# Single Crystal Growth of V-doped NbSe<sub>2</sub> Superconductor and Physical Properties Measurements

**M.Sc.** Thesis

By

Akshay Kumar Verma



### **DISCIPLINE OF PHYSICS**

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# Single Crystal Growth of V-doped NbSe<sub>2</sub> Superconductor and Physical Properties Measurements

### A THESIS

Submitted in partial fulfilment of the requirements for the award of the degree

of

**Master of Science** 

by

### **AKSHAY KUMAR VERMA**



### **DISCIPLINE OF PHYSICS**

## INDIAN INSTITUTE OF TECHNOLOGY INDORE

**JUNE 2017** 



# INDIAN INSTITUTE OF TECHNOLOGY INDORE CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "Single Crystal Growth of V-doped NbSe<sub>2</sub> Superconductor and Physical Properties Measurements" in the partial fulfilment of the requirements for the award of the degree of MASTER OF SCIENCE and submitted in the DISCIPLINE OF PHYSICS, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from July-2016 to June-2017 under the supervision of Dr. Parasharam M. Shirage, Associate Professor.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

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Thank you all!

Dedicated To



### Abstract

In this work we represent the effect of V atoms in the superconducting properties of NbSe<sub>2</sub> single crystal. The V atom is successfully intercalated in the layered structure of NbSe<sub>2</sub> and is stable at the low concentration of V atoms. The XRD pattern of V-NbSe<sub>2</sub> single crystal shows the high purity of the samples along with the highly directional alignment of the planes along the *c*-axis. The Rietveld refinement of the XRD data of NbSe2 and V-NbSe2 superconductors have been done with FullProf software. The lattice parameters which were extracted after refinement show a decrease in lattice constants and volume of NbSe<sub>2</sub> with the increasing V concentration, that confirms the intercalation of V atoms in the interlayer spacing of NbSe<sub>2</sub>. The critical temperature  $(T_c)$  of NbSe<sub>2</sub> decreases with increasing the V concentration, which might be due to change of band structure and an extra influence due to the attractive electron coupling through an electron excitation interaction. The magnetization measurements have been used to determine the effect of V impurities on the different parameters such as upper critical field  $(H_{c2})$ , irreversible field  $(H_{irr})$ , coherence length, critical current density  $(J_c)$  and the pinning mechanism in NbSe<sub>2</sub> single crystals. The upper critical field decreases with increasing V concentration in NbSe<sub>2</sub>. The  $J_c$  values were calculated using the Critical Bean Model. Upon increasing the concentration of V impurities, the superconducting critical current density  $(J_c)$  has been enhanced appreciably compared to the pure NbSe<sub>2</sub>. We obtained  $J_c$  (0) (2K) ~ 541084, 389668, 841546 Acm<sup>-2</sup> respectively for V<sub>0.0007</sub>NbSe<sub>2</sub>, V<sub>0.001</sub>NbSe<sub>2</sub>, V<sub>0.0015</sub>NbSe<sub>2</sub> samples and decreases with increasing temperature and magnetic field, indicating the presence of weak pinning phenomena occurring at the surrounding of the impurities which act as pinning point centers. The disorder created in NbSe<sub>2</sub> single crystal due to V impurity shows  $\delta l$  flux pinning, stating that defects are small and point sized. A low value of  $h_{max}$  in the studied single crystals of V-NbSe<sub>2</sub> suggests that pinning in V-NbSe<sub>2</sub> superconductor is due to the presence of a large density defect centres. Furthermore, the field dependence behaviour of the pinning force density of Vincorporated NbSe<sub>2</sub> represents the existence of both surface pinning and the

point pinning effect. We figured the flux pinning force density and shown the existence of point core pinning of the normal centres in the low field regime. The present outcomes are significant in understanding of the layered NbSe<sub>2</sub> superconductors and its applications.

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## Acronyms

$T_c$	Critical transition temperature
CDW	Charge density wave
RRR	Residual resistance ratio
H <sub>c1</sub>	Lower critical field
H <sub>c2</sub>	Upper critical field
H <sub>irr</sub>	Irreversible field
J <sub>c</sub>	Critical current density
ZC	Field cooled
ZFC	Zero field cooled
SQUID	Superconducting quantum interference device
VSM	Vibrating sample magnetometer
CVT	Chemical vapour transport
XRD	X-ray diffraction
SEM	Scanning electron microscopy

# **Chapter 1**

# **1.1 Introduction to Superconductivity**

### **1.1.1 History of Superconductivity**

The quest for low temperature started in 1800 when Charles & Gay Lussac (from P-T relationship) proposed the lowest temperature -273°C. The period of low temperature physics was well-advanced after 1908 when Onnes liquefied helium, which boils at 4.2K at standard pressure. In 1911, Dutch physicist Heike Kamerlingh Onnes, first observed that the resistance of mercury (Hg) sample dropped sharply at 4.15K to unmeasurable amount [1]. Onnes choose names "Superconductivity" for the new phenomenon of perfect conductivity.

The next great achievement in understanding superconductivity occurred with the discovery of expulsion of magnetic field by Meissner and Ochsenfeld in 1933[2]. Significant advances were made toward such a hypothesis of superconductivity with advancement of London theory [3] in 1935 and Ginzburg-Landau theory [4] in 1950. The first widely accepted theoretical understanding of superconductivity was recommended in 1957 by John Bardeen, Leon Cooper, and John Schrieffer [5], called BCS theory for which they were awarded Nobel Prize in 1972.

A veritable leap forward was accomplished in high temperature superconductivity study with the discovery of superconductivity in the cuprates in 1986 [6]. These ceramic superconductors have higher  $T_c$  than 77K in Yba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> [7] (93K). The highest value of  $T_c$  was observed in HgBa<sub>2</sub>CaCu<sub>2</sub>O<sub>6-x</sub> [8] at 133K at ambient pressure. Another period started in superconductivity when research started in Fe-based compound showing superconductivity at  $T_c$  of 26K. The discovery of superconductivity in most common ferromagnetic atom Fe was opened a new path of research towards the understanding the mechanism behind these high temperature superconductors. Further, many superconductors were discovered in the subsequent years.

### **1.2 Theory of Superconductivity**

### **1.2.1 Zero Resistance and Perfect Diamagnetism**

The perfect conductivity (zero resistance) is the first hallmark for the superconductors (fig. 1.1). The resistance of certain materials decreases to zero below certain temperature called critical temperature ( $T_c$ ). In 1933 Meissner and Ochsenfeld noted that magnetic field is expelled from the interior of the superconductors, B = 0, stating that they are perfect diamagnets<sup>3</sup>. Superconductor expels magnetic fields by forming surface currents. Surface currents induced on superconductor, generate magnetic field that precisely cancels the externally applied field inside superconductor. At a point when a material is cooled below  $T_c$  and then



Figure 1.1 Plot of resistance versus temperature of normal metal and superconductor.

magnetic field is applied, current will be induced in order to have an unaltered magnetic field in the inside of the material (fig. 1.2) and when temperature is increased above  $T_c$ , magnetic field enters through the

material. But when first we apply magnetic field and then cool below  $T_c$  then again the magnetic field is expelled from the interior and the magnetic field is trapped and when again temperature is increased, magnetic field tries to penetrate through the material. The material shows superconducting properties up to a certain value of magnetic field and above that limit, it loses its superconducting property.



Figure 1.2 The difference between perfect conductors and superconductors. (a) Perfect conductors when cooled below  $T_c$  and then applied magnetic field, flux does not pass through conductor but when first applied field and then temperature is decreased, flux passes through the conductor. (b) Superconductor expels magnetic flux below  $T_c$ , whether a field was applied or not.

