of the electrons in these films. The effect of the smaller gap is also manifested in the observed disappearance of superconductivity, consistent with Anderson’s prediction. The higher activation energy ($E_{g2}$) arises from the potential barrier present at the insulating grain boundary and accounts for the inter-granular transport, i.e. hopping of electrons across the grains. The critical grain size ($d_{XRD}$) at which an insulating energy gap opens up is $\approx 8$nm and corresponding grain boundary width is $\approx 1.1$nm. These values, obtained from our model, match our observations very well. Hence, we can justify the existence of the two activation energies and explain the observed transport behaviour in these nanostructured Nb films with particle size less than 8nm.

Our results help to explain satisfactorily the evolution of the superconducting properties such as $T_c$, $\Delta(0)$ and $H_{C2}$ as well as the normal state transport properties as a function of particle size in the nanostructured Nb films.
Appendix 3.1

Fitting of the temperature dependence of the PCAR spectra for the nanostructured Nb films using the BTK theory

In the point contact regime, the current-voltage curves are simulated using the expression of Andreev reflection current flowing through a ballistic point contact of a normal metal and a superconductor given by:

\[
I(V) \propto N(0) v_F \int_{-\infty}^{\infty} \left[ f(E - eV, T) - f(E, T) \right] \left[ 1 + A(E) - B(E) \right] dE
\]

Here, \(v_F\) is the Fermi velocity, \(N(0)\) is the density of states at the Fermi level of the normal metal, \(f(E)\) is the Fermi distribution function and the coefficients \(A(E)\) and \(B(E)\) are given by:

\[
A(E) = \sqrt{\left(\alpha^2 + \eta^2\right)\left(\beta^2 + \eta^2\right)} \quad (A3.1.2)
\]

\[
B(E) = Z^2 \left[ \left(\alpha - \beta\right)Z - 2\eta \right]^2 + \left[ 2\eta Z + \left(\alpha - \beta\right) \right]^2 \quad (A3.1.3)
\]

Where the coefficients \(\alpha, \beta, \gamma, \eta\) can be expressed in terms of the Bogoliubov coherence factors, \(u\) and \(v\) given by:

\[
u^2 = \alpha + i\eta \quad (A3.1.4)
\]

\[
v^2 = \beta - i\eta \quad (A3.1.5)
\]

\[
\gamma = u^2 + \left( u^2 - v^2 \right) Z^2 \quad (A3.1.6)
\]

The Bogoliubov coherence factors are given by:

\[
u^2 = \frac{1}{2} \left[ 1 + \frac{\sqrt{(E+i\Gamma)^2 - \Delta^2}}{E+i\Gamma} \right] = 1 - v^2 \quad (A3.1.7)
\]

Using the above equations (A3.1.1 to A3.1.7), the I-V curves are simulated for a given temperature \(T\) with \(\Delta(T)\), \(\Gamma(T)\) and \(Z\) as the fitting parameters. This is then differentiated to obtain \(G(V) = dI/dV\) which is divided by \(dI/dV\) obtained for a large bias voltage \((V>>\Delta/e)\). This gives \(G(V)/G_N\) as a function of bias voltage \(V\) and is used to fit the experimental PCAR spectrum.
### The fitting parameters used to fit the PCAR spectrum

1. **Particle size** \(d_{\text{XRD}} = 60\text{nm}; \ T_c = 9.4\text{K}; \ \Delta(0) = 1.6\text{meV} \)

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<tr>
<th>Temperature (K)</th>
<th>Barrier parameter ((Z))</th>
<th>Energy Gap ((\Delta)) (\text{meV})</th>
<th>Broadening parameter ((\Gamma)) (\text{meV})</th>
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2. **Particle size** \(d_{\text{XRD}} = 11\text{nm}; \ T_c = 5.9\text{K}; \ \Delta(0) = 0.9\text{meV} \)

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3. Particle size ($d_{XRD}$) = 17nm; $T_c$ = 7.2K; $\Delta(0)$ = 1.0meV

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<th>Broadening parameter ($\Gamma$) meV</th>
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<td>6.0</td>
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<td>0.72</td>
<td>0.082</td>
</tr>
<tr>
<td>6.5</td>
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<tr>
<td>7.0</td>
<td>0.545</td>
<td>0.496</td>
<td>0.06</td>
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4. Particle size ($d_{XRD}$) = 18nm; $T_c$ = 7.6K; $\Delta(0)$ = 1.1meV

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Barrier parameter ($Z$)</th>
<th>Energy Gap ($\Delta$) meV</th>
<th>Broadening parameter ($\Gamma$) meV</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.94</td>
<td>0.567</td>
<td>1.1</td>
<td>0.42</td>
</tr>
</tbody>
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References

40 V. I. Kozub, V. M. Kozhevin, D. A. Yavsin and S. A. Gurevich, JETP Lett. 81, 226 (2005)
Chapter 4

Size Dependence of the Superconducting Properties in the Strong Coupling Type I Superconductor: Lead

4.1 Introduction

In the bulk state, Pb is a Type I superconductor with strong electron-phonon coupling strength \(2\Delta/k_B T_c \sim 4.4\).\(^1\) Phonon softening\(^2,3\) (due to increased ratio of surface to volume atoms) and quantum size effects\(^4\) (arising from the quantization of the electronic wave vector) affect the \(T_c\) in fine particles of elemental superconductors as discussed in detail in Section 1.2.3. However, there is a third mechanism which can also influence the superconducting properties. The lower cut-off for the phonon frequency (\(\omega\)) shifts to higher values with decreasing particle size due to the quantization of the phonon wave vector.\(^5\) As a consequence, the low frequency phonon modes no longer contribute to the phonon spectrum. Pb is a strong coupling superconductor with phonons present at very low frequencies in bulk (The LA phonon energy of Pb is as low as \(\hbar \omega = 5\text{meV}\))\(^6\). The influence of surface modes in fine particles of Pb will cause additional phonons to appear at lower frequencies (\(\hbar \omega < 5\text{meV}\)) compared to the bulk phonons. However, the raising of the lower cut-off for the phonon frequency will compete with phonon softening with decrease in particle size. These competing effects should eventually influence the electron-phonon coupling strength in strong coupling superconductors, thereby affecting the superconducting properties. Hence, it is important to make a detailed study of the size effects on the superconducting properties in a strong coupling superconductor such as Pb so as to identify the dominant mechanism influencing these properties. We expect a different behaviour compared to the weak coupling superconductors like Al, Sn etc and the intermediate coupling one (Nb) discussed in the previous chapter.

The evolution of superconducting properties in Pb has been studied previously as a function of particle size in systems prepared by varied methods. The earliest reports were on small particles of Pb deposited by evaporation in controlled amounts of oxygen\(^7,8\) It was believed that oxygen diffused to the grain boundaries and formed oxides at the interface, though there was no direct evidence for the same. No change in \(T_c\) was observed with
reduction in particle size. Recently Reich et al have used a novel method to prepare small particles of Pb. They have grown Pb fine particles of different sizes using polycarbonate nucleopore membranes of different pore diameters. They have observed the existence of the Meissner transition in different samples with particle size down to 10 nm, with almost no change in $T_c$. The critical size for the disappearance of superconductivity was found to be 6 nm. Li et al have carried out a detailed study on the superconducting properties of Pb small particles. They synthesized Pb nanoparticles by evaporation in an Ar atmosphere and deposited them on stainless steel plates kept at liquid nitrogen temperatures. The particle size was controlled by varying the rate of evaporation. The powder was then scraped off the stainless steel plate and compressed into pellets to carry out different measurements such as DC transport and specific heat. They observed almost no change in $T_c$ down to 6 nm, below which the $T_c$ was found to drop sharply to zero at around 2 nm. From the measurements of the critical fields ($H_C$) as a function of temperature for different particle sizes, they claim that there is an increase in the electron phonon coupling strength with decreasing particle sizes. However, there appears to be no direct measurements of the superconducting energy gap ($\Delta$) as a function of particle size, which would directly indicate the evolution of the coupling strength as a function of particle size. In this chapter, I will present our results on the measurement of the superconducting properties ($T_c$ and $H_{C2}$) with decreasing particle size in Pb. We have studied the evolution of the superconducting energy gap ($\Delta$) as a function of particle size as measured from tunneling spectroscopy. Our results indicate that the coupling strength in Pb increases with a reduction in particle size and the temperature variation of the gap deviates from the weak coupling BCS relation. From our results we conjecture that the small decrease in $T_c$ for Pb nanoparticles just above the critical size may be due to competing effects arising from the different mechanisms influencing the superconducting properties, since an increase in electron-phonon coupling strength alone would have led to an increased $T_c$ with decreasing particle size.

4.2 Synthesis

Nanostructured Pb was prepared by high pressure DC magnetron sputtering. The process parameters were varied to control the particle size. For Pb, depositing at low DC powers (10-20 W) with the substrate kept at room temperature and relatively high (~200-400 mtorr) pressures of the Ar gas yielded small particle sizes. The Ar gas used was of 99.999% purity. The substrates used were single crystals of Si [110]. The deposition was done at a base
Figure 4.1: XRD pattern of the (a) as grown film (Pb1) showing the FCC phase of Pb (b) same film after 3 days of exposure to air showing the presence of lead monoxide (PbO)

Figure 4.2: Sputtering system used for depositing nanocrystalline Pb
pressure of $3 \times 10^{-7}$ torr. The Pb films were characterized immediately after deposition by X-ray Diffraction (XRD). The films showed a FCC phase of pure polycrystalline Pb. (Fig. 4.1(a)). However, leaving the films exposed to air for a couple of days oxidized the films. XRD done on the films after a couple of days showed the presence of an extra peak at $2\theta = 28.5^\circ$ which matched with the [110] line of the PbO phase (Fig. 4.1(b)). In order to prevent ex-situ oxidation, we needed to deposit in situ a thin overlayer of another substance on top of the Pb surface. For this, we modified the magnetron sputtering system to accommodate two sputtering guns mounted at $180^\circ$ to each other. A new substrate holder was designed with a Wilson seal which could be rotated by $180^\circ$ in vacuum. The deposition system used is shown in Fig. 4.2. Overlayers of different metals were tried. Interestingly, growth of thin metal overlayers of Au, Ag and Pt on the Pb film was found to reduce the $T_c$ of the film because of the superconducting proximity effect\textsuperscript{11}. Hence, we decided on a semiconducting overlayer, (Si). Si was sputtered on the Pb film in situ at a low Ar pressure ($\sim 5 \times 10^{-3}$ torr), under the conditions described in Table 4.2. The optimized thickness of the overlayer was $\sim 40$nm. In presence of the Si overlayer, the nanostructured Pb films of all particle sizes remained free from oxidation at least over several months. The process parameters for the samples synthesized with different particle sizes are tabulated in Table 4.1.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Base pressure (Torr)</th>
<th>Pressure of Ar (mtorr)</th>
<th>Sputtering Voltage (V)</th>
<th>Current (mA)</th>
<th>Substrate Temp.</th>
<th>Deposition Time (min)</th>
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</thead>
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<tr>
<td>SPbSi1</td>
<td>$1.9 \times 10^{-6}$</td>
<td>15</td>
<td>270</td>
<td>49</td>
<td>RT</td>
<td>5</td>
</tr>
<tr>
<td>SPbSi2</td>
<td>$3.5 \times 10^{-6}$</td>
<td>20</td>
<td>210</td>
<td>65</td>
<td>RT</td>
<td>5</td>
</tr>
<tr>
<td>SPbSi3</td>
<td>$6.7 \times 10^{-6}$</td>
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<td>200</td>
<td>49</td>
<td>RT</td>
<td>5</td>
</tr>
<tr>
<td>SPbSi4</td>
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<td>290</td>
<td>200</td>
<td>47</td>
<td>RT</td>
<td>5</td>
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<tr>
<td>SPbSi5</td>
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<td>211</td>
<td>49</td>
<td>RT</td>
<td>4</td>
</tr>
<tr>
<td>SPbSi6</td>
<td>$4.8 \times 10^{-6}$</td>
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<td>200</td>
<td>50</td>
<td>RT</td>
<td>4</td>
</tr>
<tr>
<td>SPbSi7</td>
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<td>375</td>
<td>200</td>
<td>37</td>
<td>RT</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 4.1: Synthesis (dc sputtering) conditions for the nanostructured Pb films. (RT = room temperature)

<table>
<thead>
<tr>
<th>Gas pressure (mtorr)</th>
<th>RF Power (W)</th>
<th>Substrate Temperature</th>
<th>Time of deposition (min)</th>
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</thead>
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<td>4.3-6.5</td>
<td>60</td>
<td>RT</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 4.2: Synthesis (RF sputtering) conditions for deposition of Si overlayer
4.3 Structural properties

The as-deposited nanostructured Pb films with Si overlayers were characterized by XRD, atomic force microscopy (AFM) and transmission electron microscopy (TEM). The particle size ($d_{\text{XRD}}$) was determined from an x-ray line profile analysis using WINFIT software, correcting for the contribution from the K\textsubscript{a2} line and the instrument broadening. The WINFIT software uses the Warren Averbach technique\textsuperscript{12} to find the strain corrected particle size and the size distribution. This particle size will be referred to as $d_{\text{XRD}}$ from now on. The average particle size ($d_{\text{XRD}}$) was between 5 and 60 nm with a dispersion of ±15% about the mean size. The full width at half maximum (FWHM) of the [110] line of Pb, particle size ($d_{\text{XRD}}$), the strain and the spread in the particle sizes are tabulated in Table 4.3. Fig. 4.3 shows the XRD spectra obtained for some of the films with different particle sizes. No impurity phases were observed in any of the samples. The AFM micrographs of the films with particle sizes, $d_{\text{XRD}} = 60$ nm and $d_{\text{XRD}} = 12$ nm are shown in Figs. 4.4(a) and 4.4(b) respectively. The films were further characterized by TEM. The selected area electron diffraction patterns of the films with $d_{\text{XRD}} = 40$ nm, 14 nm and 7 nm are shown in Figs. 4.5(a)-(c). The decrease of the particle size is seen clearly from these figures. For $d_{\text{XRD}} = 40$ nm, distinct spots are seen in the diffraction rings for each of the allowed reflections, which are characteristic of large grained polycrystalline samples. For $d_{\text{XRD}} = 14$ nm, the spots merge to form clear rings. These rings become very broad for the film with $d_{\text{XRD}} = 7$ nm. The decrease in particle size can also be distinctly seen from the bright field TEM images for these three films, shown in Figs. 4.6(a)-(c). The particle sizes can be obtained from the dark field TEM images for the films with $d_{\text{XRD}} = 14$ and 7 nm (Figs. 4.7(a) & (b)). It appears that the actual particle size is slightly

<table>
<thead>
<tr>
<th>Sample name</th>
<th>FWHM (degree) of [110] line</th>
<th>$d_{\text{XRD}}$ (nm)</th>
<th>Spread in $d_{\text{XRD}}$ (nm)</th>
<th>Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPbSi1</td>
<td>0.187</td>
<td>60</td>
<td>±8.0</td>
<td>0.26%</td>
</tr>
<tr>
<td>SPbSi2</td>
<td>0.253</td>
<td>40</td>
<td>±6.0</td>
<td>0.22%</td>
</tr>
<tr>
<td>SPbSi3</td>
<td>0.513</td>
<td>18</td>
<td>±3.3</td>
<td>0.44%</td>
</tr>
<tr>
<td>SPbSi4</td>
<td>0.661</td>
<td>14</td>
<td>±3.0</td>
<td>0.61%</td>
</tr>
<tr>
<td>SPbSi5</td>
<td>1.01</td>
<td>11</td>
<td>±2.5</td>
<td>0.54%</td>
</tr>
<tr>
<td>SPbSi6</td>
<td>1.191</td>
<td>7</td>
<td>±2.0</td>
<td>0.76%</td>
</tr>
<tr>
<td>SPbSi7</td>
<td>1.201</td>
<td>5</td>
<td>±1.0</td>
<td>0.81%</td>
</tr>
</tbody>
</table>

Table 4.3: Structural parameters for the nanostructured Pb films with different values of average particle size ($d_{\text{XRD}}$). The spread in $d_{\text{XRD}}$ has been obtained from x-ray diffraction line shape analysis.
Figure 4.3: XRD spectra of nanostructured Pb films of different particle sizes ($d_{XRD}$).

