Experimental Superconductivity: Growth and characterization of single crystals of superconducting

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Experimental Superconductivity: Growth and characterization of single crystals of superconducting $NbSe_2$*

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In this one credit experimental class, Tianli Liu and I collaborate on this project. We grow the $NbSe_2$ crystal by chemical vapor transport(CVT) and determine the lattice structure of our samples by X-ray diffraction(XRD), both powder and piece samples conformity the standard sample. We also test the electronic transport properties by PPMS and find that the resistance drop to zero around 7.14K, which consist of previous works. The result supports the existence of superconductivity(SC) in this material and suggests potential applications.

I. INTRODUCTION

Transition metal chalcogenide $NbSe_2$ is an ideal kind of materials for studying the superconductivity and charge density wave(CDW). This properties attracted many researchers to focus. Recently, many research groups try to grow this material and characterize the superconductivity of $NbSe_2$. There has been many experimental methods to prepare for single crystal of transition metal chalcogenide. Considering the high melting point of $NbSe_2$, we choose the chemical vapor transition(CVT), which is a widely used method. We also characterize physical properties, including lattices constant, electron transport, and superconductivity by X-ray powder diffraction(XRD) and physical property measurement system(PPMS)

The report is structured as follows: In Sec.II, we will discuss the background of our research, we will introduce the $NbSe_2$ in that section. In Sec. II the experimental methods like CVT, XRD and Four-terminal sensing(4T sensing) will be introduced briefly. In Sec.III we will discuss our result and also our uncertainty. In Sec.IV we will show the main implications of the experimental results.

II. BACKGROUND

$NbSe_2$ is a transition metal dichalcogenide. It is a superconductor at temperatures below 7.2 K that exhibit a charge density wave (CDW). In this experiment we just follow the superconductivity of $NbSe_2$. $NbSe_2$ is metallic material with hexagonal structure as Fig.II(a) suggests. In single unit cell, Nb occupies the corner of parallelogram and Se atom inlay the space of Nb.

The DFT calculation [1] Fig. IIb suggest the metallicity of $NbSe_2$, whose Fermi energy is occupied. The metallicity is also verified in our experiment by evidence of low resistance and bring some difficulties for measurements. When characterize the material, we use 4 terminate sensing to measure the resistance to minimize the error to partially overcome the difficulties.

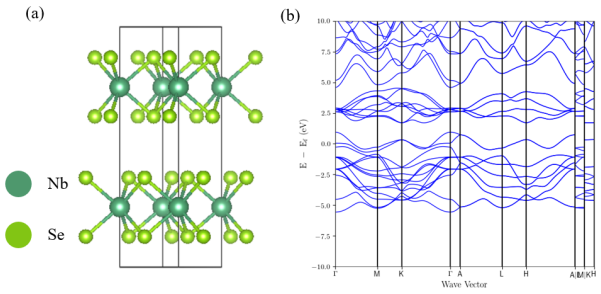

FIG. 1. (a)The crystal structure of the data is cited from material project [1]. Nb occupies the corner of parallelogram and Se atom inlay the space of Nb. (b). The band structure of $NbSe_2$ by DFT calculation[1]

III. EXPERIMENTAL METHODS

A. Chemical vapor transport

The growth of single crystal $NbSe_2$ is based on Chemical methods including CVD and CVT. CVT is a widely used technique to grow single crystal. The apparatus has two temperature zone like Fig.2 which is prepared for the gasification of source and condensation of sink. The illustration of apparatus The reaction can be decomposed to two reactions in different zone. In our reaction, we use Nb and Se to combine $NbSe_2$. However, the boiling points of Nb and Se are 5017K and 985K[2, 3], the high melting and boiling point of Nb prevent the touch of reagents and discourage the reaction. CVT try to use transport agent(in our experiment we use iodine) to react with the source and get a intermediary with lower boiling point.

$$Nb(s) + I_2(g) \longrightarrow NbI_5(g) \text{ (source)}$$
$$NbI_5(g) + Se(g) \longrightarrow NbSe_2(c) \text{ (sink)}$$

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* The two authors collaborated on this experiment but independently write the reports.