The perfect diamagnetism is essential property of superconductor only if the magnetic field and the temperature are below the critical values  $H < H_c$ ,  $T < T_c$ , where  $H_c$  depends on temperature according to expression

$$Hc(T) = Hc(0)[1 - \left(\frac{T}{Tc}\right)^2]$$
 .....(1.1)

### **1.2.2 London Penetration Model**

The basic electrodynamic properties which gave superconductivity its unique properties, were described in 1935 by London brothers. London equations are consistent with the Meissner effect and can be used Maxwell's conditions to calculate the surface current and magnetic field variation with magnetic with distance from the surface of a superconductor. They described the Meissner effect mathematically by assuming that the current density J in the superconducting state is directly proportional to the vector potential A of the magnetic field. The two equations which govern the electric and magnetic fields are:

$$\nabla \times \mathbf{Js} = \frac{1}{\mu o \lambda^2} \mathbf{B}$$
 (1.3)

Where  $\lambda_L$  is the london penetration depth. The extent to which magnetic field penetrates into the superconductor is given by penetration depth. Magnetic field *B* decreases exponentially from external value to zero, given as

Here *B* is the magnetic field at the surface and x is the distance from the surface to inside point. The value of  $\lambda$  ranges from 10 to 100 nm. Penetration depth changes with temperature according to expression

Where  $\lambda_0$  is the depth at OK. As T tends to  $T_c$ ,  $\lambda$  becomes infinite. Further with T tending  $T_c$ , magnetic field penetrates into the sample and sample becomes normal.

### 1.2.3 BCS Theory

In 1957 Bardeen, Cooper and Schrieffer presented a microscopic theory of superconductors that had success in explaining the features of superconductors, known as BCS theory. A key conceptual element in this theory is the pairing of electrons close to the Fermi level into Cooper pairs though electron-phonon interaction. This pairing results from a slight attraction between the electrons related to lattice vibrations; the coupling to



Figure 1.3 The schematic picture of electron-phonon interaction. Electron 1 attracts the positive ions, leaving a distorted region of the lattice having a positive charge and hence electron 2 is attracted to it.

the lattice is called a phonon interaction. The idea of pairing of electrons at first appears to be nonsense since electrons ordinarily repel each other in view of like charges.

Pairs of electrons can act very differently from single electrons which are fermions and must comply with the Pauli Exclusion Principle. These act more like bosons which can condense into the same energy level. At sufficiently low temperature, ground state becomes unstable towards condensing in the Superconducting phase. The electron pairs have a somewhat lower energy and have an energy gap above them of the order of 0.001 eV which prevents the kind of collision interactions that lead to ordinary resistivity. Material exhibits zero resistivity when the thermal energy is less than the band gap at certain temperatures. Fig.1.3 shows electrons moving in the lattice. The motion of one electron attracts nearby ions to move towards the electron, causing increase in the concentration of positive charge in the lattice. Thus the equilibrium positions of the electrons is distorted, giving rise to net attractive force. The attractive force between two cooper pair is an electron-phonon-electron interaction, where crystal lattice acts as a mediator.

#### 1.2.4 Ginzburg-Landau Model

In 1950, Ginzburg and Landau introduced a scientific model for superconductors that focused totally on superconducting electrons. It is not based on excitations as in the BCS theory. The London theory did not take into account the quantum effects. Thus the first quantum theory was given by Ginzburg and Landau. GL theory considers  $\psi$  (r) as an order parameter. It is based on second order phase transitions developed by Landau. Two characteristic length scales appear from Ginzburz-Laudau (GL) theory. The phase of the wave function is critical for relating currents in the superconducting electrons. The GL coherence length ( $\xi$ ) is the characteristic distance over which  $\psi$  changes. According to this theory, a phase transition of second order occurs when the state of the body changes gradually while symmetry changes discontinuously at the transition temperature. The GL theory manages a transitional state of superconductors, where superconducting and normal state exist together in presence of magnetic field. It was further demonstrated that wave function is relative to a constraint of the energy gap in BCS theory.

#### **1.2.5 Flux-pinning and Flux Flow**

Properties of superconducting materials are changed by the presence of defects in a materials. When the magnetic flux lines are trapped or pinned in the vortex state inside a superconducting material, such phenomenon is

called Flux pinning. Meissner state, states the effect of magnetic field on a superconductor. At a point when magnetic field is strong, superconducting properties were distorted and some of the magnetic field enter into the superconducting materials to form vortices. The vortices resemble tubes that go penetrate the sample from one side to other such that material is no longer superconducting as the magnetic field can enter. The material grows super currents coursing around this pillar in spiral motion, in order to enable this magnetic field go through the vortex. These represent a region where superconducting electron density is suppressed and vortex is actively favourable to accommodate on one of these defects. Such behaviour is known as flux pinning. This flux pinning causes a field gradient in the superconductor and offers a net current in the material.

There are two types of material defect pinning in type-II superconductors. Point defect pinning, which is due to irregularities in the crystal structural. Such point defects were proposed by Pastoriza (1992) in Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>O<sub>8-x</sub> at 15K. In order to understand the vortex pinning mechanism, It is necessary to calculate the pinning force density ( $F_p$ ) from the critical current density and applied field, using the formula  $F_p =HJ_c$  at low temperatures. Dew-Hughes [9] proposed a formula in order to explain single vortex pinning mechanism, the pinning force  $f_p=F_p/F_p$ , max as a function of reduced field (H/H<sub>irr</sub>).

#### **1.2.6 Critical Current**

When flux lines passes through the superconductors in the Meissner state in the form of vortices, it produces Lorentz force upon each vortex. These vortices stay in their state as far as the Lorentz force is not as much as the pinning force. At some value of  $J_c$ , the Lorentz force overwhelms the pinning force such that the field goes through the vortices. This is called flux flow. In type-II superconductor the critical current is practically  $J_c$ times the cross-section through which the current flows. The vortices can likewise begin to move due to a reduced pinning force that originates in thermal initiation of the lattice. The movement is ordinarily more irregular and much slower. This is named as flux creep.

#### **1.2.6.1 Bean Critical State Model**

Bean in 1962 presented a model that depends on experimental observations [10, 11]. This model permits only two states that are perfect diamagnetism and mixed state, with a sharp change. Therefore, it has been named as the critical state model. The Bean critical-state model provides a phenomenological description for the hysteretic magnetization of type-II superconductors in a varying external magnetic field. The magnetic field penetrates into these superconductors in the form of superconductive electron current vortices. Each of the vortices transports a similar amount of magnetic flux, thus the magnetization relies upon the vortex distribution. As per Bean model, in a type-II superconductor the distribution of vortices is determined by the balance between electromagnetic driving forces and forces pinning the vortices to material in homogeneities. At whatever point the external magnetic field is altered, magnetic vortices enters or leave the superconductor through its boundary. When the region appears where the driving forces overcome the pinning, the arrangement of vortices relocates itself into another meta-stable state to such an extent that all vortices are pinned again and the balance with the external field at the boundary is restored. As the unpinned vortices move quickly, the system rapidly alters itself to the changing external conditions, and thus a quasi-stationary model with immediate interactions is acceptable.

#### **1.2.7 Upper Critical Field**

In Type-II superconductor there exist a mixed state of normal and superconducting regions. This is called vortex state. This upper limit of field up to which type-II superconductor shows superconducting properties is called upper critical field. The quantized flux penetrates in to the material and the flux is concentrated in the normal core which is surrounded by circulating supercurrents and in the limit of zero applied field, it declines to zero in a distance from the core equal to the penetration depth. With increasing field, the number of these flux lattice increases and at upper critical field  $H_{c2}$  the flux lattice vanishes and bulk superconductivity is destroyed. The resistance does not change until  $H_{c2}$  because continuous superconducting path exist through the material. The decimation of magnetic field in type-II superconductor can be clarified by two type's pairbreaking mechanism. The first, orbital pair breaking, happens when there is immense cover of the vortex cores and the upper critical field. The other is the paramagnetic limiting effect. When the magnetic field is applied to the band of electrons, the degenerate bans split into spin-down and spin up bands and brings down the energy of the system.