Figure 4.4: Representative AFM images of nanostructured Pb films with particle sizes: (a) $d_{XRD} = 60$nm and (b) $d_{XRD} = 12$nm, shown at the same scale.
Figure 4.5: Selected area electron diffraction pattern for the nanostructured Pb films with particle sizes (a) $d_{\text{XRD}} = 40 \text{nm}$ (b) $d_{\text{XRD}} = 14 \text{nm}$ (c) $d_{\text{XRD}} = 7 \text{nm}$

Figure 4.6: Bright Field TEM images for the nanostructured Pb films with particle sizes (a) $d_{\text{XRD}} = 40 \text{nm}$ (b) $d_{\text{XRD}} = 14 \text{nm}$ (c) $d_{\text{XRD}} = 7 \text{nm}$
Figure 4.7: Dark Field TEM images for the nanostructured Pb films with particle size (a) $d_{XRD} = 14\,\text{nm}$ (b) $d_{XRD} = 7\,\text{nm}$

Figure 4.8: High resolution TEM image of the Pb film with particle size $d_{XRD} = 7\,\text{nm}$
less than those obtained from XRD. A careful analysis of the high resolution TEM micrograph of the film with $d_{XRD} = 7$nm, shows small Pb grains (4-8nm) separated by large disordered regions. The grains can be distinguished clearly as they appear darker compared to the surrounding disordered matrix. A close look at the grains shows the presence of different crystallographic domains of size ~ 1-2nm within each grain. This microstructure is not completely understood and more careful studies are required.

4.4 Size dependence of Superconducting properties

4.4.1 Nature of the decrease in $T_c$

The superconducting transition temperature ($T_c$) was determined from (a) magnetization measurements using a home made planar coil AC susceptometer and (b) DC transport measured in a custom made set-up. These techniques have been described in detail in Section 2.3. The criterion used for the estimation of $T_c$ from transport measurements was as follows. The $T_c$ was identified as the temperature at which the resistance dropped to 10% of the normal state resistance (Fig. 4.9(b)). From the AC susceptibility measurements, the temperature where the real part of susceptibility ($\chi$) deviated from zero was taken as the $T_c$ (Fig. 4.9(a)). The $T_c$ obtained from both these methods matched almost exactly (Fig. 4.10).

![Figure 4.9](image)

**Figure 4.9** (a) Real part of susceptibility ($\chi$) vs temperature for the Pb nanostructured films with different particle size (b) Resistance vs temperature for the same Pb films

The measured resistance was the sum of the resistances of the Pb film and the Si overlayer. Since, the thickness of the Si overlayer was kept almost constant for all the films, the normal state resistance ($T>T_c$) monotonically increases with decreasing particle size (Fig. 4.5(b)). This can be explained on the basis of the increase in the grain boundary scattering resulting

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from the increased fraction of grain boundaries with decreasing particle size. The variation of $T_c$ with particle size is shown in Fig. 4.10. We observe that the $T_c$ remains same as that of bulk Pb ($T_c = 7.25$K) when $d_{XRD}$ is reduced from 60nm to 14nm. Thereafter, $T_c$ decreases by only $\sim$10% down to $d_{XRD} = 7$nm. Below this size, we see a sharp crossover to non-superconducting behaviour. The critical particle diameter ($d_C < 7$nm) for the disappearance of $T_c$ ($d_C \sim 5$nm is obtained from the Anderson criterion$^{13}$) matches with the critical particle size reported by other groups$^{9,10}$ and also observed by us. Clearly, the variation in $T_c$ with particle size in Pb is very different from what we have observed in nanostructured Nb.$^{14}$ In Nb (which is an intermediate coupling superconductor), we have observed a $\sim$50% decrease in $T_c$ as the particle size is reduced from 60nm to 8nm, below which it becomes non-superconducting as per the Anderson criterion. The variation of $T_c$ in Pb with $d_{XRD}$ is also contradictory to the increase in $T_c$ observed in small particles of Type I superconductors like Al,$^{7,15}$ Sn$^{16}$ etc. To understand the size dependence of $T_c$ down to $d_{XRD} = 14$nm and the small (10%) decrease till $d_{XRD} = 7$nm, we need to investigate the size dependence of $2\Delta/k_BT_c$, which is a measure of the electron-phonon coupling.

We measured the superconducting energy gap ($\Delta$) using the method of tunneling spectroscopy.$^{17}$ Since Pb is a very soft metal we could not perform point contact measurements as the sharp tip of the normal metal punctured the Pb film and it was not

![Figure 4.10: Variation of $T_c$ with particle size ($d_{XRD}$). The solid circles are obtained from transport measurement while the triangles are obtained from AC susceptibility](image-url)
possible to establish ballistic point contacts. Therefore, we fabricated planar tunnel junction devices using the following technique. We used glass slides as substrates, which were dipped in boiling water, followed by acetone and methanol (in that order) repeatedly to clean them. An Al strip of width 1mm and thickness ~200nm was sputtered at the center of the glass slide using a stainless steel mask. The deposition parameters for Al sputtering are listed in Table 4.4. During sputtering at low Ar pressures, there was heating of the substrate. Hence, after deposition, the Al film was left in vacuum for 2 hours so that it could cool down to room temperature. Thereafter, the Al film was exposed to air for 15-20 minutes for surface oxidation of the Al layer. Stainless steel masks were used to deposit Pb (with the Si overlayer in situ) so that the Pb strips (of width 2mm and thickness ~200nm) were deposited

<table>
<thead>
<tr>
<th>Ar gas pressure (mtorr)</th>
<th>DC Voltage (V)</th>
<th>Current (mA)</th>
<th>Substrate Temperature</th>
<th>Time of deposition (min)</th>
</tr>
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<tr>
<td>4.0-6.5</td>
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<td>360</td>
<td>Ambient</td>
<td>3</td>
</tr>
</tbody>
</table>

**Table 4.4:** Synthesis (DC sputtering) conditions for Al for the fabrication of Al-Al$_2$O$_3$-Pb tunnel junction

![Diagram](image)

**Figure 4.11:** Pb/Al$_2$O$_3$/Al tunnel junction device on a glass plate with gold contact pads showing two tunnel junctions (a) The real device (b) Schematic of the device.
perpendicular to the Al strip. At a time two junctions were made. The typical junction area was $0.1 \times 0.2 \text{ cm}^2$. A photograph of the fabricated tunnel junction device is shown in Fig. 4.11. The $I$-$V$ connectors are shown only for the upper device. $I$-$V$ characterizations of the tunnel junctions were measured by the standard 4 probe method at temperatures below the $T_c$ of the Pb films. For good tunnel junctions, we obtained the usual $I$-$V$ curve as shown in Fig. 4.12(a). This curve was differentiated to obtain the differential conductance $G(V) = dI/dV$ of the junction. The tunneling spectrum (Fig. 4.12(b)) was plotted by normalizing $G(V)$ with the conductance at high biases ($V > 4 \text{ mV}$). The tunneling spectra were fitted using Eq. 2.3 obtained from the theoretical model for tunneling between a superconductor and a normal metal as discussed in Section 2.3.4. Since we have a slight distribution in the particle sizes, there is also a corresponding distribution in the superconducting energy gap. This is accounted for in the broadening parameter $\Gamma$ which is included in the theoretical model used to fit the data. Including $\Gamma$, the BCS density of states can be expressed as:

$$N(E, \Gamma) = \frac{E + i\Gamma}{(E + i\Gamma)^2 - \Delta^2} \quad \text{for} \ E > \Delta$$

$$= 0 \quad \text{for} \ E < \Delta$$

As discussed in Section 2.3.4, a finite value of $\Gamma$ can also arise from the finite lifetime of the quasiparticles ($\Gamma = 1/\tau$ ; $\tau$ is the quasiparticle lifetime). Thus, there are two fitting parameters, $\Delta$ and $\Gamma$ for any given temperature. In this context, I should point out that sometimes we obtained spectra which showed Andreev reflection features instead of tunneling features (Fig. 4.13). This can be understood in the following way. Due to incomplete oxidation of the Al surface layer, minute pin holes may be present in the oxide layer. When these pin-holes are
Andreev reflection spectra obtained for the tunnel junction device fabricated with the Pb film with particle size \((d_{\text{XRD}}) 60\text{nm}\), occurring due to the presence of minute pin holes in the oxide barrier. Smaller than the mean free path of the electrons, ballistic point contacts are established resulting in Andreev reflection. These spectra were analyzed under the Blonder-Tinkham-Klapwijk (BTK) theory\(^{18}\) discussed in Section 2.3.5 and Section 3.4.1 with \(\Delta, z\) and \(\Gamma\) being the fitting parameters. We fabricated tunnel junctions for different particle sizes and measured the I-V characteristic of the junctions for different temperatures below the \(T_c\) of the device. The spectra obtained for the films at the lowest attainable temperature of 4.3K for all the particle sizes are shown in Fig. 4.14. The success rate of obtaining good tunneling spectra from the devices was around 20%. Most of the time we did not obtain any non-linearity in the \(I-V\) characteristics (Fig. 4.15(d)), indicating that the tunnel barrier formed was too thick. At other times, though a non-linearity was obtained, large dips were seen at high biases \((V > 4\text{meV})\) in the differential conductance vs bias voltage spectrum (Fig. 4.15(a),(b)&(c)). These dips are due to large pin holes present in the aluminum oxide barrier (due to incomplete oxidation of the Al layer) which prevents the Al-Pb contact from being in the ballistic regime. (The details of the origin of the dips have been discussed in Sections 2.3.5 and 3.4.1). This leads to heating at the contact. When the voltage bias is high enough for the dips to appear, the critical current of the superconductor is reached, which causes a large change in the voltage of the contact and leads to peaks in the differential resistance vs bias voltage (or dips in the differential conductance vs bias voltage). The success rate of obtaining good spectra can be increased by reducing the junction area. Since we obtain an average gap for the film, we improved the statistics by making two measurements for each particle size on two different junction devices. The two values of \(\Delta(T)\) obtained for each particle size did not differ by more than 5%. The spectra obtained at different temperatures for two of the films.
Figure 4.14: Tunneling spectra showing the variation of the differential conductance \((G(V)/G_N)\) with the bias voltage \((V)\) for the Pb films with different particle sizes \(d_{XRD}\) at the temperature \(T = 4.3K\). For \(d_{XRD} = 60, 25\) and \(15\) nm, the tunnel junction was in the point contact regime (due to the impartial oxidation of the aluminum). The open circles denote the data points and the solid lines as fits using the BTK theory. For \(d_{XRD} = 40, 18\) and \(11\) nm, the junction was in the tunneling regime. Again, the open circles are the data points while the solid lines are the theoretical fits.
Figure 4.15: Examples of some typically bad spectra \((G(V)/G_N \text{ vs } V)\) obtained in the measurement of the Al/Al_2O_3/Pb tunnel junctions at a temperature of \(T = 4.3K\)

Figure 4.16: Tunneling spectra showing the differential conductance \((G(V)/G_N)\) of the junction as a function of the bias voltage at different temperatures \((T)\) for (a) \(d_{XRD} = 60\text{nm}\) (Tunnel junction is in the point contact regime due to impartial oxidation of the aluminum) and (b) \(d_{XRD} = 18\text{nm}\) (Tunnel junction is in the tunneling regime.)
with particle sizes 60 and 18nm are shown in Fig. 4.16(a)-(b). While the film with a particle size of 60nm showed the Andreev reflection feature, the film with particle size of 18nm showed the tunneling feature. The fitting parameters for a set of measurements for 5 films with different particle sizes are given in Appendix 4.1.

The temperature variation of the energy gap in the bulk film (with the largest particle size of 60 nm) followed the BCS relation (given by Eq. 1.11) with \( \frac{2\Delta}{k_B T_c} \approx 4.4 \) which is the same as for bulk Pb. The \( \Delta(T) \) vs \( T \) curves for films with \( d_{\text{XRD}} \) down to 25nm all follow the BCS relation. However, with decreasing particle size below 25nm, the temperature variation of the gap deviates progressively from the BCS relation as shown in Fig. 4.17. This observation has an important implication as it appears to indicate that the electron phonon coupling strength (\( \lambda \)) increases with reduction in particle size, i.e. Pb becomes a stronger coupling superconductor in the nanocrystalline state.

To cross check this conclusion from an independent experiment, we carried out magneto-resistance measurements on the nanostructured Pb films to obtain the critical field \( (H_{C2}) \) as a function of temperature. The details of the measurement and analysis are given in Section 4.4.2. We plotted the \( (H_{C2}-T) \) phase diagrams ((Fig. 4.18(a)) for films with different particle sizes and fitted the data with the relation:

\[
H_{C2} = H_{C0} \left[ 1 - \left( \frac{T}{T_c} \right)^2 \right]^{\alpha}
\]

where \( H_{C0} \) and \( \alpha \) are fitting parameters. The exponent \( \alpha \) equals 2 for a weak coupling BCS superconductor. Interestingly, an analysis of our data clearly indicates that the exponent progressively deviates from 2 with decreasing particle size, showing that Pb no longer remains a BCS superconductor for small particle sizes (\( d_{\text{XRD}} < 20nm \)). This is shown more clearly from the plot of \( H_{C2}/H_{C0} - \left[ 1 - \left( \frac{T}{T_c} \right)^2 \right]^{\alpha} \) vs \( T/T_c \) (Fig. 4.18(b)). It is obvious that for \( d_{\text{XRD}} < 20nm \), a deviation from the weak coupling BCS relation becomes pronounced.