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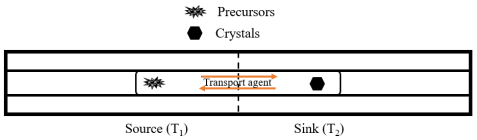

FIG. 2. The illustration of apparatus.

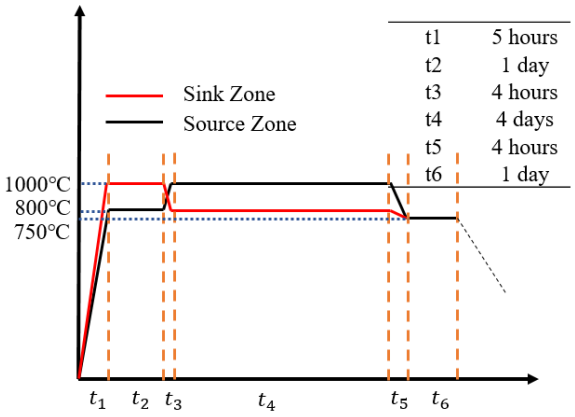

FIG. 3. (a)The temperature-time relation in our experiment. Reactions mostly proceed in t_4. In t_1, the source temperature is lower than sink zone, during which we transport the impurity from sink zone to source to private pollution of crystals

The CVT method can produce high quantity crystal with less impurity. However, seeking for more active reaction we use excess Se, which unavoidably introduce $NbSe_3$ impurity. We can see this result later. The critical parameter of CVT is the temperature in two individual zone and the dosage ratio of raw materials. We suggest an experiencing parameter which can grow good quantity $NbSe_2$ crystals.

In our experimental we use the same dosage ratio of raw materials to prepare three tubes of crystal. See Tab.III A

TABLE I. The dosages of raw materials

Nb	0.1852g
Se	0.3648g
I_2	0.04g

After prepare the raw materials in the glove box, we vacuumize the tubes and melt the glass to seal up the tubes. Then we send the source to the CVT stove. We choose the temperature in two zone as a function of time which is more convenient and controllable. The temperature function we used in experiment is shown in Fig.III A

B. XRD

The XRD (Fig.III B) is a widely used methods in detecting the crystal structure of materials which is based on interference of monochromatic X-rays. When condition satisfy Bragg's Law the reflected beam will be significantly large. By scanning the sample through a range of angle, we can get the patterns of materials, after compares with the standard diffraction patterns, we can determine our materials.

XRDs consist of three basic elements: X-ray tube, a sample holder, and an X-ray detector. The X-ray tubes can provide X-ray by heating the filament to produce electrons and accelerate the electrons to the target(usually metals). Bombarded by electrons, the target radio the X-ray. The X-ray beam can be reflected by samples and detected by the probe. The detector is usually a Geiger-Muler counter and can provide us with the counting rate of x-ray.

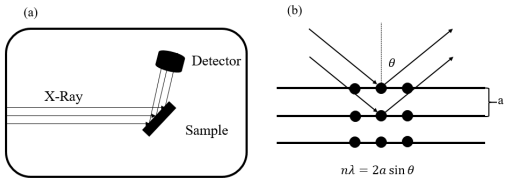

FIG. 4. (a) The XRD consists of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. (b) The Bragg's law. If this law is satisfied, the aptitude of the beam can be extraordinary large which implied the peak in x-ray patterns

C. PPMS and 4T-sensing

In this experiment, we use the apparatus provided by Quantum Design company. The PPMS allows for measurements of the resistivity, magnetic susceptibility, thermal properties and heat capacity. In this experiment, we use the resistivity measurement option, which is based on the 4T-sensing.

To avoid the effects of touch resistance in classical two-terminal sensing, we using the 4T-sensing. The principle of 4T-sensing is easy. Because the internal resistance of volt gauge is huge compared with contact resistance, so the current flow in volt gauge is small, so the potential drops when through the resistance is also small. The Fig.III C

However, there is also some problem with 4T-sensing, the first is the disorder current inside the sample. the current may rotate, twist, and flow disorderly. So, not all current which takes responsibility for reflecting resistance can be detected by volt gauge causing smaller or even negative resistance. So, when you have a homogeneous, clean, and big sample with high-resistance, the

2T-sensing could work well than 4T-sensing. In our experiment, we using 4T because of $NbSe_2$ is a metal which has low resistance and can be neglected when considering the contact resistance.