#### **1.2.9 High Temperature Superconductors**

Bednorz and Muller in 1986 found a ceramic that shows superconductivity at a critical temperature of 35K. This discovery of high temperature superconductors started the search for much higher critical temperatures. The mechanism for high temperature superconductor is not exactly clear but



Figure 1.4 shows the timeline of superconductivity with high  $T_c$  [71].

rather experiments demonstrate that the supercurrents comprises of paired electron with respect to for metallic low temperature superconductors.

### **1.3 Applications**

Superconductivity can be applied in diverse areas [12]. The variety of present and future products using different features is listed. High temperature superconductivity prompt numerous innovative technological advances, for example highly efficient and lightweight motors. Using the property of zero resistivity keeping in mind the end goal to bring down losses and lessen size of regular equipment. SQUID and magnetometers are exceptionally sensitive magnetic flux detectors used in accuracy instrument. Superconducting magnets are utilized in different experiment and medical gear to produce high magnetic fields, for example MRI (magnetic resonance imaging) and SMES (superconducting magnetic energy storage). Transformers and cables with superconducting windings can be used with reduction of losses. Magnetic levitation is used in the Maglev trains. Further superconducting magnet is becoming component in particle accelerators.

The future of superconducting applications is very positive from the technological perspective. The different research Labourites are working to develop superconducting motors and generators for power generation purpose. The great deed of work is in progress around the world to explore new high temperature superconductors and to understand the mechanism behind these high temperature superconductors.

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# **Chapter 2**

## **Studies of Layered Superconductors**

### 2.1 Layered Transition Metal Dichalcogenides

During past few years, transition metal dichalcogenides (TMDCs) have been studied extensively for the layered structure, charge density wave (CDW) and superconductivity [13] that arises due to their low structural dimensionality. These two- dimensional layered material have shown extraordinary physical properties and promising applications for example, being the reason for superconductors [14], solar cells [15], thin-film transistors [16], battery systems [17], and many others. These TMDCs, having formula MX<sub>2</sub>, where M is a transition metal (M=Ti, Zr, Hf, V, Nb, Ta, Mo, W or Te), and X is a chalcogenide (X= S, Se, or Te) [18-21] are studied extensively for understanding of fundamental physics among two dimensional materials. These materials show promising properties in electrical [22], mechanical [23] and optical devices [24]. The structures are formed by three atomic thick layers (X-M-X) stacked in repeating patterns along the *c*-axis like the sandwich sort, held together by weak van der Waals (VdW) bonding, bringing about a low coupling consistent between the layers. These LTMDs including the different polymorphs and polytypes, are a particular group of materials having a hexagonal layer structure with a genuinely strong intralayer covalent bonding and weak interlayer van der Waals bonding. The valence state and d electron arrangement of the metal, attached to the chalcogen, are in charge of the various electrical, magnetic and optical properties. The quasi 2D nature of MX<sub>2</sub>, give ascent to distinct anisotropy in physical properties. Despite having similarity in structures, these TMDC's present a range of electronic behaviour from semiconductors  $(MOS_2)$  to semimetals  $(TeS_2)$  and real metals  $(NbSe_2)$  [25]. The structural and physical properties can be enhanced by low doping levels [26-27].

To the extent we concerned, doping is one of viable approaches to enhance material performance in many research fields, for example, photocatalytic material [27] information materials [28], lithium ion batteries [29], magnetic materials [30] and so forth. Over the past decades, various test and hypothetical reviews have devoted to adjust LTMD's properties through the doping strategy predominantly because of the appealing outcomes carried by the dopants. Xiaopeng Qin et al. [31] studied the microstructure, mechanical and tribological study of Ti-doped MoS<sub>2</sub> composite coatings, which shows the hardness and grip of the composite coatings achieved its most extreme inside a specific scope of Ti substance and doped Ti enhanced the tribological properties of pure MoS<sub>2</sub> as well. As of late, the infrared vibrational properties of Re-doped MoS<sub>2</sub> nanoparticles have been investigated, demonstrating that phonon lifetime decreases further while the phonon lifetime of unadulterated 2H-MoS<sub>2</sub> is like that of customary polar semiconductors like GaAs, are significance for comprehension carrierphonon communications in low-dimensional semiconducting nanomaterials.

Any impurity material can be doped in two ways, substitution and intercalation in layered structure.

#### 2.2 Substitution Compounds

When any impurity or doping material is doped in any material such that it replaces any atom, such type of doping is known as Substitution. Such type of doping is more energetically favourable due to the presence of van der Waals forces which exists in the interlayer spacing which prevents any atom to be doped in to the interlayer. The lattice parameters are changed with the doping. In the substituted structure, the *c*-axis extends, since the distance between layers increases to some extent. Tao et al. [32] showed that the substitution of Te in NbSe<sub>2</sub>, influences the superconducting properties, stating that both  $T_c$  and RRR value decreases with increasing Te content. The substitution Nb atom by V atom in NbSe<sub>2</sub> is shown in fig. 2.1.



*Figure 2.1. The structure of NbSe*<sub>2</sub> *with Nb atom replaced by a V atom.* 2.2 Intercalation

In layered MX<sub>2</sub> the vacant lattice sites that exist between the feebly bonded X-M-X slabs are possible 'gaps' which can be filled somewhat or totally by additional metal (M=metal) atoms, ions, or molecules, to offer ascent to stoichiometric or nonstoichiometric compounds. Such a process of filling-up is called intercalation, a word essentially used to recognize it from the substitutional doping and demonstrate that the intercalated atom or molecule bonded to the layer of MX<sub>2</sub> may be weak. The weak interlayer bonding contributes intercalation very likened to other layered materials by which it is conceivable to introduce various metal atoms, ions, organic and inorganic molecules between layers to frame stoichiometric or nonstoichiometric compounds. Fig. 2.2 shows the interlayer of V atom in between the Se layers in NbSe<sub>2</sub>. Dependent on the intercalate species, very normal and intense changes in the physical properties of the host happen and this energizing possibility has stimulated a considerable measure of research enthusiasm for the decades. The transition temperature ( $T_c$ ) of the

parent  $MX_2$  is changed on intercalation either due to the change in the density of states at  $E_F$  or due to rearrangement of electrons between the overlying conduction bands or changes in the electron phonon interaction.



Figure 2.2. The structure of NbSe<sub>2</sub> with a V atom embedded into the interlayer.

#### 2.1.2 Synthesis of layered structures

MCh2 materials can be prepared in powder form by various strategies which include direct combination of elements in evacuated and sealed quartz tube at high temperature. Mostly they and decompose and melt above 1000°C and henceforth single crystals are developed by the chemical vapour transport methods utilizing chalcogen, halogens or phosphorus as the transport agents. Only slight measures of the carriers get incorporated into the lattice of MX<sub>2</sub>. The chemical reaction of intercalation in transition metal dichalcogenides MX<sub>2</sub> is given by:

$$TX_2 + xI = T.X_2$$

The  $T_c$  of TaS<sub>2</sub> was raised from 0.8K by intercalation with pyridine and in NbSe<sub>2</sub> and MoS<sub>2</sub> metal-insulator transitions were induced by intercalation with Na-NH<sub>3</sub> [33].