This observed increase in the electron-phonon coupling strength with decreasing particle size implies that phonon softening plays an important role in influencing \( T_c \) in this strong coupling superconductor. However, as we have discussed in Section 1.2.3, an increase in the coupling strength (\( \lambda \)) should imply an increase in \( T_c \) with decrease in particle size. Hence, the question that arises is what causes the observed size dependence of \( T_c \) down to \( d_{\text{XRD}} = 14nm \) followed by a 10% decrease in \( T_c \), though there seems to be a continuous increase in electron phonon coupling strength (\( \lambda \)) with decreasing particle size for \( d_{\text{XRD}} < 20nm \).
Figure 4.17: Temperature variation of the superconducting energy gap ($\Delta(T)$) for the Pb films with different particle sizes ($d_{XRD}$). The black solid line is obtained from the BCS relation. For films with $d_{XRD} < 20$nm, there is a gradual deviation from the BCS variation.

Figure 4.18(a) Phase diagrams ($H_{c2}(T)$ vs $T$) for the Pb films with different particle sizes ($d_{XRD}$) (b) Plot of the deviation from the BCS relation ($H_{c2}(T)/H_{c0} - [1-(T/T_c)^2]$) vs reduced temperature ($T/T_c$). Films with particle size ($d_{XRD}$) less than 20nm show a considerable deviation from the BCS relation.
To understand this we try to correlate our results with the theoretical work of Fenton and Leavens on the variation of $T_c$ with particle size in small Pb particles. They numerically solved the detailed Eliashberg theory for a 5nm Pb nanoparticle assuming the electron-phonon coupling strength of the bulk to be the same as that of the surface. Their simulations yielded no change in $T_c$ of Pb nanoparticles from its bulk value when there was a 5% increase in $\Delta$. However, it must be pointed out that, experimentally it is very difficult to detect a 5% increase in $\Delta$. In fact, in our measurements there is an error of about 5% in the $\Delta$ values. They have neglected any changes in the electronic density of states arising from the discretization of energy levels and also argued that the effect of the quantization of the phonon wave vector (which would increase the lower cut-off for the phonon frequency contributing to the phonon spectrum and hence $\lambda$), is negligible in this size regime. Under these approximations, their calculations match qualitatively our observed variation of $T_c$ and $\Delta(0)$ with decreasing particle size, though we observe a higher (>5%) increase in $\Delta$ as particle size is reduced from 60 to 7nm. However, it remains to be understood why the electron phonon coupling strength of the surface should equal that of the bulk and whether this is related to the fact that Pb is a strong coupling superconductor in the bulk, since the $T_c$ shows a large change with particle size for weak coupling and intermediate coupling superconductors.

Another plausible explanation for the observed null size effect on $T_c$ could be due to the opposing influences of the phonon softening mechanism and quantum size effects. Fenton and Leavens had neglected the quantization of the electronic wave vector arising from the discretization of the energy levels with decreasing particle size. However, this effect cannot be altogether neglected since the Anderson criterion originates from it and the Anderson criterion actually predicts a destabilization of $T_c$ at 5nm in Pb (which is also experimentally observed). Also we have seen from our measurements of $T_c$ and $\Delta$ in nanostructured Nb that the quantum size effect plays a dominant role in influencing $T_c$ by decreasing the density of states at the Fermi level for small particles. Therefore, it is possible that the phonon softening effect (which increases $T_c$) is exactly offset by the quantum size effect (which decreases $T_c$) with decrease in particle size.

It is also possible for the increase in the lower cut-off for the phonon frequency to offset the effect of phonon softening, thereby leading to a size independent $T_c$ (till $d_{XRD} \sim 14$nm). Below $d_{XRD} = 14$nm, quantum size effects start dominating and $T_c$ gets suppressed. Thus, our results indicate that all the three mechanisms, namely phonon softening, quantum
size effect due to discretization of the electronic wave vector and phonon wave vector can influence \( T_c \) for small particles in the strong coupling superconductor, Pb.

However, to understand the observed small variation in \( T_c \) below 14nm, one requires more detailed theoretical work that incorporates the contribution from both the phonon softening and quantum size effects to \( T_c \) in small particles of strong coupling superconductors.

### 4.4.2 Enhancement of \( H_C^2 \) with decreasing particle size

Bulk Pb is known to be a Type I superconductor. However, with decreasing particle size, the coherence length \( (\xi_{GL}(0)) \) for a “dirty” \( (l_{eff} \ll \xi_0) \) superconductor decreases. Since \( \xi_{GL}(0) \approx \left(\frac{\xi_0}{l_{eff}}\right)^{1/2} \), the mean free path \( (l_{eff}) \) and hence the coherence length decreases with decreasing particle size. The parameter which is used to distinguish Type I and Type II superconductors is the Ginzburg Landau parameter, \( \kappa = \frac{\lambda_L}{\xi_0} \), where \( \lambda_L \) is the penetration depth and \( \xi_0 \) is the intrinsic coherence length. By convention, Type I superconductors correspond to \( \kappa < 1/2 \), whereas Type II superconductors correspond to \( \kappa \geq 1/2 \).

With decreasing particle size or increasing disorder, there is a decrease in the coherence length \( (\xi_{GL}) \) and \( \kappa \) increases. Thus, Pb may start to behave as a Type II superconductor at small particle sizes. This can be experimentally confirmed from the hysteresis observed in the magnetization vs magnetic field (M-H) loop, measured in a

![Figure 4.19](image_url)

**Figure 4.19:** Four quadrant M-H loop at \( T = 5K \) for the Pb film with particle size \( (d_{XRD}) = 41nm \).
Figure 4.20: Resistance ($R$) vs applied magnetic field ($H$) at different temperatures for the nanostructured Pb films with particle sizes ($d_{XRD}$) = 40nm, 18nm, 14nm and 10nm.

Figure 4.21: Variation of the upper critical field ($H_{c2}(0)$) with particle size ($d_{XRD}$). Note that there is an enhancement of 3.2 times in the $H_{c2}$ of the film at the smallest particle size ($d_{XRD} = 9$nm) as compared to that of the largest particle size film ($d_{XRD} = 60$nm).
Vibrating sample magnetometer (VSM). Such hysteresis is characteristic of a Type II “dirty superconductor”\textsuperscript{1}. Fig. 4.19 shows the hysteresis observed in the $M-H$ loop for the film with $d_{XRD} = 40$nm. Since, all our Pb films are in the “dirty limit” (i.e. $l_{\text{eff}} < \xi_o$) the effective coherence length ($\xi_{\text{GL}}(0)$) for the bulk films ($d_{XRD} > 20$nm) also gets reduced from the bulk coherence length of 38nm. Thus, all our nanostructured Pb films (with $d_{XRD}$ between 60 to 5nm) behave as Type II superconductors. Hence, we will refer to the critical field measured as the upper critical field ($H_{C2}$) for these nanostructured Pb films.

The $H_{C2}$ was obtained from magneto-transport measurements using the standard four probe method. Resistance of the Pb films was measured as a function of the magnetic field at fixed temperatures ($T$) below $T_c$. $H_{C2}$ was taken to be the field at which the resistance dropped to 90% of the normal state resistance. Fig. 4.20 (a)-(d) shows the isothermal plots of $R$ vs $H$ for the film with $d_{XRD} =$ 40nm, 18nm, 14nm and 10nm respectively. The $H-T$ phase diagrams were plotted for the films with different particle sizes (Fig. 4.18(a)). The curves were fitted to Eq. 4.1 to obtain $H_{C0}$ which denotes the upper critical field at zero temperature. The variation of $H_{C0}$ with particle size is plotted in Fig. 4.21. There is a remarkable (3.6 times) enhancement as the particle size is reduced from 60 nm to 7nm. Note also that there is a monotonic increase in $H_{C2}$ in nanostructured Pb, contrary to nanostructured Nb where we had observed a non-monotonic variation of $H_{C2}$ with reduction in particle size. The Ginzburg Landau coherence length $\xi_{\text{GL}}(0)$ and the mean free paths ($l_{\text{eff}}$) were evaluated in the case of nano Nb from the following two expressions,

\begin{equation}
\xi_{\text{GL}}(0) = \left[ \frac{\phi_0}{2\pi H_{C2}} \right]^{1/2}
\end{equation}

\begin{equation}
\xi_{\text{GL}}(0) \approx 0.85 \left( \xi_o l_{\text{eff}} \right)^{1/2}
\end{equation}

where $\xi_o$ for Pb is taken as 80nm. The experimental values of $H_{C2}$ and $T_c$ and the calculated values of $\xi_{\text{GL}}(0)$ and $l_{\text{eff}}$ for the films with different $d_{XRD}$ are tabulated in Table 4.5.

To understand why the nature of variation of $H_{C2}$ with particle size is qualitatively different in Pb and Nb, we refer back to the variation of the $H_{C2}$ with $l_{\text{eff}}$ as determined from the WHH theory\textsuperscript{19}. According to this theory for “dirty superconductors” ($l_{\text{eff}} < \xi_o$):

\begin{equation}
H_{C2} \propto \left[ T_c N(0) \right] \rho_N
\end{equation}

where $N(0)$ is the density of states at the Fermi level and $\rho_N$ is the normal state resistivity. With decreasing particle size, $l_{\text{eff}}$ is expected to decrease and hence $\rho_N$ should increase due to increased grain boundary scattering.
Since $\rho_N$ increases with decreasing particle size, Eq. 4.4 implies an increase in $H_{C2}$ with decreasing particle size as long as there is no appreciable change in the product of $T_c$ and $N(0)$. We expect quantum size effects to become pronounced at low particle sizes, which should decrease $N(0)$. However, we have seen in Section 4.4.1 that due to the competing effects of phonon softening and quantum size effects, we observe only a small (~10%) decrease in $T_c$ as $d_{XRD}$ reduces from 60 nm to 7 nm in nanostructured Pb. This is contrary to the case of nanostructured Nb where there is an almost 50% decrease in $T_c$ as $d_{XRD}$ reduces from 60 nm to 8 nm, which causes a decrease in $H_{C2}$ at low enough particle size. Therefore, in nanostructured Pb, the increase in $\rho_N$ with decreasing particle size overrides the small decrease in the product $T_c$ and $N(0)$ and hence causes $H_{C2}$ to only increase monotonically with reduction in particle size till the system finally becomes non-superconducting.

### Table 4.5: Particle size dependence of $T_c$, $H_{C2}$, $\xi_G(0)$ and $l_{eff}$ of nanostructured Pb films

<table>
<thead>
<tr>
<th>$d_{XRD}$ (nm)</th>
<th>$T_c$ (K)</th>
<th>$H_{C2}(0)$ (T)</th>
<th>$\xi_G(0)$ (nm)</th>
<th>$l_{eff}$ (nm)</th>
</tr>
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<tr>
<td>60</td>
<td>7.24</td>
<td>1.62</td>
<td>11.48</td>
<td>1.94</td>
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<tr>
<td>41</td>
<td>7.23</td>
<td>1.57</td>
<td>11.51</td>
<td>1.95</td>
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<tr>
<td>18</td>
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<td>2.472</td>
<td>9.69</td>
<td>1.38</td>
</tr>
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<td>14</td>
<td>7.14</td>
<td>3.18</td>
<td>8.41</td>
<td>1.04</td>
</tr>
<tr>
<td>10</td>
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<td>7.14</td>
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</tr>
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<td>7</td>
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<td>6.46</td>
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</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

4.5 Conclusions

Nanostructured Pb films were synthesized by high pressure DC magnetron sputtering with the average particle size ranging between 5 and 60 nm. Pb shows no change in $T_c$ as particle size is reduced from 60 to 14 nm and thereafter a 10% decrease as particle size is reduced from 14 to 7 nm. Below 7 nm, the films are non-superconducting, as predicted from the Anderson criterion. Measurements of the superconducting energy gap and the critical fields in nanostructured Pb indicate a deviation from the weak coupling BCS behaviour. This is indicative of the fact that the electron phonon coupling strength increases with reduction in
particle size in nanostructured Pb. This shows that the phonon softening mechanism is effective in this system. This should have led to an increase in $T_c$ with reduction in particle size. However, this effect appears to be almost exactly offset by the quantum size effects (which is pronounced below $d_{XRD} < 20\text{nm}$) that tends to decrease $T_c$. These competing effects cause only a 10% decrease in $T_c$ as the particle size is reduced from 60 to 7nm. Below 7nm, quantum size effects dominate and superconductivity is destroyed, consistent with the Anderson criterion.

Nanostructured Pb films show a 3.6 times enhancement of the upper critical field as the particle size is reduced from 60 to 7nm. The monotonic enhancement in $H_{C2}$ with reducing particle size is contradictory to what was observed in nanostructured Nb. This is because Pb shows a very small decrease in $T_c$ with reduction in particle size. Therefore, though the density of states [$N(0)$] decreases for small particle sizes due to quantum size effects, the decrease in the product of $T_c$ and $N(0)$ is not substantial enough to override the effect of the decrease in the mean free path with decreasing particle sizes. This explains the observed monotonic increase (3.6 times from the $H_{C2}$ of the bulk Pb film) in $H_{C2}$ as particle size is reduced from 60 to 7nm in nanostructured Pb films.
Appendix 4.1

Fitting of the temperature dependence of the spectra \((G(V)/G_N \ vs \ V)\) for the nanostructured Pb films using the tunneling theory for a normal metal-insulator-superconductor junction (when the junction is in the tunneling regime) and the BTK theory (when the junction is in the point contact regime).

In the tunneling regime, the current-voltage curves are simulated using the expression for the tunneling current given by:

\[
I \propto |T|^2 N_S(0) \int_{-\infty}^{\infty} N_S(E) \left[ f(E - eV) - f(E) \right] dE
\]

(A4.1.1)

Here, \(|T|\) is the transmittivity of the junction, \(N_S(E)\) is the density of states of the superconductor and \(N_N(E)\) is the density of states at the Fermi level of the normal metal which is taken as constant. \(f(E) = \frac{1}{\exp((E - eV)/kT) + 1}\) is the Fermi distribution function.

\(N_S(E)\) satisfies the condition:

\[
N_S(E) = \frac{E + i\Gamma}{\sqrt{(E + i\Gamma)^2 - \Delta^2}} \quad E > \Delta
\]

\[
= 0 \quad \text{otherwise}
\]

(A4.1.2)

Here, \(\Gamma = 1/\tau\), is the broadening parameter.