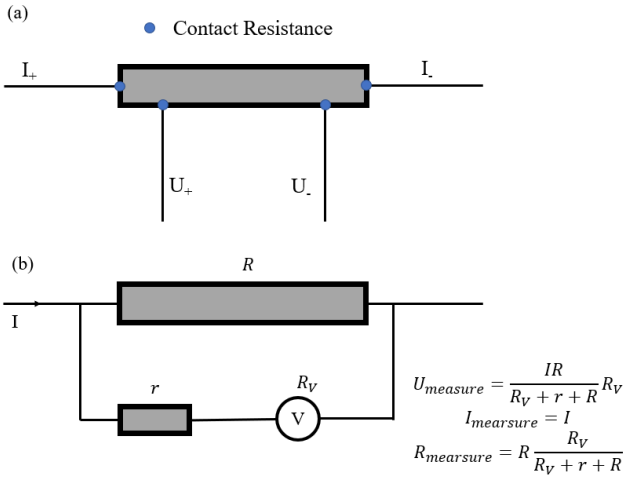

FIG. 5. (a)The schematic layout of circuit inside the PPMS. We annotate the contact resistance by blue dots. (b)Equivalent circuit diagram, in the right corner we give the measurement R in experiment. Mostly, the contact resistance is far smaller than R_V which means no effect with our results.

The PPMS by Quantum design company using the 4T-sensing and automatically control the temperature by liquid Helium, liquid Nitrogen, refrigerators, and the heating system inside PPMS. The range of temperature can various from 1.8K to 300K, which is enough for low temperature physics. By sending the samples in to the PPMS, the researchers can automatically get the resistance-temperature relation of materials and focus on theirs properties including SC or CDW.

D. The Crystal and the superconducting devices

In this section, we would like to introduce the method we used in preparing the experimental devices. The samples are shown in Fig.III D. Because the two typical impurity on the surface of $NbSe_2$ can affect our result dramatically, we should use ethanol the clean the surface of samples, the iodine can dissolve in ethanol while pseudo-1D material $NbSe_3$ can be flowed away from surface.

We think the impurity on the surface is unavoidable, because the Chemical reaction is hardly to control as well as the condensation of I_2 gas. But they do not harmful to our further experiments after cleans. However, the insider impurity like Nb may play harmful role in experiment as we can see in next section.

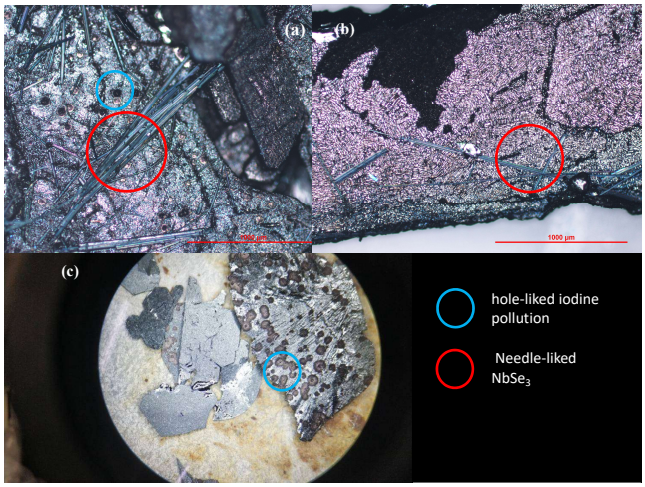

FIG. 6. (a, b)Two original samples growth by CVT, the blue circles and red circles display two typical impurity of our samples. The hole-liked iodine pollution is originate from the coagulation iodine on the surface of samples. And $NbSe_3$ is another chalcogenide of Nb which has superconductivity only in high pressure[4, 5].(c)The zoom out view of samples on which there is a serious iodine pollution.