### 2.2 NbSe<sub>2</sub> Superconductor (a true 2-D superconductor)

### 2.2.1 Crystal Structure

The quasi two-dimensional compound NbSe<sub>2</sub> belongs to the family of metallic layered MX<sub>2</sub>. NbSe<sub>2</sub> is one of the widely studied TMDC's, which shows both a charge density wave (CDW) and superconducting properties at transition temperature  $T_{CDW} = 33$ K [34-36] and  $T_c = 7.4$ K respectively at a temperature of 7.2K, highest among the group V transition metals. NbSe<sub>2</sub> has a layered hexagonal structure. The unit cell consist of two sandwiches of Se-Nb-Se. The crystal typically cleaves between the weakly coupled neighbouring Se layers and the top Se layer is imaged by STM. The following fig. 2.3 shows the structure of NbSe<sub>2</sub>.



Figure 2.3 The crystal structure of NbSe<sub>2</sub> shows Nb atoms between the Se layers.

#### 2.2.2 NbSe<sub>2</sub> properties

The single layer of NbSe<sub>2</sub> is a two-dimensional superconductor, which was a major breakthrough in the field of two-dimensional materials. Not very many 2D superconductors exist in nature, and single-layer NbSe<sub>2</sub> is the first among them that remaining parts a superconductor in its detached, 2D frame without the need of an exceptional substrate NbSe2 was found to have experimental and theoretical interest owing to its essentially anisotropic system, which undergoes a charge density-wave (CDW) transition at a temperature near 33K [34-36]. A CDW is a periodic variation in the conduction electron density that is necessarily accompanied by the periodic lattice distortion, both having the same wave vector. The wave vector is determined by the details of the fermi surface. The CDW transition is observed in low dimensional metals and recent studies indicate that it develops due to the Fermi surface nesting in the electronic band [37]. D. E. Monc et al. [38, 39] confirmed CDW through Neutron Scattering, B. Giambttish et al. [40] by scanning tunnelling microscopy and by C Bertheir et al. [41] through NMR. NbSe<sub>2</sub> shows a large anisotropy in its electrical, mechanical and magnetic properties due to its layered structure. The studies of the superconducting order parameters of NbSe<sub>2</sub> have recently increased in number, due to recent new concepts of s-wave pairing in cuprates and two gap superconductivity in MgB<sub>2</sub> [42]. It becomes a prototypical anisotropic s-wave superconductor below a temperature Tsc = 7.2K. Different experiments performed on NbSe<sub>2</sub>, reveal specific heat [43], thermal conductivity [44], magnetization [45], penetration depth, tunnelling spectroscopy [46] and angle resolved photoemission spectroscopy (ARIES) [47, 48]. The studies of intercalation by Cu, Co, and Fe in NbSe<sub>2</sub> [48] showed that intercalates fill selectively the available interstitial sites. Luo et al. [49] studied the superconducting behavior of Cu-intercalated NbSe<sub>2</sub> resulting in decrease of  $T_c$  with increasing Cu concentration with an inflection point. Wang [50] revealed the consequence of Te doping in NbSe<sub>2</sub>, showing that  $T_c$  and RRR value decrease with increasing Te content.
Mohammed Kars et al. [51] also revealed the examination on the structures of intercalation compounds Ge<sub>0.2</sub>NbSe<sub>2</sub> and Ge<sub>0.3</sub>NbSe<sub>2</sub> resulting in different superstructures by electron microscopy, high resolution electron microscopy and single crystal X-ray diffraction and X-ray microanalysis. The magnetic exchange studies on interaction in resistivity on 2H-Nb<sub>1</sub>-<sub>x</sub>VxSe<sub>2</sub> found that magnetization at low temperature is due to the presence of localized magnetic moments of vanadium(V<sup>4+</sup>) accompanied with exchange interaction [52]. Chen et al. [53] showed by first principles PBE-GGA calculations the changes in structure, chemical bonding and electronic properties due to V doping into 2H-NbSe<sub>2</sub>. The different doping in NbSe<sub>2</sub> resulted in change in structural properties and upper critical field  $(H_{c2})$  and critical current density  $(J_c)$  associated with different pinning mechanism [54]. To explain superconducting mechanism, single crystals with significant value of  $J_c$  are required. Such crystals assist to evaluate the applicability of TMDC's utilizing high current density. The  $J_c$  values depends on the density, type of, and arrangement of pinning centers. It is necessary to increase the flux pinning strength in order to increase the critical current density, which can be improved by doping with foreign atoms and irradiation. In type-II superconductors, the magnetic field penetrates the bulk of superconductor in the form of vortices or flux lines, while each vortex is like tube that go through the sample from side to side and superconducting currents circulating around this vortex in spiral motion. The defects created due to the addition of a impurity atom change the elasticity of the vortex lattice, which suffers the change in the pinning force density [55]. The defects or the disorder created due to destabilization leads to a different types of pinning regimes such as strong collective pinning regime and weak pinning regime [56]. The doping of NbSe<sub>2</sub> single crystal with Fe impurity enhances the superconducting critical current density and the disorder created by Fe atoms shows  $\delta l$  flux pinning [57].

#### 2.3 V-doped NbSe<sub>2</sub>

Vanadium (V) occupies a position in the group V of the transition metals in d-block with Niobium, thus indicating to have same properties to some extent. The ionic radius of Nb<sup>4+</sup> (68pm) is greater than that of V<sup>4+</sup> (58pm). In the present work, V is doped in NbSe<sub>2</sub> to study the changes in structural, electrical and magnetic properties. V can be doped in two methods in our sample, one Nb atom is changed by the V atom while the other in which V is inserted in between the Se layers. The V doping brings about obvious changes in the lattice parameters and surrounding atoms. When Nb atom is substituted by V atom, the Se atoms adjacent to V atom come nearer to the V atom so that the distance between layer and layer decreases, thus increasing the *c*-axis. In case of V intercalated between the Se layers, V forms chemical bond with the nearby Se atoms which constricts the distance between layer and layer and layer, decreasing *c*-axis.

# **Chapter 3**

## **Experimental techniques**

#### 3.1 Sample Growth Technique

All the samples were grown utilizing the in-campus facilities available at IIT Indore.

#### 3.1.1 Polycrystalline and Single Crystals

Polycrystalline are solids that are composed of many crystals of varying size and orientation. Single crystals are well-arranged atomic arrays, two dimensional arrangements of atoms that have a tremendously high level of crystalline excellence. Crystals play a crucial part in research industries of intrinsic properties and crystalline structure and also in innovative applications. Large portion of the superconducting compounds are vastly anisotropic, so single crystals have been basic for deciding the directionality of key properties, for example lower and upper critical fields,  $H_{c1}$  and  $H_{c2}$ , coherence length, penetration depth and critical current density  $J_c$ ,. Intrinsic estimations of high quality crystals have given the premise for scheming a variety of magnetic imaging and storage, electronic power transmission and high speed signal propagation on strip lines. Single crystals have likewise allowed full determination of the fundamental structures of pure superconducting phases, along these lines making ready to understanding the mechanism for superconductivity and forecasting the existence of unfamiliar superconducting compounds. Subsequently, examinations of single crystal growth have given strategies for characterizing processing conditions in some bulk and thin film development methods, such as melt texturing and liquid phase epitaxy.

#### **3.1.2 Single Crystal Growth**

Crystal growth is a procedure through which the atoms, molecules or ions arrange themselves in repeating pattern. There are various methods to prepare crystals, any number of which is relevant to a given compound. A large tail of methods exist for crystal growth from a small inexpensive technique to sophisticated growth process with crystallization times ranging from minutes, hours, days and to months. Single crystals might be created by the transport of crystal constituents in the solid, liquid or vapour phase. Crystal growth techniques can be classified as solid growth, vapour growth, melt growth and solution growth on the basis of phase transformation.

The development of single crystal material from vapour phase is likely the most flexible of all crystal development forms. High purity crystals can be developed from vapour phase by condensation, sublimation and sputtering of essential materials. This method can be used to grow single crystal of high melting point. The most often used technique for the growth of single crystal is chemical transport reaction in which a reversible reaction is utilized to transport the source material as a volatile material to the crystallization region. Finding an appropriate transporting agent is an impressive, issue in this procedure.