Hence, to simulate the I-V curves for a given temperature \((T)\) (using equations A4.1.1 and A4.1.2), \(\Delta(T)\) and \(\Gamma(T)\) are taken as the fitting parameters. The simulated I-V data for a given \(\Delta(T)\) and \(\Gamma(T)\), is then differentiated to obtain \(G(V) = dI/dV\) which is divided by \(dI/dV\) obtained for a high bias voltage \((V >> \Delta/e)\). This gives the simulated \(G(V)/G_N\) as a function of bias voltage \((V)\) and is used to fit the experimental spectrum \((G(V)/G_N \ vs \ V)\) in the tunneling regime.
In the **point contact regime**, the current-voltage curves are simulated using the expression of Andreev reflection current flowing through a ballistic point contact of a normal metal and a superconductor given by:

\[
I(V) \propto N(0)v_f \int_{-\infty}^{\infty} \left[ f(E-eV,T) - f(E,T) \right] [1 + A(E) - B(E)] dE \tag{A4.1.3}
\]

Here, \(v_f\) is the Fermi velocity, \(N(0)\) is the density of states at the Fermi level of the normal metal, \(f(E)\) is the Fermi distribution function and the coefficients \(A(E)\) and \(B(E)\) are given by:

\[
A(E) = \sqrt{\left( \alpha^2 + \eta^2 \right) \left( \beta^2 + \eta^2 \right) \over \gamma^2} \tag{A4.1.4}
\]

\[
B(E) = Z^2 \left[ \left( \alpha - \beta \right) Z - 2\eta \right]^2 + \left[ 2\eta Z + \left( \alpha - \beta \right) \right]^2 \over \gamma^2 \tag{A4.1.5}
\]

Where the coefficients \(\alpha, \beta, \gamma, \eta\) can be expressed in terms of the Bogoliubov coherence factors, \(u\) and \(v\) given by:

\[
u^2 = \alpha + i\eta \tag{A4.1.6}
\]

\[
v^2 = \beta - i\eta \tag{A4.1.7}
\]

\[
\gamma = u^2 + \left( u^2 - v^2 \right) Z^2 \tag{A4.1.8}
\]

The Bogoliubov coherence factors are given by:

\[
u^2 = {1 \over 2} \left[ 1 + \sqrt{\left( E + i\Gamma \right)^2 - \Delta^2 \over E + i\Gamma} \right] = 1 - v^2 \tag{A4.1.9}
\]

Using the above equations (A4.1.3 to A4.1.9), the I-V curves are simulated for a given temperature \(T\) with \(\Delta(T), \Gamma(T)\) and \(Z\) as the fitting parameters. This simulated curve is then differentiated to obtain \(G(V) = dI/dV\) which is divided by \(dI/dV\) obtained for a large bias voltage \((V >> \Delta/e)\). This gives \(G(V)/G_N\) as a function of bias voltage \((V)\) and is used to fit the experimental spectrum \((G(V)/G_N vs \ V)\) in the point contact regime.
Table A4.1: Fitting parameters used for fitting in the point contact regime
Particle size ($d_{\text{XRD}}$) = 60nm; $T_c = 7.25\text{K}$

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Table A4.2: Fitting parameters used for fitting in the point contact regime
Particle size ($d_{\text{XRD}}$) = 25nm; $T_c = 7.25\text{K}$

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Table A.4.3: Fitting parameters used for fitting in the tunneling regime  
Particle size (d$_{\text{XRD}}$) = 18nm; $T_c =$ 7.2K

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<tr>
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<td>-</td>
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Table A4.4: Fitting parameters used for fitting in the point contact regime  
Particle size (d$_{\text{XRD}}$) = 15nm; $T_c =$ 7.18K

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Table A4.5: Fitting parameters used for fitting in the tunneling regime  
Particle size (d$_{\text{XRD}}$) = 11nm; $T_c =$ 7.0K

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<th>Temperature (K)</th>
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<th>Energy Gap ($\Delta$) meV</th>
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<td>-</td>
<td>0.3</td>
<td>0.23</td>
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</table>
References

11. P. G. De Gennes, Rev. Mod. Phys. 36, 225 (1964)
Chapter 5

Superconducting Proximity Effect in Biphasic Nanostructured Systems

5.1 Introduction

It is well known that when a superconductor and a normal metal are in good electrical contact, the microscopic mechanism of Andreev reflection\(^1\) leads to a leakage of Cooper pairs and phase coherence into the normal metal. At the same time, unpaired electrons from the normal metal diffusing into the superconductor have a strong influence on the properties of the latter. This is the classic superconducting proximity effect (SPE), which leads to superconductivity being weakened in the superconductor and induced in the normal metal. It is well described within the framework of the de Gennes–Werthamer model\(^2,3\) as discussed in Section 1.3. There are a large number of studies of SPE in bilayers and multilayers (with alternating superconducting and normal metal layers) with the thickness of each component being less than its respective coherence length. However, our understanding is much more limited for the case of nanometer scale superconducting particles embedded in a metallic (normal or superconducting) matrix. In such cases, besides the constraint of size, the matrix may also play a crucial role in dictating the onset of superconducting transition. We may expect the superconducting properties of such multi-component systems to be controlled by superconducting proximity effect (SPE)\(^4,5,6,7,8\) when the size of the superconducting particles is less than the coherence length.

Random three dimensional dispersions of granular superconductors have been studied in the past with respect to percolation theory.\(^9\) However, such granular systems consist of superconducting particles in an insulating matrix and do not involve proximity effect. A few of the earlier reports on random mixtures of superconducting particles in normal (conducting) matrices,\(^10\) involve the theory of Hsiang\(^11\) \textit{et al.}, who have estimated the superconducting transition temperature \((T_c)\) of clean SNS junctions in the thick limit, in which the \(T_c\) is a function of the critical current density \(J_c\). There is a very recent report on a 3D random mixture of a strongly coupled superconductor (Pb) and normal metal (Cu), in which the particles of both the components are smaller than their respective coherence lengths.\(^12\) The authors have shown that in this case it is justified in replacing the ratio of the thicknesses of
the superconductor and normal metal \((d_S/d_N)\) in the de Gennes-Werthamer theory by the ratio of the volume fractions of the two components. There are a few other reports of the superconducting behavior of nanometric dispersions of metallic particles in conducting matrices.\(^{13,14,15}\) Tsai et al have discussed the influence of the matrix phase on the superconducting properties of the dispersion and suggested that proximity effect can be a possible reason for the observed decrease in \(T_c\). However, there was no quantitative explanation of the data with respect to proximity effect. Clearly, it is important to explore in further detail the behavior of such random dispersions.

We wanted to determine whether, if the theory of SPE for bilayers and multilayers is at all valid in such random dispersions. If it is, then which are the relevant parameters that determine the \(T_c\) in such systems? With this in mind, we carried out a study of the superconducting properties in two different types of 3D random mixture systems as a function of component fraction and particle size. The first system consists of 3D nanocomposite films of randomly interdispersed Pb and Ag nanoparticles. Here, we have tried to understand the evolution of \(T_c\) as a function of the ratio of the volume fractions of the two components. The second system consists of Pb/Sn biphasic nanoparticles randomly distributed in an Al matrix. Here, again we have invoked the modified theory of SPE to explain the observed \(T_c\) of the system.

### 5.2 Superconducting / normal metal nanocomposites – Random distribution of Pb and Ag nanoparticles

#### 5.2.1 Synthesis and Structural Characterization

The Pb/Ag nanocomposites have been prepared by co-sputtering of the two elements, using an axial magnetron gun in a vertical geometry (bottom-up) as shown in Fig. 5.1.1. Initially we mounted a silver target (99.999% pure from Kurt and Lesker Co.) on the sputtering gun and kept small rectangular (~1cm×0.5cm) pieces of Pb (cut from a Pb sheet, 99.99%) on the annular ring of the Ag target, from where the rate of sputtering is the highest. P-type Si (100) wafers were used as substrates. By keeping the pressure of the Ar gas as high as ~0.1mbar, we could control the particle sizes of Pb and Ag such that they remained lower than the coherence length of Pb (~80nm). It was however difficult to independently control both particle size and the composition of the two elements in the films. Also in this geometry, we could not grow Pb-Ag nanocomposite films with more than 25 atomic % of Pb (even when the Pb pieces almost covered the annular ring). Hence, to increase the Pb:Ag ratio in the
films, we used a commercial Pb target (99.999% pure from Kurt and Lesker Co.) with small pieces (~1cm × 0.5cm) of Ag (99.99% pure) placed on the annular ring on Pb. As before, the pressure of the Ar gas and the amount of the Ag pieces were varied to control the particle size and the composition of the films. The substrate was kept at room temperature for all depositions. We also employed a liquid nitrogen trap (prior to deposition) to improve the base vacuum and also condense out any residual oxygen. We also used a Ti wire in the deposition chamber which was kept red hot during deposition. This acted as a getter and absorbed any residual oxygen present in the chamber and in the Ar gas. The above two steps were essential to prevent oxide formation. The sputtering conditions of the Pb-Ag nanocomposite films and the relative compositions of Pb and Ag are given in Table 5.1.1.

The composition of the as-deposited films was determined from Energy Dispersive X-ray Absorption (EDX) done in a JEOL JSM-840 SEM. The EDX was done from 5 different regions of the films and the composition differed by 2-3%, showing that the films were homogenous. Elemental mapping confirmed a uniform distribution of Pb and Ag in all the samples. The average composition (from EDX) of the different nanocomposite Pb-Ag films was in the range of Pb(9%)-Ag(91%) to Pb(100%), as shown in Table 5.1.1.

The films were further characterized by X-ray Diffraction (XRD). The XRD patterns of some of the films are shown in Fig. 5.1.2. The XRD spectra do not show the
<table>
<thead>
<tr>
<th>Sample</th>
<th>Gas Pressure (mbar)</th>
<th>Voltage (V)</th>
<th>Current (mamp)</th>
<th>Time of deposition (minutes)</th>
<th>Atomic ratio (Pb:Ag)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbAg01</td>
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<td>260</td>
<td>25</td>
<td>5</td>
<td>100 : 0</td>
</tr>
<tr>
<td>PbAg12</td>
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<td>230</td>
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<td>5</td>
<td>93 : 7</td>
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<tr>
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<td>35</td>
<td>10</td>
<td>86 : 14</td>
</tr>
<tr>
<td>PbAg14</td>
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<td>40</td>
<td>10</td>
<td>84 : 16</td>
</tr>
<tr>
<td>PbAg06</td>
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<td>270</td>
<td>100</td>
<td>10</td>
<td>81 : 19</td>
</tr>
<tr>
<td>PbAg05</td>
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<td>300</td>
<td>100</td>
<td>10</td>
<td>75 : 25</td>
</tr>
<tr>
<td>PbAg10</td>
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<td>280</td>
<td>60</td>
<td>10</td>
<td>67 : 33</td>
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<tr>
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<tr>
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<td>5</td>
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<tr>
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<td>5</td>
<td>16 : 84</td>
</tr>
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<td>340</td>
<td>54</td>
<td>10</td>
<td>9 : 91</td>
</tr>
</tbody>
</table>

Table 5.1.1: List of samples studied with their composition (obtained from EDX), and sputtering conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic ratio (Pb:Ag)</th>
<th>P_s/P_N</th>
<th>T_c(K)</th>
<th>Particle size of Pb (nm)</th>
<th>Particle size of Ag (nm)</th>
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</thead>
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</tr>
<tr>
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<td>7.0</td>
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<td>-do-</td>
</tr>
<tr>
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<td>-do-</td>
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<td>6.52</td>
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<td>-do-</td>
</tr>
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<td>7.59</td>
<td>6.4</td>
<td>45</td>
<td>-do-</td>
</tr>
<tr>
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<td>5.34</td>
<td>6.1</td>
<td>21</td>
<td>5.4</td>
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<td>5.4</td>
<td>56</td>
<td>11</td>
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</tr>
<tr>
<td>PbAg03</td>
<td>16 : 84</td>
<td>0.33</td>
<td>-</td>
<td>18</td>
<td>11</td>
</tr>
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<td>-</td>
<td>no XRD line</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 5.1.2: List of samples studied with their composition (obtained from EDX), volume fraction (P_s/P_N) and T_c
presence of any impurity phase. The particle size was determined from an x-ray line profile analysis (after Rachinger correction and instrumental broadening) using the WINFIT software which corrected for the strain in the films. Films with particle sizes greater than 80nm were discarded for further studies since we required the particle size to be lower than the coherence length of Pb to invoke the theory of proximity effect. The particle size of Pb ($D_{\text{Pb}}$) varied between 20-60nm and that of Ag ($D_{\text{Ag}}$) varied between 7-25nm. The particle sizes, strains and relative composition of Pb and Ag is given in Table 5.1.2. The film thickness was typically between 200 and 500nm implies that the films were three dimensional dispersions. X-ray line profile analysis showed that there was a 15-20% dispersion about the mean particle size. This is therefore the upper limit to the size distribution.

**Figure 5.1.2:** Representative XRD pattern of some of the Pb-Ag nanocomposite films. The composition of Pb denoted is the atomic %.

The homogeneity, particle sizes and the size distribution in the nanocomposite films were further examined using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The SEM images were obtained using a Zeiss Ultra 55 field emission scanning electron microscope (FE-SEM) based on a Gemini lens while the AFM images were obtained from a Digital Instruments multimode scanning probe microscope (SPM). The Zeiss FE-SEM has an energy selective back scatter detector (ESB) in addition to the in-lens secondary electron (SEI) detector. The ESB detector gives local compositional information since it provides contrast between elements with different atomic numbers. This is important for the Pb-Ag nanocomposite films as it helps in understanding if Pb and Ag nanoparticles form a random mixture at the microscopic level. A typical, low-resolution SEM image of a
Figure 5.1.3: SEM image (×100,000) of a Pb-Ag nanocomposite sample with 63 at % Pb, showing perfectly uniform microstructure, obtained using (a) a normal (in-lens) secondary electron (SEI) detector, and (b) an energy selective backscatter (ESB) detector. The ESB image (b) shows only the Pb nanoparticles.

Figure 5.1.4: SEM image (×100,000) of a Pb-Ag nanocomposite sample with 81 at % Pb, showing perfectly uniform microstructure, obtained using (a) a normal (in-lens) secondary electron (SEI) detector, and (b) an energy selective backscatter (ESB) detector. The ESB image (b) shows only the Pb nanoparticles.