After clean the surface, we using the GE-vanish and silver glue to fix our sample on the sapphire bases and using the golden wire to transmit the current. The device are prepare by following steps:

First, we prepare for the sapphire bases, the sapphire is an ideal material for low temperature physics which request the base should be insulators for current but conductors for heat. As we know, in low temperature, the electronic contributions to the heat transmission overwhelm the phonon's. However, electrons also contribute to the current transmission, which implies the difficulty to satisfy both condition. Fortunately, the sapphire can work well in these experiments.

Second, we use small plastic bulk to hold the golden wire because the golden wire is fragile and possibly break off during the experiment. The golden wires are fixed by AB silver glues on the holders.

Third, we fixed the sample onto the bases by GE-vanish which is a special glues and valid in low temperature and set the golden wires to the sample and fix them on the samples by silver glues.

Fourth, we place the device on the PPMS sensor and connect the circuit.

The device under the microscopes is Notice that gold and silver are not superconductors which will not affect the measurement of samples. The devices are prepared for further measurements of transmission properties.

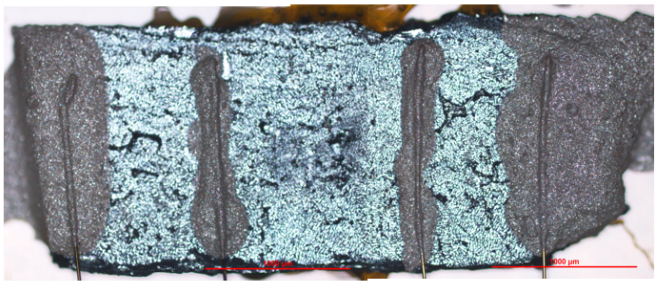

FIG. 7. The microscopic device, the impurity on the surface is clean in picture. The figure is spliced by two pieces. Grey parts is the silver and the green-blue zone is the cleaned samples.

IV. RESULTS

Our sample were sent to Analyze and Measurement Center of Shanghai Jiao Tong University. The diffraction patterns are given in IV. As we mentions in SecIII The different samples are from three different tubes.

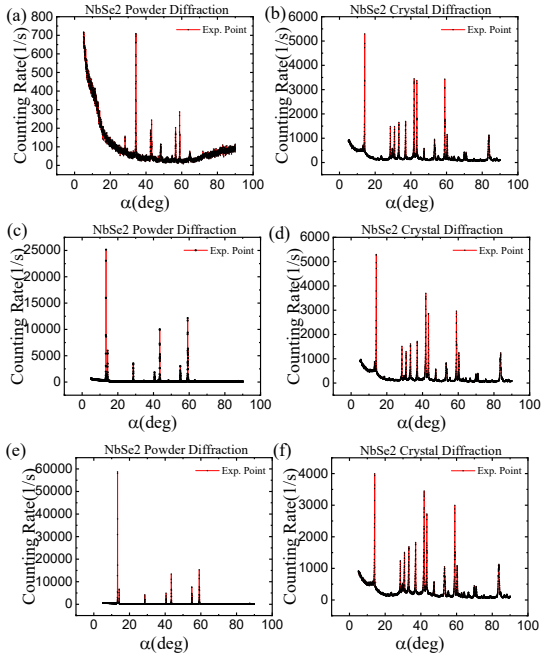

FIG. 8. (a, c, e)The powder diffraction patterns of $NbSe_2$ Fig.a behave abnormally we will discuss it in next section. (b, d, f) The crystal surface of $NbSe_2$ and some abnormal small peaks raised in the figure because of the impurity

We analyze the data by Jade 6.5. The result shows FOM value of $NbSe_2$ is about 2.3 which is considerable small. Further analyze of crystal abc value of the sample suggests

TABLE II. The possible crystal structure of sample 1.

Direction	Sample	Standard[1]
a	6.87	6.978
b	6.87	6.978
c	12.51	13.757

The superconductivity of $NbSe_2$ is also tested by PPMS the results can be get in Fig.IV. As we can see in the picture, there is a significant resistance drops around 7K. Meanwhile when temperature is high, the relation respects to temperature is linear. However, even considered the error bar, the resistance is significant non-zero which inspires the further discuss. The more precise measurement also suggest another phase transform during the 10K, which is also interesting phenomenon.