#### 3.1.3 Procedure

Single crystals of pure NbSe<sub>2</sub>, V<sub>0.1</sub>NbSe<sub>2</sub>, V<sub>0.15</sub>NbSe<sub>2</sub>, V<sub>0.01</sub>NbSe<sub>2</sub>, V<sub>0.01</sub>NbSe<sub>2</sub>, V<sub>0.001</sub>NbSe<sub>2</sub>, V<sub>0.001</sub>NbSe<sub>2</sub>, V<sub>0.0007</sub>NbSe<sub>2</sub> compound were prepared by the chemical reaction of high purity elements V=99.99%, Nb=99.8% and Se=99.999% powder in stoichiometric proportions by chemical vapour transport method. The precursors were mixed in a stoichiometric ratio in an agate mortar and the circular pellets of diameter 1.0 cm were made by applying pressure of 8 ton using a hydraulic press. The pellets were sealed in a quartz tube at a pressure of  $2.5 \times 10^{-5}$  mbar with iodine as a transport agent. The synthesis takes place by chemical vapour



Figure 3.1 The schematic diagram for synthesis of single crystal through chemical vapour technique. (a) Shows ampoule in which precursors are kept. (b) two zone furnace in which ampoule is placed at high temperature.

transport (CVT) when heated in two zone furnace for 15 days with charge zone and heat zone temperature of 800 °C and 720 °C, respectively. The set up consist of two zone furnace (source  $T_1$  and  $T_2$ ), the reactant and transport agent sealed in a small sealed quartz tube. All the samples were prepared using the same temperature profile.

#### **3.1.3.1** Chemical Vapour Transport method

In the process of CVT, a solid is volatilized in the presence of a gaseous reactant (transport agent) and deposited elsewhere in the form of crystals. Transport agents include halogens and halogen compounds such as iodine. The various parameters that must be optimized for a successful CVT are growth temperature, transport direction, rate of mass transport, choice of the transport agent and the free energy of the reaction. Transport is governed by two processes –convection and diffusion. Though larger crystals can be obtained by increasing the transport rates favouring convection, the crystals are inhomogeneous and are prone to having more defects. Depending on the free energy of the reaction between the species, the source and sink

temperature must be altered. Single Crystal of transition metal dichalcogenides have been obtained by this process.

#### **3.2 Characterization Techniques**

#### **3.2.1 Laue Diffraction**

The Laue Diffraction method is primarily used to govern the alignment of single crystals. The diffracted beam form sets of points that lie on the curve. The spots on any curve are reflections from planes corresponding to the zone. Laue reflections from planes of the same zone lie on the surface of an imaginary cone whose axis is the zone axis. There are two different methods by which Laue diffraction pattern can be obtained, the back-reflection and the transmission Laue method. In back-reflection technique, the sample is put between the x-ray source and the crystal. The diffracted beam in backward direction are recorded. In case of transmission Laue technique, the sample is put behind the sample to record the beams which are transmitted through the sample. Sample orientation is resolved from the position of the spots. The Laue technique can likewise utilized to access crystal perfection from the size and state of the spots

#### 3.2.2 Powder diffraction

Powder diffraction is utilized for classification of polycrystalline materials. A polycrystalline sample contains a substantial number of crystallites. Along these, all possible peaks are observed. The basic theory of powder diffraction is that for each arrangement of planes, there are measurably pertinent number of crystallites that are suitably arranged to diffract the incident beam. The diffraction pattern is the unique fingerprint of any crystalline phase which rely upon the position, width shape, intensity, and intensity of the diffraction lines giving us data on the specimen. Diffraction data can be lessened to a list of peak positions and intensities. Each  $d_{hkl}$  corresponds to a family of atomic planes. The limitation of powder

diffraction over single crystal diffraction is that the individual planes cannot be resolved.

#### **3.2.3 X-ray Diffraction**

The X-ray diffraction (XRD) pattern of a crystalline substance is a unique analytical technique primarily used for phase identification of a crystalline material which can provide information on unit cell. X-ray diffraction t4echnique is used for the study of crystal structures and atomic spacing. It is based on constructive interference of monochromatic x-rays and a crystalline sample. Bragg's law gives the conditions required for interference. According to Bragg's law

Where *d* is spacing between two crystal planes, *n* is an integer,  $\lambda$  is the wavelength of the X-ray beam,  $\theta$  is acute angle between the incident ray and the scattering. Fig. explains the Bragg's law. A diffraction pattern is obtained by determining the intensity of scattered waves as a function of scattering angle ( $2\theta$ ). The family of crystal planes produces a diffraction peak at specified angle. The spacing between the diffracting planes of the



Figure 3.2 The diffraction process in direct lattice (left) and reciprocal lattice (right) space. Parallel rays are incident on the atomic planes and are scattered as shown. In reciprocal lattice space, planes of atom are signified by single point and the reciprocal lattice points which are intersected by the Ewald sphere (red) satisfy the bragg condition.

atoms determines the peak positions. The intensity of the plane is determined by the number of atoms present in the diffracting plane. The ray diagram of the diffraction process is shown in fig. 3.1. The diffraction process is also expressed in reciprocal space lattice. Reciprocal lattice space is the Fourier transform of the real lattice. Planes of atoms (having inter planar distance d) in real space are defined by points in reciprocal space are described by wave vector.

Let, x-rays are incident from infinity along direction k with wave vector  $k_1 = 2\pi k/\lambda$ . Assuming scattering to be elastic in  $k_2$  direction with same  $\lambda$ , so that the wavevector  $k_2 = 2\pi k'/\lambda$ . The scattering vector is then  $\Delta k$ =  $k_2 - k_1$ . These wavevector will construct a sphere, called Ewald sphere. The reciprocal lattice points intersecting the Ewald sphere will satisfy the Bragg condition and contribute to scattering. Fig.3.2 shows the two dimensional Ewald sphere.

#### **3.2.3.1 Instrumentation**

A Bruker D8 Advance X-ray diffractometers with  $CuK_{\alpha}$  radiation ( $\lambda = 1.54$ Å) was used to analyse the phase formation, phase purity and composition presented in this thesis. An x-ray beam of single wavelength is used to analyse the specimens. In this diffractometer incident angle of X-ray beam is changed continuously to record a spectrum of intensity versus angle between incident and diffracted beam.

It consist of an X-ray tube, incident beam optics, sample holder, receiving side optics and a detector as shown in fig. 3.3.  $\theta$  is the angle between the incident beam and the detector. The X-rays are produced in cathode ray tube by heating filament to high energy electrons, accelerated towards the



Figure 3.3 Schematic diagram of X-ray diffractometer.

object by applying electric field and bombarded on the target specimen. These X-rays are diffracted by the sample and are converged at the receiving slits before they enter a detector. The diffracted X-rays are passed through a monochromatic filter to supress wavelengths other than  $K_{\alpha}$ .

#### **3.2.4 Scanning Electron Microscopy**

Scanning electron microscopy is used to study the structure and topographies of the specimen surfaces at very high magnifications. Image of the sample is produced by the secondary electrons produced by the specimen which contains topological features of the specimen. Figure shows a schematic diagram of a SEM. The electrons are produced by electron gun which are guided and focused by the magnetic lenses on the sample. The beam of electrons is than raster scan across the surface. The number of secondary electrons produced by the sample at each scanned point are plotted to give a two dimensional image. Any other signal like backscattered electrons and electron-excited characteristics X-rays can also be detected by most of the detector. A secondary electron detector is given positive potential to attract low energy secondary electrons. (When the



Figure 3.4 The schematic diagram of Scanning Electron Microscopy.

specimen is exposed with a fine electron beam called electron probe, secondary electrons are emitted from the specimen surface. Topography of the surface can be observed by two dimensional scanning of the electron probe over the surface and gaining of an image from the detected secondary electrons). The schematic diagram of SEM is shown in fig. 3.4.