Figure 5.1.5(a): High resolution energy selective back scattered (ESB) SEM image of the Pb-Ag nanocomposite with 81% Pb. (b) Line profile taken across three grains (as shown by the line in (a)) to find the particle size of Pb nanoparticle.
sample with 63 at % Pb was obtained using the in-lens SEI detector [Fig. 5.1.3(a)]. The image shows uniform microstructure with a narrow particle size distribution. However, this image does not allow one to distinguish between Pb and Ag particles. A compositional image of the nanoscale two-phase dispersion was obtained using the ESB detector, also operated at a relatively low voltage (~1.8 kV). Fig. 5.1.3(b) shows an ESB image of the same region as Fig. 5.1.3(a), but the Pb and Ag particles here display different contrasts. It is clear that the Pb nanoparticles (showing lighter contrast) are intimately mixed with the Ag particles, which have much darker contrast and are virtually invisible. Similar SEM images of the sample with 81 at % Pb are shown in Fig. 5.1.4. As before, Fig. 5.1.4(b) is an ESB image showing elemental contrast. It is apparent from Figs. 5.1.3(a) and 5.1.4(a) that the nanoparticles are largely aggregated into small clusters. Since, the particles in sputter deposited films lie close to each other and are stacked together to form 3D films, often in low resolution SEM and AFM images, they appear as a cluster having a size larger than the primary particle size. This is the reason why the particle sizes as determined from XRD may appear smaller than those seen in the SEM image. Also the size distribution appears larger than it actually is as seen from low resolution image. Hence, to get an estimate of the proper particle size and size distribution a high resolution image needs to be analyzed. We carried a detailed analysis of the high resolution SEM images (using ImageJ and WSxM software) of the nanocomposite films. Shown in Fig. 5.1.5(a) is the high resolution SEM image with 81% of Pb. Taking a line profile over three particles (shown by the line in the image) gives a particle size ~ 50nm.

**Figure 5.1.6:** Particle size distribution obtained from high resolution SEM images for two representative nanocomposite samples: with 63 atomic % Pb (left) and 81 atomic % Pb (right). The standard distribution is typically about 15% of the mean.
5.1.5(b)). We have used the ESB image to do the analysis since the normal SEM image cannot distinguish between the Pb and Ag particles. Since the Ag particle size is less than that of Pb, analyzing the normal SEM image will give wrong information of the particle size and its distribution. The size distribution is around 15-20% as can be seen from the histogram plot obtained from a particle size analysis of the image for the film with 63% of Pb (Fig. 5.1.6, left) and for the film with 81% of Pb (Fig. 5.1.6, right). A comparison of Fig 5.1.6 and Table 5.1.2 shows that the coherently diffracting x-ray domain size matches quite well with the mean primary particle size obtained from SEM.

5.2.2 Results and Discussions
The superconducting transition temperature ($T_c$) of the nanocomposite films was measured by the planar coil ac susceptibility technique. Though it does not provide the absolute value of the diamagnetic moment, it is a very sensitive technique to determine the superconducting properties of thin films. The temperature at which the real part of the susceptibility ($\chi'$) deviated from zero was identified as the $T_c$. Independent measurements show that this temperature matches closely with that at which the electrical resistivity vanishes and a macroscopic critical current density ($J_c$) can be sustained in the sample. Fig 5.1.7(a) shows the temperature dependence of the real part of the ac-susceptibility for the Pb-Ag nanocomposites with varying volume % of Pb (indicated in figure).

**Figure 5.1.7 (a):** Temperature dependence of the real part of the ac-susceptibility for the Pb-Ag nanocomposites with varying volume % of Pb (indicated in figure).

(b) Variation of $T_c$ with the volume % of Pb in the nanocomposite samples.

To see if $T_c$ is dependent on the particle size of Pb, we grew films with approximately the same
Pb fraction (~85%) but with the particle size of Pb ($D_{Pb}$) varying between 20 to 60nm. The $T_c$ was found to remain the same (~6.7K) in this size range (Fig. 5.1.8). In a separate study\cite{16} of particle size effects in pure nanocrystalline Pb as discussed in chapter 4, we found that $T_c$ does not change down to a size of 14 nm, in conformity with existing data as well as Fig. 5.1.8. Fig. 5.1.7(b)) shows that the $T_c$ decreases monotonically with decreasing volume concentration of Pb. Hence, it is the ratio of the volume fractions of the two components in the nanocomposites and not the particle size that plays the dominant role in controlling $T_c$. Expectedly, we also found that if particle size of Pb is greater than 80nm (coherence length of pure Pb), the corresponding $T_c$ remains the same as that of bulk Pb ($\approx$ 7.25 K).

To understand our observations on the variation of $T_c$ with the volume fraction of the superconducting and normal components, we adopt an approach similar to that of Sternfeld \textit{et al}\cite{11} for the case of the Pb-Cu system. Following this approach, we substitute the ratio of the thickness of the superconductor and the normal metal in the SPE formalism for bilayers and multilayers, by the ratio of the volume fractions of the two components in the nanocomposite system (say, $P_S$ and $P_N$). Thus, the modified expression for $T_c$ is:

$$\ln\left(\frac{1.14\Theta_D}{T_c}\right) = \frac{1 + \alpha (P_N/P_S)}{N_S(0)V}$$

in the weak coupling limit ($\lambda < 1$), where $\Theta_D$ is the Debye temperature, and:

$$\ln(1.45T_c) = \frac{\lambda_S \ln \Theta_S + \lambda_N \ln \Theta_N \alpha (P_N/P_S)}{\lambda_S + \lambda_N \alpha (P_N/P_S)} - \frac{\lambda_S + 1 + (\lambda_N + 1) \alpha (P_N/P_S)}{\lambda_S - \mu + (\lambda_N - \mu) \alpha (P_N/P_S)}$$

in the strong coupling limit ($\lambda > 1$).
Here $\alpha = N_N(0)/N_S(0)$, where $N_N(0)$ and $N_S(0)$ are the density of states at the Fermi energy for the normal metal and the superconductor respectively, while $\lambda_N$, $\Theta_N$, $\lambda_S$ and $\Theta_S$ are the electron phonon coupling constants and the Debye temperatures of the normal metal and the superconductor, respectively. $V$ is the inter-electron attractive potential due to phononic interaction and $\mu$ is the effective electron-electron repulsion term.

Theoretical curves for $T_c$ vs $P_S/P_N$ the strong and weak coupling limits were calculated using the following parameters from literature: $\Theta_{Pb} = 105K$, $\Theta_{Ag} = 215K$, $^7\mu = 0.11$, $N_{Pb}(0) = 0.276N_0$, $N_{Ag}(0) = 0.098N_0$, $^8\lambda_{Pb} = 1.013$, and $\lambda_{Ag} = -0.018$, where $N_0$ is the Avagadro number. The value of $N_{Pb}(0)V = 0.355$ was obtained from the weak coupling BCS expression$^9$ for $T_c$: $T_c = 1.14\Theta \exp(-1/N(0)V)$, and taking $T_c (Pb) = 7.25\text{ K}$. $\lambda_{Ag}$ has been taken from the work of Kouh and Valles$^{20}$ who studied SPE in quench condensed Pb/Ag bilayers. Their data on the variation of $T_c$ with bilayer thickness could be fitted to SPE theory only if the electron-phonon coupling for Ag was taken to be slightly repulsive.

Fig. 5.1.9 depicts our experimental data points and the calculated curves for the weak and strong coupling limits, shown respectively as a solid line and a dotted line. Though Pb is a well known strong coupling superconductor with $\lambda > 1$, our nanocomposite data fits better with the theoretical curve for the weak coupling case. Thus, in such random mixtures of Pb and Ag nanoparticles, the weaker electron phonon interaction in Ag compared to Pb appears to influence the interaction of the superconducting electrons with the lattice in the Pb nanoparticles. Such weak-coupling behavior of Pb has not been observed in bilayers or multilayers of Pb with normal metals. On the other hand, for pure nanocrystalline Pb, there

![Figure 5.1.9: Variation of $T_c$ with the ratio of the volume fractions of Pb ($P_S$) and Ag ($P_N$). The accuracy of measuring either $T_c$ or $P_S/P_N$ are no larger than the size of the data points, shown by the open circles. The theoretical curves for the strong and weak coupling limits are shown by the green and red solid lines, respectively.](image)
are reports showing that Pb tends to exhibit stronger coupling behavior with decreasing particle size.

In summary, we have shown that the superconducting transition temperature in a co-sputtered, randomly intermixed composite of Pb and Ag nanoparticles is controlled by the ratio of the volume fraction of the two components, in accordance with the predictions of proximity effect. The exact nature of the nanoparticle dispersion has been shown from high resolution electron microscopy data. The particle sizes corresponding to each phase should be smaller than the relevant coherence length for proximity effect to be observable. Quantum size effects due to the discretization of the energy bands are not important above \( \approx 10\text{nm} \). We further show that Pb behaves as a weak coupling superconductor when randomly distributed with a normal metal such as Ag.

5.3 Biphasic superconducting nanoparticles (Pb-Sn) in bulk superconducting (Al) matrix

5.3.1 Synthesis and measurement of structural and superconducting properties

The nanocrystalline Pb-Sn alloy (in nominally equi-atomic proportion) embedded in an Al matrix was prepared by rapid quenching of the ternary melt containing high purity (99.99\%)

![Figure 5.2.1: Binary phase diagram of Pb-Sn](image)

Al, Pb and Sn metals. The as-cast alloy was prepared by melting the metals in an alumina crucible using a 12 kW induction furnace. For rapid solidification, the ternary alloy melt was ejected through a 0.5 mm quartz nozzle onto the surface of a polished copper wheel rotating with a velocity of 24 m/s. The sample thus obtained was in the form of ribbons of 60 \( \mu \text{m} \) thickness and 2.5 mm width. The melt phase separates during cooling through the ternary
miscibility gap yielding nanodroplets of Pb-Sn binary melt. The equilibrium lead-tin phase diagram (Fig. 5.2.1) shows the presence of face centered cubic Pb and body centered tetragonal β-Sn at the two ends. These phases evolve from the melt by a eutectic reaction, which corresponds to a temperature of 183.3°C and a composition of Pb-73.9at% Sn. The solid solubility of both Pb and Sn in Al is less than 0.1 mass% at the binary eutectic temperature. The strategy for the synthesis of biphasic alloy nanoparticles of Pb-Sn embedded in an Al matrix relies on the fact that both Sn and Pb exhibit positive heat of mixing with Al, indicating a tendency toward repulsive interaction and subsequent phase separation in the liquid as well as in the Al-rich solid. The formation can be explained as follows. The first solid phase to form in the nanodroplet is Pb, which undergoes heterogeneous nucleation on the surrounding Al matrix. The Pb phase catalyses the nucleation of Sn and the eutectic reaction and hence the bi-phasic nanoparticles of Pb-Sn is formed. The schematic of the formation of the nanodroplets of Pb-Sn from the ternary melt is shown in Fig. 5.2.2.

X-ray diffraction (XRD) using a JEOL JDX 8030 machine with CuKα radiation was used for phase identification. Fig. 5.2.3(a) shows the XRD data for the as-cast Pb-Sn alloy.
Figure 5.2.3: X-ray diffraction data showing the presence of (a) Sn and Pb peaks in the as-cast alloy, and (b) Sn, Pb and Al reflections in the rapidly solidified sample.

Figure 5.2.4 (a) Bright Field TEM image of the Pb-Sn nanoparticles in Al matrix (b) High resolution of the same region showing distinctly the bi-phasic nanoparticles of Pb-Sn.
The XRD data for the rapidly solidified sample (Fig. 5.2.3(b)) indicate the presence of FCC Pb and tetragonal Sn phases in addition to FCC Al reflections. Detailed microstructural characterization of the sample was carried out using a JEOL 2000 FX-II transmission electron microscope (TEM) operating at 200 kV. The local composition was analyzed using energy dispersive x-ray absorption (EDX) (Oxford) attachment. A microstructural analysis of the rapidly solidified sample shows composite particles of Sn and Pb dispersed within the Al matrix. The typical morphology of the dispersion is shown in the bright field transmission electron micrograph (TEM) of Fig. 5.2.4(a). The biphasic particles can be seen more clearly in the TEM micrograph of Fig. 5.2.4(b). We observe that every particle has a distinct two-phase contrast within it, clearly suggesting a composite substructure. Composition analysis using EDAX reveals the average composition of the particles to be 54 at% Pb + 46 at% Sn. The Pb-Sn biphasic nanoparticles form 2% by volume of the Al matrix. The size distribution of the Pb-Sn nanoparticles in the Al matrix, calculated using the Sigma-scan Pro software, is shown in Fig. 5.2.5. The peak of the distribution occurs at 20 nm. The distribution is markedly skewed and has a long tail at larger sizes. The volume-weighted mean is \( \approx 100 \text{ nm} \).

![Size distribution histogram of the two phase Pb-Sn particles obtained from TEM data.](image)

An Oxford MagLab vibrating sample magnetometer (VSM) was used to investigate the superconducting properties of the samples via magnetization measurements under field-cooled (FC) and zero field-cooled (ZFC) conditions as a function of temperature and applied magnetic field. The sample was first cooled down to the lowest temperature (typically 1.6 K) in zero field. The ZFC data was then recorded by warming the sample at the rate of 0.2
Kmin\(^{-1}\) up to 10K in the presence of the measuring field. Finally, the FC data was recorded while cooling the sample at the same rate and under the same field as during the ZFC cycle.

### 5.3.2 Results and Discussions

Fig. 5.2.6 shows the zero-field cooled magnetization (M) as a function of temperature (T) for the as-cast binary Pb-Sn alloy (of the same composition as the nanodispersed particles) measured at a low applied magnetic field (H) of 45G. The observed \(T_c\) of 6.9 K suggests the solid solution consists of a Pb-rich phase. This is consistent with the fact that there is a limited solubility of Sn in Pb under equilibrium conditions. The criterion for the determination of the superconducting transition temperature \((T_c)\) from the magnetization measurements is to equate it with the temperature of the onset of the Meissner transition. Fig. 5.2.7 shows the temperature dependence of the magnetization measured under ZFC conditions for the Pb-Sn biphasic particles nanodispersed in Al, measured at a low applied field of H = 45 G. The M-T data for nanodispersions in Al indicates a weak onset of superconducting transition at 3.1 K, which is much lower than the \(T_c\) of either Pb (7.2 K) or Sn (3.7 K).

Our results indicate a large reduction in the \(T_c\) of the nanodispersed system. The detailed TEM data do not show the formation of either metastable phases or large interphase boundaries which can be invoked to explain this reduction. Decrease in the \(T_c\) with decreasing particle size has been observed in some superconductors as discussed in Chapter 3.\(^{22}\) However, in the case of Pb, recent measurements\(^{23}\) as well as our own data (chapter 4)
have established that a decrease in $T_c$ can be expected only when the particle size is below $\approx 10$ nm. In the present situation, it is quite clear from the particle size distribution (Fig. 5.2.5) that the large majority of particles are well above this size. Hence, it is likely that some other mechanism is responsible for the large suppression of $T_c$. The biphasic (Pb/Sn) system nanodispersed in Al exhibited an onset of $T_c$ of $\sim 3.1$ K, which is much lower than the $T_c$ of either bulk Pb ($T_c = 7.25$ K) or Sn ($T_c = 3.7$ K). Hence, the possibility of proximity effect between Pb and Sn alone cannot explain the observed $T_c$. We show that it is essential to take account of the effect of the Al matrix in proximity with the composite to explain our observations.