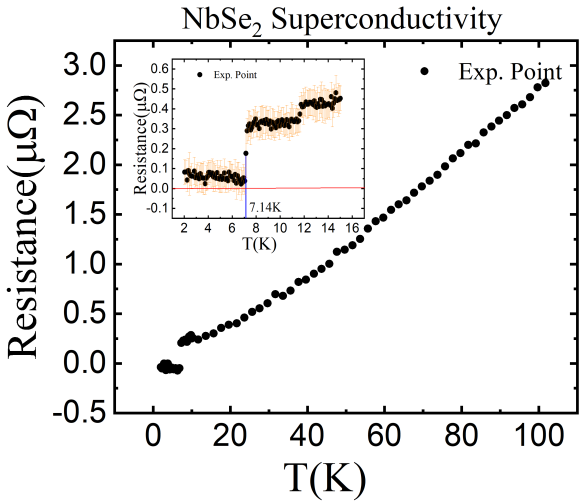

FIG. 9. The Superconductivity of $NbSe_2$ .The big picture reflects the resistance relation respects to temperature from 2K to 300K. The overall property show linear relation when T¿7.2 but a significant drops near 7.2K. If we focus on the 2-15K relation in small picture at the corner(Orange line is the error bar given by PPMS.), the translation temperature is 7.14K in our experiment. However, the resistance has a considerable distance to zero even take the error into account.

V. DISCUSSION

In this section we discuss the abnormal behavior of XRD and PPMS results. In XRD, the powders of sample 1 performs badly. The reasons which need to be considered are discussed below:

Experimental errors: The abnormal behaviors are caused by some mistakes of technicians. The ev-

idences support this ideas is: 1. The counting rate is very small($800 \ll 20000$ in sample 2 and 3.) which can be originated from X-ray is not focus on the samples. 2. Another two samples have nothing strange. And disapproval evidence is that some peaks consist with the other samples.

Impurity of sample: Some impurities in the sample affect the result. The evidences support this ideas is: 1. The peak patterns of samples 1 is mismatch with other samples, which can be provide by impurities. But there is a disapproval evidence that bulk sample perform as good as others.

The above discussion suggests that these may be caused by some mistakes but not the defect of samples. I think we can repeat the experiment to verify my guess. But because of the limitation of time, we can not do it.

In PPMS the non-zero superconducting resistance is also strange. We should emphasize that it is must not overlooked because the non-zero resistance is considerable large when compared with normal state. We also have some reasonable guesses.

Impurity of sample: The non-zero resistances are originated from Se or I_2 impurities which does not have superconducting state. However, if we can using the equivalent circuit as Fig.III C. Unless all paths are jammed by those non-superconducting impurities, the resistance should always be zeros. As Tony mentioned in the lecture, the nonmagnetic impurity has a little to do in superconducting.

Contact resistance: the contact resistance of the system may causing some residue resistance when superconductive state. But I think it is impossible because the contact resistance should not contribute to the potential drops. When the materials is a superconductor, there is no current flow through the volt sensors, that is V=0. And the contact resistance is about 3Ω, far from the residue resistance.

AC current: In this experiment we use the AC current to test the sample, but SCs have finite AC resistance. This is also impossible because only when AC frequency is near the Debye frequency which is nearly 10^7 Hz.

So, I think although impurities are the most reasonable guess, I still can't given a good explain to it. The further research should be processed in these fields: 1. repeat experiment. 2. Using the DC current.

We also see a twice phase transform in experiment. Prof. Liu raised that the PPMS may not be closed perfectly. I think the superconducting impurities could play role. The argument support this ideas is that if the impurities are superconducting, the resistance of whole samples will drop a bits. But the translation temperatures of Nb or other possible impurities are not 11K. Quantitative model should be built to explain this phenomenon.

In conclusion, more deep experiment and quantitative model should be processed. Better experimental apparatus are required.

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