#### **3.2.5 Energy Dispersive Analysis using X-rays**

Energy Dispersive X-ray spectroscopy (EDAX) is an x-ray technique used to obtain the elemental conformation of a materials. At a point when a beam of electron strikes with the specimen, an electron from an internal nuclear shell is excited to an external shell while making a hole in place electron. The higher energy electron at that point fills the hole and energy is emitted as X-ray. The discharged energy will be characteristic of the energy difference between the two energy levels, thus the characteristic for the electronic structure of the component is included. The information generated by EDX examination comprise of energy spectra indicating peaks relating to the elements compromising the components of the sample being analysed.

#### **3.2.5 Magnetic and Physical Properties Measurements**

The magnetization measurements were made using the Vibrating Sample Magnetometer option in the Physical Property Measurement System (PPMS-VSM) (Quantum Design, USA). The PPMS by Quantum Design allows the measurement of several functional properties with high resolution. The PPMS can be utilized to measure electrical properties, heat capacities and magnetic properties, in addition to other things. A threewalled Dewar permits the chilling of the measurement chamber off to around 5K by utilizing liquid nitrogen and liquid helium as refrigerants. A temperature range from 2K to 400K is feasible for various kinds of measurements when combined with special heating elements. The schematic diagram of the physical property measurement system is shown in fig. The instrument is extremely delicate to a small magnetic signal, making it perfect for measuring elusive alterations in the magnetic conduct of a sample when it is exposed to various temperatures, magnetic fields or pressures. The temperature dependence of the magnetization can be measured in two distinctive applied field circumstances, called ZFC and FC modes. In ZFC measurement the sample is first cooled from the high temperature state to low temperature and after that magnetic field is applied to the specimen. In a FC measurement, the field is connected in advance. There can be a critical contrast between the ZFC and FC data relying on the way of the magnetic order existing in a material.

#### 3.2.6.1 The SQUID Magnetometer

The SQUID magnetometer is the utmost profound instrument to measure the magnetic property of a specimen. It consist of a second-order gradiometer (counter-coiled spontaneous coils) in a superconducting ring associated to two parallel Josephson junctions. When the specimen moves through the superconducting pick up coils, which is placed at the middle of a superconducting magnet, the variation in magnetic flux density delivered by the specimen is measured. The SQUID magnetometer is shown schematically in figure 3.5. The specimen is placed in a non-magnetic sample holder which is held toward the end of a non-magnetic sample rod. The rod is embedded in the specimen space in a liquid He Dewar, toward the termination of which there is a stepper motor used to place the specimen at the centre of the pickup coils. It acts as an efficient current to voltage converter, giving the change measured in magnetic flux by the pick-up coils.



Figure 3.5 The schematic diagram of a Quantum Design SQUID magnetometer. It detect the change in current, based on superconducting loops containing Josephson junctions and yield a voltage response.

Accordingly, the variation in the current in the detection coils create variants in the SQUID voltage which is relative to the magnetic moment of

the specimen. At last, there are PC schedules which fit the SQUID profile and extract the magnetic moment of the sample from the SQUID output. SQUID magnetometers are equipped for measuring small magnetic moments.

#### **3.2.6.2** Vibrating Sample Magnetometer (VSM)

The PPMS is equipped with a VSM option. The schematic diagram of VSM is shown in figure 3.6. This can be utilized to measure magnetic hysteresis loops and perform temperature- dependent magnetization measurements with a static applied magnetic field. The working principle of the VSM to measure the rate of the change of magnetic flux due to the magnetized specimen which produces an induced emf in a detection coil system. The specimen is put in a uniform dc magnetic field given by the superconducting magnet, which is made to oscillate sinusoidally with small fixed amplitude. The PPMS-VSM used can be varied within the temperature range of 2K-400K and magnetic field up to 8T.



Figure 3.6 The schematic diagram of Vibrating Sample Magnetometer (VSM)

# **Chapter 4**

## **Results and Discussion**

Single crystals of V–doped NbSe<sub>2</sub> samples were grown by chemical vapour transport technique discussed in Chapter 3 with starting precursors of Nb (99.95%), Se (99.999%) and V (99.99%) in stoichiometric proportion.

The following photo shows the (a) single crystal were grown in quartz tube and (b) shows the dimension of the single crystal. The size of the single crystal is more than 1 cm and thickness is about few micron. The single is very flat and shiny.



Figure 1.1 Shows the photograph of (a) single crystal grown in quartz tube and (b) photo graph of single crystal on graph paper

#### 4.1 XRD analysis

The phase formation, phase purity and composition were confirmed by Xray diffraction (XRD, Bruker D8 Advance X-ray diffractometers) with  $CuK_{\alpha}$  radiation ( $\lambda = 1.54$ Å). Fig.4.2 shows the



Figure 4.22 The XRD pattern of NbSe<sub>2</sub>,  $V_{0.0007}NbSe_2$ ,  $V_{0.001}NbSe_2$  and  $V_{0.0015}NbSe_2$  single crystals.

X-ray diffraction (XRD) pattern of NbSe<sub>2</sub>, V<sub>0.0007</sub>NbSe<sub>2</sub>, V<sub>0.001</sub>NbSe<sub>2</sub>, V<sub>0.0015</sub>NbSe<sub>2</sub> single crystals.

The XRD peaks were indexed by considering hexagonal crystal structure (JCPDS card no. 01-070-5612) of NbSe<sub>2</sub> (space group P63/mmc). All samples indicate that the XRD pattern consist of very clean phase with no impurity peaks. The indexing of the XRD pattern reflect that only *c*-axis oriented (*001*) peaks are present indicating the single crystals are highly oriented along *c*-axis and high quality. The Rietveld refinement of the powered samples with FullProf software reveals the absence of any impurity peak. The calculated lattice parameters are summarized in table 4.1.

Sample	a = b(Å)	<i>c</i> (Å)
NbSe <sub>2</sub>	3.44(7±5)	12.56(0±4)
V <sub>0.0007</sub> NbSe <sub>2</sub>	3.42(5±3)	12.56(7±7)
V <sub>0.0015</sub> NbSe <sub>2</sub>	3.40(0±2)	12.42(3±5)
V <sub>0.001</sub> NbSe <sub>2</sub>	3.40(0±7)	12.40(8±4)

Table 4.1 The structural parameters of V-doped NbSe<sub>2</sub> single crystals.

From table 1, it is evidenced that small variation is observed in *a* and *c* lattice parameters due to incorporation of V atoms in NbSe<sub>2</sub>. The decrease in lattice parameter suggest that V atoms are successfully intercalated in between the Se layers [55].



Figure 4.3 The reitveld refinement of V-doped NbSe<sub>2</sub>, XRD data in powered form.

The decrease in c lattice parameter indicates that the intercalated V atom form chemical bonds with surrounding Se atoms which limits the separation between layers.

### 4.3 SEM and TEM Analysis

SEM images of the NbSe<sub>2</sub> single crystal show the layer by layer growth of the single crystals along the c-axis direction. The SEM images of the single crystals





Figure 4.3 Represents the SEM image and (b) TEM image NbSe<sub>2</sub> single crystals.

are shown in fig. 4.3(*a*). Figure 4.3(*b*) shows the SAED TEM pattern of NbSe<sub>2</sub> single crystal. The dotted line like pattern confirms the high quality single crystalline nature. The single crystal is oriented along (00l) direction and agree with the results of XRD pattern.