We will first investigate how the proximity effect between Pb and Sn alone affects the $T_c$ of the system. For a strong coupling superconductor in contact with a normal metal, as discussed in Section 1.3, the effective $T_c$ predicted by proximity effect is:

$$\ln T_c = \frac{\langle \lambda \ln \Theta \rangle}{\langle \lambda \rangle} - \frac{1}{\lambda^*} - \ln 1.14 \tag{5.2.1}$$

where $\Theta$ is the Debye temperature. $\langle \lambda \rangle$ is the effective electron phonon coupling strength and $\lambda^* = \frac{\langle \lambda \rangle - \mu^*}{(1 + \langle \lambda \rangle)}$; with $\mu^*$ being the Coulomb pseudopotential term. Silvert has shown that for a strong coupling superconductor of thickness $d_S$ in contact with a normal metal or a superconductor with a lower $T_c$ of thickness $d_N$,

$$\langle \lambda \rangle = \frac{d_S N_S \lambda_S + d_N N_N \lambda_N}{d_S N_S + d_N N_N} = \beta_S \lambda_S + \beta_N \lambda_N \tag{5.2.2}$$

$$\langle \lambda \ln \Theta \rangle = \beta_S \lambda_S \ln \Theta_S + \beta_N \lambda_N \ln \Theta_N \tag{5.2.3}$$
where: \( \beta_S = \frac{d_S N_S}{d_S N_S + d_N N_N} = 1 - \beta_N \)

Here \( N_S \) and \( N_N \) are the densities of states at the Fermi level from obtained from the free electron theory of the superconductor and the normal metal respectively.

**Figure 5.2.8:** Variation of \( T_c \) with volume % of Pb for the Pb/Sn nanocomposite

For the Pb/Sn nanocomposites with 54 atomic% of Pb, we can find the average volume per cent of each component within a single particle of a specific size and hence obtain the ratio of the length of the sides of each component within the particle assuming a cuboid geometry. TEM study indicates that this estimation is reasonable. Assuming \( N_{Sn}(Sn) = 0.212N_0 \) and \( N_{Sb}(Pb) = 0.276N_0 \) \( (N_0 = \text{Avagadro number}) \), \( T_c \) was evaluated from (Eqs. 5.2.1-5.2.3) for the Pb/Sn nanocomposite as a function of the volume% of Pb (see Fig. 5.2.8). It is also clear from the above equations that the \( T_c \) remains the same as long as \( d_S/d_N \) is constant (provided \( d_S \) and \( d_N \) are within the ‘Cooper limit’\(^{25} \)). Fig. 5.2.8 indicates that for 57% by volume of Pb, the \( T_c \) for the Pb/Sn nanocomposite should be \( \approx 6.16 \)K, which is much higher than the observed value of 3.1K. Note also that the observed onset of \( T_c \) is even less than the lower of the \( T_c \)’s of the two components \( (T_c(Sn) = 3.7 \)K). Since such a situation is not predicted by proximity effect, it is clear that the Al matrix \( (T_c(Al) = 1.17 \)K) must significantly influence the effective onset of \( T_c \) of the entire system.

We know that the total amount of Pb+Sn nanocomposite in the Al matrix is about 2% by volume. For all practical purposes, the Al matrix can therefore be taken to be of infinite extent with respect to the Pb/Sn composite particles of average size \( \approx 20 \)nm. We can then compare this situation to the case where a thin superconducting metal is in contact with a thick normal/superconducting metal (of lower \( T_c \)) and find out how proximity effect...
influences the effective $T_c$ of such a system. The proximity effect theory for a N/S interface in the thick clean limit has been worked out by Werthamer. For a thin superconducting metal of thickness $D_S$ in contact with a normal metal of infinite thickness, the $T_c$ is given by:

$$d_s = \left(\frac{\pi}{2}\right)\left(1-t\right)^{-1/2} \cot^{-1}\left[\frac{2}{\pi}\left(t^{-1} - 1\right)\right]^{1/2}$$

(5.2.4)

where $d_s = D_S\left(\frac{h\nu_{FS} l_s}{6\pi k_B T_{cS}}\right)^{-1/2}$ and $t = T_c/T_{cS}$ is the reduced temperature, where $T_c$ is the transition temperature for the entire system and $T_{cS}$ is the transition temperature of the superconducting layer. Here $l_s$ is the mean free path at low temperatures and $\nu_{FS}$ is the Fermi velocity for the superconducting layer. For simplicity, we first consider small superconducting particles of Pb dispersed randomly in an Al matrix (dilute limit). We assume that each Pb particle is smaller than its coherence length and compare this case to that of a thin superconducting layer in contact with a thick normal/superconducting layer. Here, we replace the thickness of the superconducting layer ($d_S$) by the particle size of the dispersed superconductor. Obviously, when the particle size of Pb is very small, the $T_c$ of the system will tend towards the $T_c$ of the Al matrix (1.2K), as shown in Fig. 5.2.9. This is consistent with the results reported earlier.

In the next step, we replace the single phase, dispersed superconductor (Pb) with the Pb/Sn composite phase (in the ratio of 54:46 by volume) dispersed in the Al matrix, where the $T_c$ of the nanocomposite phase (reduced by proximity effect) is taken to be 6.16K, as

![Figure 5.2.9: Variation of $T_c$ for Pb-Sn nanocomposite in Al matrix.](image)
obtained from Fig.5.2.5. Similarly, the Fermi velocity of the composite is taken as the weighted average of the Fermi velocities of Pb and Sn, and the mean free path is assumed to be limited by the particle size (i.e., \( l_s \approx D_0 \)). The resulting plot of \( T_c \) versus the particle size for the Pb/Sn nanocomposite dispersed in Al, is also shown in Fig. 5.2.9. It is clear that the distribution in particle size (as is the case in our system) will result in a distribution in the \( T_c \). However, the actual onset of superconductivity is expected to be governed by the larger particles since the volume average lies close to 100nm. We do find a distribution in \( T_c \), though the observed onset is slightly higher than that predicted from the theory. However, the prediction from proximity effect is quite accurate in view of the rather gross assumptions made in the estimation of the Fermi velocity and the mean free path.

In summary, we have shown that the onset of superconducting transition (~3.1K) in a random dispersion of Pb-Sn biphasic nanoparticles in an Al matrix, is governed by the proximity of the metals to each other. The maximum influence on the onset of \( T_c \) is from the Al matrix. The superconducting proximity effect as applicable to bilayers and multilayers can be invoked successfully to understand the observed superconducting transition in this complex system.

### 5.4 Conclusions

We have studied two distinct types of systems with random dispersions of superconductors and normal metals. The first system was a nanocomposite of Pb and Ag prepared by co-sputtering. We observed a monotonic decrease of the superconducting transition temperature \((T_c)\) with the concentration of Pb in the nanocomposite films. This variation in \( T_c \) can be understood on the basis of the superconducting proximity effect which is valid for bilayers and multilayers if the ratio of the thickness of the superconductors and normal metal is replaced by the ratio of the volume fractions of the superconductor and normal metal nanoparticles. We have also observed that Pb, a strong coupling superconductor in the bulk, behaves as a weak coupling superconductor when randomly distributed with a normal metal.

The second system studied is the biphasic nanoparticles of Pb-Sn randomly distributed in an Al matrix. This was prepared by rapid quenching of the ternary melt consisting of Al, Pb and Sn. The bi-phasic nanoparticles of Pb-Sn is equi-atomic proportion and were around 2% by volume of the Al matrix. The system showed a weak superconducting onset at a temperature of 3.1K which is much lower than the \( T_c \) of either Pb or Sn. This could be explained by invoking the theory of superconducting proximity effect as
valid for bilayers firstly between Pb and Sn and then between the biphasic (Pb/Sn) nanoparticles and the Al matrix. The distribution in particle size leads to a distribution in $T_c$ as well.

Thus, from the study of these two systems, we conclude that the theory of superconducting proximity effect is indeed valid for such random nano-dispersions of superconductors and normal metals.
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Chapter 6

Summary and Future Directions

6.1 Summary
In summary, the main goal of my thesis was to understand the mechanism of the evolution of superconductivity as a function of particle size in elemental nanostructured superconductors. Traditionally, finite size effects in superconductors have been attributed to two different mechanisms: (i) The discretization of energy levels arising from quantum size effects and (ii) the phonon softening at the surface of the superconducting nanoparticles due to reduced coordination number. The aim of my thesis was to study the possible interplay of these two effects in two distinct systems, namely, the intermediate-coupling superconductor Nb, and the strong-coupling superconductor Pb, in which the nature of the evolution of superconducting properties with decreasing particle size is quite different.

Nb shows a 50% decrease in $T_c$ from the bulk value of 9.4K as the particle size is reduced from 60 to 8nm, below which it becomes non-superconducting - consistent with the Anderson criterion. To understand the mechanism influencing $T_c$, we measured the superconducting energy gap of the nanostructured Nb films by point contact Andreev reflection spectroscopy (PCAR). Measurement of the superconducting energy gap and its temperature dependence in nanostructured superconductors is crucial (though so far often neglected) for the understanding of the evolution of the electron phonon coupling strength with decreasing particle size. Our results show that there is no change in the electron-phonon coupling strength with decreasing particle size in Nb and it remains an intermediate coupling superconductor down to the smallest particle size of 8nm. This indicates that it is the decrease in the density of states at the Fermi level arising from the quantum size effects that is probably responsible for the reduction in $T_c$ with decreasing particle size in this intermediate coupling superconductor. In addition, Nb also shows a non-monotonic variation in the upper critical field ($H_{C2}$) with decreasing particle size. It shows a 2.3 times increase in $H_{C2}$ as the particle size is reduced from 60 to 20nm, below which the $H_{C2}$ starts to decrease. This non-monotonic variation in $H_{C2}$ can be explained by the competing effects of the decrease in particle size and the decrease in the density of states (due to quantum size effects) at the Fermi level. Finally, Nb also shows a size induced metal-insulator transition. Films with
particle size $\geq 8$nm are metallic and superconducting while films with particle size $< 8$nm are weakly insulating and non-superconducting. From the temperature dependence of the conductivity in the weakly insulating films we found that there are two characteristic energies associated with the transport of the electrons in the nanostructured Nb films. The lower of the two energy scales arises from the discretization of the energy levels and is associated with the intra-granular transport. The higher energy arises from the potential barrier present at the grain boundary (due a physical oxide barrier at the interface of the grains) which controls the inter-granular transport.

Nanostructured Pb films, on the other hand, show only a small (10%) decrease in $T_c$ as the particle size is reduced from 60 to 7nm, below which it abruptly becomes non-superconducting, consistent with the Anderson criterion. However, the measurement of the superconducting energy gap in planar tunnel junctions of Al/Al$_2$O$_3$/Pb, shows that there is a substantial increase in the electron-phonon coupling strength with a reduction in particle size in this strong-coupling superconductor. The small decrease in $T_c$ appears to occur due to the competing effects of phonon softening and quantum size effects. Also, contrary to the case of Nb, nanostructured Pb shows a monotonic, 3.6 times increase in the upper critical field as the grain size is reduced from 60 to 7nm. I have shown that this variation in $H_{C2}$ with particle size is consistent with the observed small decrease in $T_c$.

The third part of my thesis dealt with the study of the variation of the superconducting transition temperature in nanocomposites of superconductors and normal metals. In both the systems studied, namely nanocomposites of Pb-Ag and bi-phasic nanoparticles of Pb-Sn randomly distributed in an Al matrix, we have shown that the superconducting proximity effect (which is usually invoked to explain the behavior of bilayers and multilayers of superconductors and normal metals) can be suitably modified to explain the observed dependence of the $T_c$ on the component fraction of the superconducting phase.

### 6.2 Future directions

We have studied the size dependence of the superconducting properties of two elemental superconductors in detail. From the variation of the electron phonon coupling strength with particle size we could see that the mechanism influencing the superconducting properties in Nb and Pb were quite different. Hence, it will be interesting to see how the coupling strength changes with particle size in the weak coupling superconductors like Sn, Al etc. Though there are measurements of $T_c$ in these systems as a function of particle size, there are very few
systematic studies on the variation of coupling strengths with particle size as determined from a careful measurement of the superconducting energy gap. In future, we would like to carry out a systematic study of the variation in the superconducting properties in the weak coupling superconductors such as Sn.

Our studies on Pb indicate that there is an increase in the electron phonon coupling strengths with reduction in particle size though there is only a small (~10%) change in $T_c$. In future we would like to obtain a quantitative estimate of the coupling strength. This can be obtained from the tunneling data which gives the superconducting density of states. By inverting the tunneling data (by a technique suggested by McMillan and Rowell\textsuperscript{1} it is possible to get the complete phonon spectrum which can show the occurrence of soft phonon modes in small particles. Furthermore, it is possible to eventually calculate the electron phonon coupling strengths. This calculation may further explain the reason for the observed small change in $T_c$ (~10%) with reduction in particle size, in spite of showing an increased electron phonon coupling strength. For this calculation, tunneling spectroscopy has to be carried in the Al/Al$_2$O$_3$/Pb tunnel junctions at very low temperatures (at 300 mK, to reduce the effect of thermal smearing). This would require the fabrication of fresh tunnel junctions with the nanostructured Pb films (as the previous Al/Al$_2$O$_3$/Pb tunnel junctions are unusable after thermal cycling).

In the nanostructured Nb films, we had carried out electrical transport measurements to ascertain if they were forming a random network of Josephson junctions. However, to get the proper estimate of the critical current density, $J_C$, micro bridges with a well defined geometry needs to be made by lithographic techniques on the nanostructured Nb films. In future we would like to carry on these measurements and hence, get the temperature variation of $J_C$ and see if it follows the classic Ambegaokar-Baratoff\textsuperscript{2} relations characteristic in granular superconductors.

In future, we also plan to extend our studies on 1-dimensional nanowires of Pb and Sn grown by electrodeposition through porous alumina templates. There are very few reports on the evolution of superconductivity in 1D nanowires of diameters less than 10nm. We hope to explore this by studying single superconducting nanowires of diameters less than 20nm through electrical transport measurements where the contacts will be made by electron beam lithography.

\textsuperscript{1} W. L. McMillan and J. M. Rowell, Phys. Rev. Lett. \textbf{14} 108 (1965)
APPENDIX
In addition to the main work related to my thesis, I participated in several problems in collaboration with colleagues from other departments. Two of the problems studied have resulted in publications in peer reviewed journals. I will briefly describe the main work done by me in these two areas and attach the published manuscripts for details.

Appendix 1

Size effects on the local magnetism and Kondo behavior of isolated Fe impurities in nanocrystalline metallic hosts

The aim of this work was to study size effects on the local magnetic behaviour of dilute magnetic (Fe) impurities when implanted in metallic hosts (both bulk and nanocrystalline) of Cu and Ag. The Cu and Ag nanoparticles were synthesized by DC magnetron sputtering onto Cu plates with the substrate kept at liquid nitrogen temperature. The nanocrystalline powder was removed from the substrate and pressed into pellets of 6mm diameter. Fe was implanted in these pellets (both bulk and nanocrystalline) in the Pelletron Accelerator Facility at TIFR and the hyperfine interactions were studied by the $\gamma$-ray perturbed angular distribution (TDPAD) technique. Our results showed a decrease in the Kondo temperature in the Cu nanoparticles compared to bulk Cu. In Ag, on the other hand, we observed an increase in the local Kondo temperature in the nanoparticle pressed pellets compared to that of the bulk. To explain these results, magnetization measurements were carried out in a MPMS SQUID magnetometer for the Cu and Ag bulk and nanoparticle samples. From the bulk measurements we noticed that the nanoparticle samples showed an increase in the Pauli susceptibility compared to their bulk counterparts. These results indicated that the host spin polarization influenced the Kondo behaviour of the isolated Fe impurities.

In this work, the synthesis of the bulk and nanoparticle samples of Cu and Ag, their structural characterization and magnetization measurements in MPMS SQUID were carried out by me. The Fe implantation and the TDPAD measurements and analysis were done by Prof. S.N. Mishra of the Department of Nuclear and Atomic Physics, TIFR.

The published manuscript is attached.
Size effects on the local magnetism and Kondo behavior of isolated Fe impurities in nanocrystalline metallic hosts

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Measurements of the local susceptibility and 3d spin relaxation rate of single Fe impurities embedded in Cu and Ag nanoparticles indicate a strong influence of lattice size on the magnetism and Kondo temperature, $T_K$. With a reduction in particle size, $T_K$ increases in nanocrystalline Ag, but decreases in nanocrystalline Cu. Supported by macroscopic host susceptibility data that indicate enhanced Pauli paramagnetism for Cu nanoparticles, we suggest that size-induced host spin polarization strongly influences the Kondo behavior.

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Local magnetism of $3d$ impurities in nonmagnetic metallic hosts is a subject of intense experimental and theoretical investigations. A key problem is the study of Kondo effect arising from antiferromagnetic exchange interaction between the impurity moment and host-conduction electrons leading to moment instability below a characteristic temperature $T_K$. While extensive studies have been carried out for many $d$ and $f$ impurities in bulk metallic hosts, little information is available on the Kondo behavior of single magnetic impurities in nanocrystalline materials. Recently resistivity studies in thin films and nanowires of Au(Fe), Cu(Cr), and Cu(Fe) alloys have revealed the suppression of Kondo interaction below a critical thickness and width. The results, initially interpreted as being due to confinement of the Kondo screened electron cloud, were later shown to arise from size-induced magnetic anisotropy effects.

Nanocrystalline materials have recently attracted considerable attention due to their novel physicochemical properties and practical applications. Since the energy bands of a bulk solid split into discrete levels with a reduction in size, physical properties of nanoparticles show marked differences from those of bulk materials. Size dependent changes in structural, electronic, and magnetic properties have been observed in many metals. In this context, one can ask: Does a finite host lattice size affect single impurity local magnetism? If so, how does it influence spin fluctuation and Kondo interaction? We approach this problem by studying the local magnetism and 3d spin dynamics of isolated Fe impurities in nanocrystalline Cu and Ag hosts using the γ-ray perturbed angular distribution (TDPAD) technique. Fe in noble metal nanoparticles is a typical local moment system for which $T_K$ values have been measured accurately. By comparing the magnetic behavior of Fe in bulk and nanocrystalline noble metals, we can obtain crucial information on finite size effects on local moments and Kondo interaction. Preliminary results for Fe in Ag nanoparticles have been reported earlier.

In this Brief Report we show that the local susceptibility and 3d spin dynamics of $^{54}$Fe implanted in nanocrystalline Cu and Ag reveal a strong influence of particle size on the magnetic moment of Fe, particularly on the Kondo temperature $T_K$. While size reduction in Ag leads to enhancement of $T_K$, data on Cu nanoparticles indicate a drastic suppression of the Kondo interaction. With the help of macroscopic susceptibility data for the host matrix, which reflects an enhanced Pauli paramagnetism for nanocrystalline Cu, we show that the sign and strength of the size-induced spin polarization of host conduction band electrons play an important role on the magnetism and Kondo behavior of Fe in nanocrystalline materials.

The TDPAD experiments were carried out at the Pelletron Accelerator Facility at TIFR. The magnetic response of Fe atoms in the hosts of interest was studied via hyperfine interaction of the $10^+$ isomeric state of the $^{54}$Fe nucleus ($\tau_{1/2} = 360$ ns, $g_\gamma = 0.728$) produced by the reaction $^{12}$C($^3$He,$p2n$)$^{54}$Fe. The recoiling $^{54}$Fe nuclei were implanted deep (~1 to 2 μm) inside the host matrix at concentrations well below 1 ppm. Measurements were performed within a time window of 10 ns to 2 μs immediately after implantation. These experimental conditions ensure negligible impurity-impurity interaction and the results reflect the magnetic response of a truly isolated impurity. Observations were made in the temperature range of 17–300 K and applied magnetic field of 2 T using γ-ray detectors placed at ±45° with respect to the beam direction. Further details on the TDPAD method can be found in Ref. 8.

Nanocrystalline samples of Cu and Ag were prepared by dc magnetron sputtering from a target of 99.99% pure metal onto thin (0.05 mm) Al or Cu substrates cooled to ~100 K. The sputtering was carried out in flowing argon at a pressure of ~100–200 mTorr. The deposition thickness was ~5 mg/cm$^2$. We also prepared a thin disk of the nanocrystalline sample by scraping and mildly pressing the sputter-deposited particles. The samples were characterized by x-ray diffraction and electron microscopy. Details of nanoparticle synthesis and characterization are available in Ref. 9. The mean crystallographic domain size “d” was calculated from the instrument-corrected Scherrer broadening of the [111] reflection of Cu/Ag using the formula $d = 0.94\lambda / B \cos \theta$, where $\lambda$ is the x-ray wavelength, $B$ is full width at half maximum of the peak, and $\theta$ is the Bragg angle. The sputtering targets were 99.99% pure Cu and 99.99% pure Ag.

Figure 1 shows typical spin rotation spectra, $R(t)$, and their Fourier transforms for $^{54}$Fe in bulk and nanocrystalline Cu and Ag hosts. All the spectra exhibit a single frequency
FIG. 1. Spin rotation spectra, $R(t)$ (left panel) and their Fourier transforms (right panel) for $^{57}$Fe in bulk and nanocrystalline Cu and Ag hosts.

with high anisotropy suggesting that the implanted Fe atoms occupy a well-defined lattice site that is likely to be substitutional. The narrow frequency distribution also indicates that a large majority of the Fe atoms are embedded within the nanoparticles rather than in the grain boundaries. The spectra were fitted to the function:

$$B(t) = (3/4)A_{22} \exp(-t/\tau_0) \sin[2(\omega_t t - \phi)]$$

where the Larmor frequency $\omega_t$ and the nuclear relaxation time $\tau_0$. The local susceptibility of Fe, $\chi_{loc} = \beta^{-1}$ calculated from $\omega_t \tau_0 = h^{-1} g_N \mu_B B_{ext} \times \beta$ is shown in Fig. 2. In both bulk and nanocrystalline samples, $\chi_{loc}$ shows a strong temperature dependence, which indicates a large local moment for Fe.

To examine the effect of lattice size on the local magnetism of Fe, we now compare the $\beta(T)$ in nanocrystalline and bulk hosts. The data (Fig. 2) clearly show that the magnetic properties of Fe embedded in nanocrystalline metals differ significantly from that in the corresponding bulk metal. Further, the size-induced change in $\beta(T)$ relative to bulk hosts is different for Cu and Ag. While $\chi_{loc}(T)$ is reduced in nano-Ag, it shows a substantial increase in nano-Cu. The $\beta(T)$ could be fitted to the Curie-Weiss law:

$$\beta - 1 = C/(T + T_K)$$

where the Curie constant $C = g_\mu_B (S+1) B(0)/3k_B$ provides a measure of the Fe magnetic moment $\mu_{Fe} = gS$ and $T_K$ is the Kondo temperature. Here, $B(0)$ is the magnetic hyperfine field at $T = 0$ K and $S_{imp} + S_{host}$ is the net spin due to the impurity atom ($S_{imp}$) and possible spin polarization of host conduction electrons ($S_{host}$). The derived values for $C$ and $T_K$ are summarized in Table I. The $\mu_{Fe}$ estimated using $B(0) = -46$ kG for Ag and $B(0) = -100$ kG for Cu Refs. 11 and 12 are shown in Table I. For Fe in bulk Cu and Ag the magnetic moment $\mu_{Fe} \sim 3 \mu_B$ corresponds to impurity spin $S_{imp} = 3/2$ which agrees with earlier results. In nano-Ag, the $\mu_{Fe}$ is slightly smaller than its value in the bulk metal. These results suggest that the host spin polarization in bulk Cu and Ag is negligible, and that the $S_{host}$ for Fe in nano-Ag is small and negative. In contrast, the Curie constant observed for nano-Cu yields $\mu_{Fe} = 5.82 \mu_B$ for 7 nm and 4.66 $\mu_B$ for 30 nm. Taking $B(0)$ to be as high as $-140$ kG, the Fe moment in nano-Cu (7 nm) comes out to be $3.59 \mu_B$ which is still much larger than the value of $\mu_{Fe} = 2.9 \mu_B$ in bulk Cu. This clearly indicates a large ferromagnetic spin polarization ($S_{host}$) for nano-Cu. We point out that measurements in CuO and Cu$_2$O show nonmagnetic behavior of Fe with $\beta \sim 1.0$ which assures us that the results observed in the nanocrystalline samples cannot be ascribed to extrinsic impurities but are genuine lattice size effects.

Figure 3 shows the temperature dependence of the macroscopic magnetic susceptibility ($\chi$) of the unimplanted bulk and nanoparticle samples measured using a superconducting quantum interference device magnetometer. Clearly, the nanocrystalline samples show a much higher susceptibility than their bulk counterparts. In particular, nano-Cu shows a strongly enhanced, Pauli-type susceptibility with a magnitude comparable to that for exchange enhanced metals such as Pd and Pt. Since $\chi_{Fe} \sim \mu_B^2 g(\varepsilon_F)$, the nano-Cu data imply a high density of states at the Fermi energy, $g(\varepsilon_F) \sim 1.7$ states/eV atom, probably due to a large contribution from the Cu $d$-band electrons which move closer to the

![Table I](image)

**Table I. Summary of Curie constant, Kondo temperature $T_K$, and magnetic moment $\mu_{Fe}$ for Fe in bulk and nanocrystalline Cu and Ag.**

<table>
<thead>
<tr>
<th>Host</th>
<th>Curie constant $C$ (K)</th>
<th>$T_K$ (K)</th>
<th>$\mu_{Fe}$ ($\mu_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(bulk)</td>
<td>$-11.0(10)$</td>
<td>25.5(15)</td>
<td>2.92</td>
</tr>
<tr>
<td>Cu(nano: 7 nm)</td>
<td>$-17.5(10)$</td>
<td>8.5(15)</td>
<td>5.82</td>
</tr>
<tr>
<td>Cu(nano: 30 nm)</td>
<td>$-14.9(10)$</td>
<td>16.6(15)</td>
<td>4.66</td>
</tr>
<tr>
<td>Ag(bulk)</td>
<td>$-5.2(5)$</td>
<td>2.3(8)</td>
<td>3.05</td>
</tr>
<tr>
<td>Ag(nano: 19 nm)</td>
<td>$-5.0(10)$</td>
<td>17.2(8)</td>
<td>2.86</td>
</tr>
</tbody>
</table>

$^a$Fe moment estimated using the maximum value of $B(0) = -14$ T (Ref. 11).
to the in its position due to size reduction does not contribute much.

Compared to bulk Cu, the strongly damped Korringa-like temperature dependence of host conduction electrons plays a crucial role in the Kondo behavior of Fe.

Next we discuss the spin fluctuation of Fe in nanocrystalline Cu and Ag hosts which scales with the Kondo temperature $T_K$ obtained from the Curie-Weiss fitting of the local susceptibility data. The $\beta(T)$ response of Fe in nano-Ag yields a Kondo temperature $T_K \sim 17$ K which is substantially higher than the value $T_K=2$ K observed in bulk Ag. On the other hand, compared to $T_K \sim 26$ K for Fe in bulk Cu, the $\beta(T)$ data in nano-Cu yields a significantly smaller $T_K \sim 8$ K for 7 nm concomitant to the substantial increase of the Curie constant ($\sim 17.5$ K) discussed earlier. The high $T_K$ of Fe in nano-Ag suggests a large enhancement of the Fe-3d spin fluctuation rate, $\tau_\nu^{-1}$. In contrast, our data for nano-Cu indicate a drastic suppression in $\tau_\nu^{-1}$. A reduction of $\tau_\nu^{-1}$ in nano-Cu is also visible from the $\tau_\nu$ data shown in Fig. 4. Compared to bulk Cu, the strongly damped $R(t)$ spectra in nano-Cu reflects a significantly lower value of $\tau_\nu$ which in turn implies a sharp reduction of $\tau_\nu^{-1}$. Using $\tau_\nu^{-1} = 4\pi k_B^{-1}|Jp(E_F)|^2/\Delta_g T$, the data yield $Jp(E_F) \sim 0.06$ for nano-Cu as compared to $\sim 0.11$ in the bulk metal. From the trend of Fe magnetism in bulk and nanocrystalline materials, particularly the observation of $S_{\text{host}}$ and the concomitant decrease of $T_K$ in nano-Cu, we believe that the induced spin polarization of the host conduction band electrons leading to a ferromagnetic coupling with the Fe moment can effectively reduce $Jp(E_F)$ and result in lower spin fluctuation and dimished $T_K$. The suppression of Kondo interaction observed for Fe in nano-Cu is consistent with the basic features of the results of thin films and nanowires, though the disagreement with respect to the size dependence of $T_K$ needs to be investigated further.

The magnetic behavior of Fe in nanocrystalline Cu shows a striking similarity with that of 3d impurities in exchange-enhanced d-band metals such as Pd and Pt, in which the ferromagnetic spin polarization of the host d-band electrons leads to giant moments with extremely small $T_K$. Suppression of the Kondo temperature due to ferromagnetic host spin polarization is also observed for 4d impurities in different metallic hosts. It is quite plausible that the ferromagnetic spin polarization causes a strong interatomic interaction between the impurity and host conduction electrons and competes with the usual antiferromagnetic exchange interaction, thereby successfully suppressing spin fluctuation and diminishing $T_K$. This model is also consistent with recent theoretical calculations, which predict that the ferromagnetic interaction between the impurity and host conduction electrons drastically reduces the Kondo resonance near $E_F$.