#### **4.3 Superconducting properties measurements**

Magnetization measurement, critical transition temperature  $(T_c)$  is one of the tool to measure the properties of superconductor. Application of low magnetic field (few gauss) in either cooled state (ZFC) or applied magnetic field cooling (*FC*) with temperature sweep, provides the information about the superconducting critical transition temperature ( $T_c$ ).



Fig. 4.4. Shows the temperature dependence of the magnetization of pure and V doped NbSe<sub>2</sub> in the presence of different applied magnetic fields.

Fig. 4.4 represents that even though the doped V concentration is very small 0.0007 to 0.0015 the effect on superconducting transition temperature is noticeable. The  $T_c$  decreases appreciably with increase in the V concentration in NbSe<sub>2</sub>. The effect of V doping in NbSe<sub>2</sub> is shown in Fig. 4.5. The pure NbSe<sub>2</sub> shows  $T_c$  of 6.8 K while the lowest superconducting transition temperature among the V doped NbSe<sub>2</sub> single crystal is V = 0.0015 with  $T_c = 3.8$  K. We observed that the magnetization curve do not

show any sharp transition for the samples  $V_{0.1}NbSe_2$ ,  $V_{0.15}NbSe_2$ ,  $V_{0.01}NbSe_2$ ,  $V_{0.015}NbSe_2$ , thus they do not exhibit superconductivity. Therefore no further studies were carried out for the samples.



Figure 4.5. The effect of V doping on  $NbSe_2$  single crystals superconducting transition temperature  $T_c$  (K).

Fig. 4.6 represents the temperature dependent magnetization measured at the different magnetic field in *ZFC* and *FC* modes for observing the effect of V intercalation on  $T_c$ . Fig. 4.6 indicates that the shielding effect of superconductor decreases after incorporation of V in NbSe<sub>2</sub> due to the of the presence of the crystal defects, whereas at a higher magnetic field, with increase of magnetic field both the curves are merged due to the destruction of superconductivity. The *ZFC* curve shows perfect diamagnetism in the low temperature region and the sharp transition temperature starting at 5.4 K, 4.3 K, 3.5 K was observed for the samples  $V_{0.001}$ NbSe<sub>2</sub>,  $V_{0.0015}$ NbSe<sub>2</sub>,  $V_{0.0007}$ NbSe<sub>2</sub> respectively, indicating that  $T_c$  decrease with increasing V concentration. The decrease in  $T_c$  may be due to modification in the density of states either due to electronic charge transfer to the parent NbSe<sub>2</sub> conduction bands or the changes in the band structure, increment of the electron-phonon introduction of soft phonon modes into the phonon spectrum [58-60], with an additional contribution to the attractive electron coupling through an electron excitation interaction [61], tunnelling mechanism, and the suppression of low temperature *CDW* super lattice distortions [58,59,62,63]. Fig. 4.7 presents the isothermal M (H) hysteresis loops of V doped NbSe<sub>2</sub> with different concentrations at temperatures 2 K, 2.5 K, 3 K, 3.5 K, 4 K and 5 K within the superconducting state ( $T_c = 6.4$ K). All isothermals exhibit a central peak around H = 0 at all temperature.



Figure 4.6 The temperature dependence of magnetization measurement of (a). V<sub>0.0007</sub>NbSe<sub>2</sub>, (b). V<sub>0.001</sub>NbSe<sub>2</sub> and (c). V<sub>0.0015</sub>NbSe<sub>2</sub> single crystal at 0.005T, 0.05T, 0.01T and 0.3T magnetic fields.



Figure 4.7 Isotherm magnetization hysteresis loops as a function of magnetic field are shown for (a)  $V_{0.0007}NbSe_2$ ; (b)  $V_{0.0015}NbSe_2$ ; (c)  $V_{0.001}NbSe_2$  at temperatures 2 K, 2.5 K, 3 K, 3.5 K, 4 K, 4.5 K and 5 K.

#### 4.4 Upper Critical field (*H*<sub>c2</sub>)

The upper critical fields ( $H_{c2}$ ) were calculated from the M-T characteristics, considering the onset of superconducting transition of the samples V<sub>0.001</sub>NbSe<sub>2</sub>, V<sub>0.0015</sub>NbSe<sub>2</sub> and V<sub>0.0007</sub>NbSe<sub>2</sub>. According to BCS theory, H<sub>c2</sub>(T) at low temperature is given as:

$$Hc2(T) = Hc(0)[1 - A\left(\frac{T}{Tc}\right)^2]$$
 ------ (4.1)

The upper critical field  $H_{c2}(0)$  values are obtained from M(T) curve of the samples which are plotted in Fig. 4.8. The curves are fitted with equation 4.1, where A is a constant different for samples, give values of upper critical field  $H_{c2}(0) = 3.65$  T, 3.30 T, 2.57 T for the samples  $V_{0.0007}$ NbSe<sub>2</sub>,  $V_{0.001}$ NbSe<sub>2</sub> and  $V_{0.015}$ NbSe<sub>2</sub> respectively. V doping in NbSe<sub>2</sub> decreases the  $H_{c2}$  values appreciably with respect to pure NbSe<sub>2</sub> [57] (6.23T). The decrease in  $H_{c2}$  values in the doped samples reveals that V intercalation



Figure 4.8. The temperature dependence of upper critical field  $(H_{c2})$  of the V-doped NbSe<sub>2</sub> samples and the red curve is a corresponding parabolic fit with a formula  $H_{c2}(T) = A-BT^2$ .

destroys the superconducting properties by improving the pair-breaking phenomena in the presence of magnetic field [64].

#### 4.5 Irreversible Field

The irreversible field is calculated using the criteria of  $J_c = 100 \text{ Acm}^{-2}$  due



Figure 4.9 The temperature dependence of the  $H_{irr}$  for  $V_{0.0007}NbSe_2$ ,  $V_{0.0015}NbSe_2$  and  $V_{0.001}NbSe_2$  single crystals fitted with  $H_{c2}(T) = A-BT^2$ .

to depinning [65, 66] of the magnetic fluxes. The  $H_{irr}$  curve is fitted with equation-1. The plot irreversible field  $H_{irr}$  magnetic field is shown in fig. 4.9

#### 4.6 Critical Current density

The critical current density,  $J_c$  (Acm<sup>-2</sup>) is calculated at different temperatures using Bean's critical state model [10, 11] with the assumption of field independent  $J_c$ 



Figure 4.10 The critical current density  $(J_c)$  of the sample: (a)  $V_{0.0007}NbSe_2$ , (b)  $V_{0.0015}NbSe_2$  and (c)  $V_{0.001}NbSe_2$  estimated from the M (H) curves. (d) The critical current density plot at a temperature of 2K of  $V_{0.0007}NbSe_2$ ,  $V_{0.001}NbSe_2$  and  $V_{0.0015}NbSe_2$  single crystal.

Where  $\Delta M = M_{dn}$ -  $M_{up}$ ,  $M_{dn}$  and  $M_{up}$  are the magnetization measured with decreasing and increasing applied filed, respectively, a(cm) and b(cm) are sample width (a < b). The unit of  $\Delta M$  is in electromagnetic unit per cubic

cm and the calculated  $J_c$  is in Ampere per cubic cm. The calculated  $J_c$  values are shown in Fig. 4.10. We obtain  $J_c$  (0) (2K) ~ 541084, 389668, 841546 Acm<sup>-2</sup> respectively for V<sub>0.0007</sub>NbSe<sub>2</sub>, V<sub>0.001</sub>NbSe<sub>2</sub>, V<sub>0.0015</sub>NbSe<sub>2</sub> samples and decreases with increasing temperature and magnetic field, indicating the presence of weak pinning phenomena. Figure 4.11 shows the  $J_c$  plot of (*a*) V<sub>0.0007</sub>NBSe<sub>2</sub>, (*b*) V<sub>0.0015</sub>NbSe<sub>2</sub> and (*c*) V<sub>0.001</sub>NbSe<sub>2</sub> in the log- log scale. The inset shows the collective pinning model fitting at the log-log scale at a temperature of 2 K occurring at the surrounding impurities.