In conclusion, we have studied the local magnetism and Kondo behavior of isolated Fe impurities in nanocrystalline noble metals by the TDPAD method. A comparison of the local susceptibility and 3d spin dynamics of Fe in nanocrystalline Cu and Ag with similar data from the respective bulk metals reveals a strong influence of particle size on the Fe Kondo interaction in nano-Cu while there is a large increase of $T_K$ in nano-Ag? The Kondo temperature of Fe expressed as $T_K \sim T_F [1/[\exp(-1/\rho(E_F))]$ can increase or decrease, depending on the magnitude of the effective antiferromagnetic exchange interaction $Jp(E_F)$ between Fe-3d and host conduction electrons. Here, $J \sim -\gamma^2_{kd} / \epsilon_g$ is the exchange constant which depends on the hybridization strength $\gamma_{kd}$ and the position of the Fe-3d level ($\epsilon_g$) with respect to the Fermi energy $E_F$, and $\rho(E_F)$ is the density of states (DOS) at $E_F$. As discussed earlier, the DOS for the nanocrystalline samples is expected to be larger than its corresponding bulk value. The observed magnetic behavior of Fe in nano-Ag with $T_K = 17$ K is consistent with such a model. The higher $T_K$ of Fe in nano-Ag is also supported by recent Mössbauer data. An increase in $T_K$ has also been reported for Ce in nanosized (Ce,Al) alloys. Extrapolating this trend and assuming $J$ to be antiferromagnetic, one expects Fe in nano-Cu to be nonmagnetic with $T_K \gg 10^3$ K. Instead, the $T_K$ for Fe in 7 nm-Cu turns out to be $\sim 8$ K, suggesting a sharp decrease in the effective exchange interaction strength $Jp(E_F)$. This is confirmed from our spin relaxation data (Fig. 4). Using $\tau_\nu^{-1} = 4\pi k_B^{-1}|Jp(E_F)|^2/\Delta_g T$, the data yield $Jp(E_F) \sim 0.06$ for nano-Cu as compared to $\sim 0.11$ in the bulk metal. From the trend of Fe magnetism in bulk and nanocrystalline materials, particularly the observation of large $S_{\text{host}}$ and the concomitant decrease of $T_K$ in nano-Cu, we believe that the induced spin polarization of the host conduction band electrons leading to a ferromagnetic coupling with the Fe moment can effectively reduce $Jp(E_F)$ and result in lower spin fluctuation and diminished $T_K$. The suppression of Kondo interaction observed for Fe in nano-Cu is consistent with the basic features of the results of thin films and nanowires, though the disagreement with respect to the size dependence of $T_K$ needs to be investigated further.

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FIG. 3. Temperature dependence of macroscopic susceptibility for unimplanted bulk and nanocrystalline Cu and Ag.

FIG. 4. Nuclear relaxation time $\tau_\nu$ as a function of temperature for $^{57}$Fe in bulk (open symbols) and nanocrystalline (closed symbols) Cu and Ag. The linear dependence of $\tau_\nu$ with $T$ (solid lines) is indicative of the Korringa-like relaxation process.
magnetism, and especially the Kondo temperature, $T_K$. While the magnetism of Fe in nano-Ag, with a high $T_K$, is consistent with enhanced antiferromagnetic $s$-$d$ interaction, we have shown that the magnetism and Kondo temperature of Fe in nano-Cu are strongly influenced by the ferromagnetic spin polarization of the conduction band electrons of the host. The interpretation of our results provide an important basis for the understanding of Kondo interaction of magnetic impurities in metallic hosts including nanocrystalline materials. This also illustrates the important common role of ferromagnetic host spin polarization on the spin fluctuation and the Kondo behavior of $3d$ and $4d$ magnetic impurities in bulk metals as well as nanosized solids.

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14 The value $B(0)=-140$ kG for Fe in Cu is estimated using spin and orbital moments from Ref. 11 and the hyperfine field constants $a_{CP}=-12$ T/$\mu_B$ and $a_{orb}=+50$ T/$\mu_B$ for core and orbital contributions, and valence hyperfine field $B_{val}=+17$ T.
17 Spin relaxation rate $\tau^{-1}_J$ of Fe can be extracted from $\tau^{-1}_J=2(g_S\mu_N/h)B(0)^2(S+1)^{-1}\tau_N$ (Ref. 4).
Appendix 2

**Hot ion generation from nanostructured surfaces under intense, femtosecond laser irradiation**

The aim of this work was to study the effect of nanostructured surfaces on the emission of ions and electrons from intense femtosecond laser produced plasma. A polished Cu target was half coated with Cu nanoparticles (15-20nm particle size) deposited by DC magnetron sputtering. The target was bombarded with focused 50 fs, p-polarized laser pulses (1-6 mJ) from a 806 nm, 10Hz, Ti-Saphhire laser (THALES LASER, ALPHA 10). The hard x-ray spectra in the 20 – 200 keV range were measured using a calibrated NaI(Tl) scintillation detector coupled with a multichannel analyzer. The ions emitted normal to the target surface was detected by a channel electron multiplier (CEM) and a Faraday cup (FC) arrangement. Electrons from optically polished copper targets coated with copper nanoparticles (CuNP) were observed to be “hotter” than those from uncoated polished targets. Also a nearly two-fold enhancement was observed for ions in the range 14-74 keV. However, ion yields decreased by a factor of 2 in the 74-2000 keV range. Our results further showed that the total ion yield measured was greater from the CuNP targets than those from polished Cu targets when measured with a large area Faraday Cup indicating greater beam divergence due to surface modulations.

In this work, the sputter deposition of Cu nanoparticles on polished Cu targets, and its structural characterization were carried out by me while the laser-matter interactions were studied in Prof. G. Ravindra Kumar’s group at the Department of Nuclear and Atomic Physics, TIFR.

The published manuscript has been attached.
Hot ion generation from nanostructured surfaces under intense femtosecond laser irradiation


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Studies of ion emission from nanostructured metallic surfaces excited by intense (0.5–6.3 × 10^16 W cm^{-2}) 50 fs laser demonstrate that “hotter” electrons need not to give rise hotter ions, contrary to conventional expectation. Such surfaces produce twice as many ions as planar surfaces in the moderate energy regime (16–75 keV), but their yield in the higher energy range (75–2000 keV) is substantially lower. Surface modulations also influence ion beam divergence.

The advent of ultrashort, intense solid state lasers has enabled the production of good quality particle beams with high energy and brightness. The physics of these ultrashort duration beams is very interesting in terms of their potentials in areas of fundamental research and technological applications. When an intense laser pulse interacts with the target, rapid ionization occurs at the beginning of the laser pulse and the electrons in the plasma then absorb the light by a variety of mechanisms such as resonance absorption. The electrons which gain energy through these mechanisms form a distinct “hot” bunch well separated in energy from the colder electrons in the bulk plasma. Ion acceleration occurs when the hot plasma expands and an electric field is created due to charge separation. Ion acceleration in plasma with multiple electron temperatures has been explored in simulations and in different experimental situations. Many studies have reported particle production from solid, cluster, and microdroplet plasmas. Efficient coupling of laser energy into the short-lived plasma thus plays a crucial role in ion generation. Enhanced coupling of laser energy (up to 80%) to the plasma has been achieved by the creation of a preplasma before the arrival of the main pulse, by modifying target composition in the case of clusters and by the introduction of sublaser wavelength surface modulations on solid targets. A more pertinent question is whether the optimization of the target properties will work for enhanced generation of hot electrons as well as higher energy ions. This is based on the expectation that hotter electrons should lead to hotter ions. In this letter, we report the influence of surface modulations on the characteristics of the ions emitted by a femtosecond laser produced plasma. Specifically, we present results for targets coated with copper nanoparticles.

The experiment is performed with focused 50 fs, p-polarized laser pulses (1–10 mJ) from a 806 nm, 10 Hz, Ti:sapphire laser (Thales Laser, Alpha 10). The target is a polished copper block (50×50×5 mm^3), half of which is coated with a thick layer of copper nanoparticles (CuNP) with an average diameter of 15 nm. The nanoparticles are deposited using high-pressure dc magnetron sputtering technique. The crystallite size is determined from the Scherrer broadening of the Cu [111] x-ray diffraction line. The partially coated target ensures exactly the same laser and detector conditions for measurements from the coated and uncoated portions. The typical coating thickness of the NPs is about 0.2 μm which is large compared to the optical skin depth of a few nanometers. The base pressure of the experimental chamber is 10^{-6} torr. The target is scanned across the laser beam for each shot. The laser is focused by a gold coated off axis parabolic mirror, in an f/4 focusing geometry with a spot size (full width at half maximum) of 10 μm, giving peak intensities in the (0.5–6.3) × 10^16 W cm^{-2} range.

The energy of the ions emitted normal to the target surface is measured using the time of flight (TOF) technique and the ions are detected by a channel electron multiplier, kept at a distance of 97 cm from the focal spot, along the axis of the TOF, viewing the plasma plume directly with a solid angle of 26 msr. Measurements of the ion charge state distribution have been carried out with a Thomson parabola spectrometer (TPS), into which the ions enter through a 500 μm aperture. The ions are detected by a 40 mm micro-channel plate coupled to a phosphor screen. The signal from the phosphor screen is imaged with a charge-coupled device camera. An ^{241}Am α-particle source (energy of 5.4 MeV) with known emittance is used to calibrate the setup. Four annular Faraday cups (FCs) placed at different angles (θ) of 4.6°, 8.1°, 11.6°, and 16.6° with respect to the axis of the time of flight spectrometer are used to measure the total flux as well as the divergence of the ion beam [Fig. 3(a)].

The hard x-ray spectra in the 20–200 keV range are measured using a calibrated NaI(Tl) detector. The bremsstrahlung spectra from both the polished Cu and CuNP coated surface measured at the input intensity of 3 × 10^{16} W cm^{-2} show a clear enhancement in the hard x-ray spectrum. The hot electron distribution in Cu plasma is a single Maxwellian with a temperature of 9.3±1.1 keV, whereas the CuNP plasma shows two temperatures: 9.5±1.7 and 33.9±6.4 keV, confirming that the enhanced coupling of laser energy into NP coated surface is facilitated by the nanoparticle coating in tune with the previous results.

Measured energy spectra [where n(E) is the number of ions emitted within the energy range of E to E+dE] of the ions obtained from the TOF spectrometer is shown in Fig. 1. A clear difference in the ion energy spectrum is observed from the NP coated surface compared to that from polished Cu. The polished Cu surface, at lower input intensities,
it gradually decreases to approximately 1.5 times, indicating that the yield from CuNP coated surfaces is approximately four times that from the polished Cu surfaces at laser energies, corresponding to the intensities in the range of 16–75 keV, indicating energy dependent divergence of the ion beam.

Figure 2 shows the total ion yield as well as the divergence of the ion beam, measured using multiple FCs as described above. The inset in Fig. 2 shows the ratio of the total x-ray yield from CuNP and Cu surfaces with laser energy. The arrow (↑) indicates the convergence of both the data sets at 5.5 mJ after the destruction of NPs.

At all the incident laser energies used in our studies, the maximum ion energy as well as the average energy from the CuNP coated target is lower than that from the polished Cu surfaces over the input laser energy is shown in Fig. 2. The cutoff ion energy from the Cu plasma increases from 1.58 to 3.80 MeV as the laser intensity increases from 1.0-2.0 MeV for CuNP plasma indicating a reduction of around 50% in the highest ion energy. Above an intensity of 3.2×10^16 W cm^−2, the cutoff ion energy from the CuNP plasma is almost the same as that for Cu. A similar behavior is observed in the ratio of total x-ray yield from CuNP coated surfaces to that from the polished Cu surface at different input laser energies, corresponding to the intensities in the range of (0.9–3.6)×10^16 W cm^−2 (inset of Fig. 2). The yield from NPs is approximately four times that from the polished Cu surface, up to an intensity of 2.5×10^16 W cm^−2 after which it gradually decreases to approximately 1.5 times, indicating the damage to the NP coating, in agreement with our previous results.15

We also examined the possibility that, protons could be preferentially enhanced in their energy in the nanoparticle coated target. This is ruled out by the time of flight spectra and TPS traces. This clearly shows that though more laser energy is coupled to the NP coated surface than the polished surface and generates hotter electrons, the ion emission from the NP coated surface gets enhanced only in an intermediate regime (16–75 keV) and the highest ion energy decreases for the NP coated surface. This is in contradiction to the usual expectation that the generation of hotter electrons should lead to hotter ion emission.6 To get the overall ion yield as well as the divergence of the ion beam, we measured the ion currents using multiple FCs as described above. The inset in Fig. 2 shows the total ion flux collected by the FC placed at an angle of 8°. Linear fits to the data have different slopes, indicating energy dependent divergence of the ion beam. This is reinforced by Fig. 3(b) (inset), which shows the ratio of the total charge accumulated by each FC (i.e., the angular spread) at different laser energies. It is therefore evident that the divergence of the ion beam from the CuNP plasma is larger than that from polished Cu.

To look at our results from a comparative perspective, let us first consider the ion emission from the polished (unstructured) copper targets. As per the standard conceptual picture, the hot electrons produced by the intense laser, together with the colder electrons form a two-temperature plasma.5 The two-temperature plasma gives rise to the formation of a sheath layer across which the ions are accelerated and emerge as the hot ions.5 The field developed across the sheath is $E_{\text{ac}} = k_BT/e\left[\max(L_n,\lambda_D)\right]$, where $L_n$ is the local scale length of the expanding plasma and $\lambda_D$ is the Debye length.2 The model assumes isothermal expansion which may not be strictly valid, but the general features are well reproduced even under this approximation. The critical point is that hotter electrons are expected to generate hotter ions in
optimization of each signal from the plasma requires an understanding of the actual dynamics of the process. In our case, hot electron generation is enhanced by the local field enhancements which increase the effective light intensity. This process takes place on the time scale of the laser pulse (tens of femtoseconds). The ion acceleration, however, depends on a subsequent process, namely, the plasma expansion and energy exchange. We believe that this is significantly modified by the same nanoparticles in a counteracting manner and leads to enhanced number of ions in the intermediate range (16–75 keV) and reduces the high energy ions above 75 keV.

In summary, we have presented a comparison of the ion energy and flux measurements from polished targets and those from targets coated by copper nanoparticles. A significant and surprising observation is that the nanoparticle coated targets give hotter electrons but colder ions. The enhancement of x-ray emission and selective suppression of high energy ion emission can prove very useful in designing brighter hard x-ray sources with reduced damage from ion debris. The total flux of the emitted ion beam measured at different angles indicates the energy dependent divergence of the ion beam from the nanoparticle coated surfaces resulting in the colder ions. We expect that this result will help in the design of femtosecond laser driven x-ray and ion sources. More experiments with variations in nanoparticle type, shape, and size are in progress to better understand the physics of ion emission.