Figure 4.11 The  $J_c$  plot of (a)  $V_{0.0007}NbSe_2$ , (b)  $V_{0.0015}NbSe_2$  and (c)  $V_{0.001}NbSe_2$  in the log- log scale. The inset shows the collective pinning model fitting at the log-log scale at a temperature of 2K.

The  $J_c$  values obtained from M (H) loop is enhanced due to the presence of V impurity. These values are larger than the reported values for pure NbSe<sub>2</sub> [57], 138997 Acm<sup>-2</sup> at 2K. The determined  $J_c$  values are rather as high as 8 ×10<sup>5</sup> Acm<sup>-2</sup> for the sample V<sub>0.0015</sub>NbSe<sub>2</sub>. Fig. 4.11 shows the  $J_c$  values

plotted in the log-log scale, showing the field independent behaviour of  $J_c$  in the single vortex pinning. The  $H_{irr}$  is obtained from the magnetization loop using the criterion of  $J_c$  (H) = 100 Acm<sup>-2</sup> due to depinning [65, 66] of the magnetic fluxes.

#### 4.7 Pinning force density

In order to understand the vortex pinning mechanism in V- NbSe<sub>2</sub>, pinning force density ( $F_p$ ) is calculated from the critical current density ( $J_c$ ) and applied field, using the formula  $F_p = HJ_c$  at low temperatures. Dew-Hughes [9] proposed a formula in order to explain single vortex pinning mechanism, the pinning force  $f_p = F_p/F_{p-max}$  as a function of reduced field  $h=H/H_{irr}$ follows a scaling relation  $f_p = Ah^p(1-h)^q$  where  $F_{p,max}$  is the maximum pinning force, A is coefficient related with the material properties of the



Figure 4.12 The filed dependence of the reduced pinning force for the samples: (a)  $V_{0.0007}NbSe_2$ , (b)  $V_{0.001}NbSe_2$  and  $V_{0.0015}NbSe_2$ . The inset plot shows the fitted results using the scaling law at temperature 2K.

sample and p and q are the exponents that depend on the pinning mechanism. In our analysis we have used  $H_{irr}$ , the irreversible magnetic field which is obtained by using the criterion of  $J_c$  (H) = 100 Acm<sup>-2</sup>. This model states, p = 1 and q = 1 as volume pinning, p = 1 and q = 2 normal point pinning with  $h_{max} \sim 0.33$ , p = 0.5 and q = 2 normal surface pinning mechanism with  $h_{max} \sim 0.2$ . The position of peak  $(h_{max})$  in fp (h) as well as the extracted fitting parameters p and q provide information about the nature of pinning and its origin. Fig. 4.12 shows the plots of  $f_p$  versus h at different temperatures for V doped samples, with fitted curve at 2 K in inset. Fig. 4.12 exhibit a similar scaling behaviour to the MgB<sub>2</sub> samples [68]. The field dependence behaviour of the reduced pinning force  $(f_p)$  of V-NbSe<sub>2</sub> at temperature 3.5 K and 4 K deviates significantly from the curves at lower temperatures, therefore, a single pinning mechanism cannot explain the pinning mechanism in V doped samples. From the fitted curves of V<sub>x</sub>NbSe<sub>2</sub> at 2 K with Dew-Hughes model, p = 0.97 and q = 3.46 describes the presence of point pinning mechanism but could not describe the value of r= 1.15 and s = 12.81 in the form,

$$fp = Ah^{p}(1-h)^{q} + Bh^{r(1-s)^{s}}$$
(4.3)

which is shown in the inset of Fig. 4.12. Due to the core interaction in the vortex lattice in type-II superconductors, the nature of pinning mechanism in crystal structure is classified as  $\delta l$  and  $\delta T_c$  pinning [68]. The  $\delta l$ -type pinning is associated with spatial variation in mean free path (l) near lattice defects of charge-carriers while  $\delta T_c$ -type pinning is caused by spatial variation in the critical temperature ( $T_c$ ). The defects in case of  $\delta l$  are small, point sized while they are extended, usually larger than coherence length in case of  $\delta T_c$ . From fig. 4.12  $h_{max} \sim 0.14$ , 0.16, 0.18 values corresponding to  $f_{p, max}$  are observed for V<sub>0.0007</sub>NbSe<sub>2</sub>, V<sub>0.001</sub>NbSe<sub>2</sub>, V<sub>0.0015</sub>NbSe<sub>2</sub> samples at 4 K. According to Dew-Hughes model [9], a high value of  $h_{max}$  (>0.5) indicates a  $\delta T_c$  type pinning whereas the low value of  $h_{max}$  corresponds to  $\delta l$ 

pinning. Therefore, a low value of  $h_{max}$  in the studied single crystals of Vdoped NbSe<sub>2</sub> suggests that pinning in the V-NbSe<sub>2</sub> samples is due to the presence of a large density defect centres [69] i.e.  $\delta l$  pinning. Similarly, the pinning mechanism is observed in single crystals of MgB<sub>2</sub> and polycrystalline YBCO, is  $\delta T_c$  while in C substituted MgB<sub>2</sub>,  $\delta l$  pinning is observed due to decrease of mean free path due to C substituted atoms.

# **Chapter 5**

## **Conclusion and Future Work**

### **5.1 Conclusion**

In summary, we have successfully synthesized single crystals of V<sub>0.0007</sub>NbSe<sub>2</sub>, V<sub>0.001</sub>NbSe<sub>2</sub> and V<sub>0.0015</sub>NbSe<sub>2</sub> through chemical vapour transport method to investigate the variation of lattice parameter,  $H_{c2}$ ,  $J_c$  and pinning properties due to the addition of V impurity atoms. The XRD results confirm the single crystalline nature of V doped NbSe<sub>2</sub> samples. The current result reveal the intercalation of V in NbSe<sub>2</sub> with the decrease of lattice parameters due to the van der Waals forces which exist between the layers. A subsequent decrease in the critical transition temperature is observed with increasing V concentration due to the change in the band structure. There is significant enhancement of the  $J_c$  values due to V doping, whereas  $H_{c2}(0)$  is reduced to a much lower value revealing the enhancement of the defects in the crystal structure which increases the pair- breaking phenomena as well as the pinning of the magnetic flux. The enhanced current density reveals the use in various applications. We calculated the flux pinning force density and have shown the existence of point core pinning of the normal centres in the low field regime. The current results are important in understanding of the V-doped NbSe<sub>2</sub> superconductors and its applications.

#### 5.2 Future Work

Here, we are only study the magnetization properties of the NbSe<sub>2</sub> single crystal at the different concentration of V atoms. Further we will study the effect of V atoms on the electrical and other transport properties of NbSe<sub>2</sub> superconductor to improve the fundamental parameters of superconductivity. V atoms are added to the layered structure to increase

the disorder of the vortex dynamics and decrease the dissipation of the supercurrent due to the Lorentz force. Another parameter that can also increase the disorder of the superconducting system is pressure. Further we will try to modulate the order parameter of NbSe<sub>2</sub> superconductor by application of both pressure and the addition of foreign atoms and increases the practical application of NbSe<sub>2</sub> in the family of transition metal dichalcogenides. The magnetic susceptibility data and the ac susceptibility need to be studied further to get more information on the doping in NbSe<sub>2</sub>. The study of CDW with V doping in NbSe<sub>2</sub> will be studied. The optical properties and the band diagram study to see the effect of V in NbSe<sub>2</sub> will be studied.

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