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Physics

ELECTRICAL PROPERTIES OF NIOBIUM DISELENIDE SINGLE CRYSTALS

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ABSTRACT A study of structural, optical, electrical and superconducting properties of the layered compounds of the group II-VI have aroused a widespread interest and attention of the material scientists all over the world during the last few decades. Currently, the growth of super conducting material NbSe2 single crystals was grown by chemical vapour transport technique. The electrical resistivity parallel and perpendicular to the growth axis were measured at high temperature. In temperature range 303 K to 423 K, the resistivity, both normal as well as along the basal plane are decreases with increase in the temperature. But beyond 423 K temperature the resistivity parallel to growth axis was increase with increasing temperature. The activation energy and anisotropy measurements have been carried out for grown crystal. The variation of electrical resistance was monitored in a Bridgman opposed anvils setup up to 8 GPa pressure to identify occurrence of any structural transition. These crystals do not possess any structural transitions up to pressure limit examined.

KEYWORDS : Semiconductor, single crystal, resistivity, High pressure resistivity, High temperature resistivity

1. Introduction

Transition metal dichalcogenides (TMDCs) are among the most studied layered compounds that have been isolated in monolayer form. Compounds in the TMDC family exhibit a wide range of electrical properties, depending on polytype and the number of transition metal d-electrons, and include metallic[1], half-metallic[2], semicon ducting[3-5], superconducting[6], and charge density wave[7] behavior. In particular, molybdenum and tungsten based TMDCs are semiconductors with band gaps ranging from the visible to the near-infrared. Besides Mo and W, chalcogenides of Nb, Ti, Sn, and Zr are also predicted to be semiconducting but little to no experimental evidence exists on their isolation in monolayer form, stability, or performance in devices [8-12]. $NbSe_2$, a superconducting dichalcogenide, has been used to study the changes in the superconductivity by field effect doping and may be used in superconducting field effect devices [13].

TMDCs have the chemical formula MX_2, where M is a transition element and X is a chalcogen. A monolayer is defined here as a hexagonally ordered plane of metal atoms sandwiched between two hexagonally ordered planes of chalcogen atoms, where the formal oxidation states of the metal and chalcogen elements are +4 and -2, respectively. The structure of layered TMDCs is similar to that of graphite and each layer has a thickness of 6 – 7 Å with strong in-plane covalent bonding and weak out-of-plane van der Waals interactions. Bulk TMDCs are found in several structural polytypes depending on the stacking order of the layers, while single layers of TMDCs are found in two polytypes, depending on the position of the chalcogen with respect to the metal element in the X-M-X structure.

In the past few years, studies of materials with layered structures such as graphite [14], transition metal dichalcogenides (TMDCs) [14-18], metal oxychlorides [19] and clay minerals [20-22] have received an ever increasing attention. Among all these, most of the studies have been focussed on TMDCs elements of group IVB, VB and VIB, e.g., TiS_2, NbS_2, $NbSe_2$, MoS_2, $MoSe_2$, WS_2 and WSe_2, etc., due to their unique and attractive properties based on the extreme degree of anisotropy in their structures [14,15]. They find applications as high pressure-high temperature lubricants, catalysts, as electrode materials for solar energy conversion purposes and in the development of primary and secondary batteries [23-25].

Since $NbSe_2$ possesses a superconducting nature, it was decided to study their electrical properties. In this research paper attention has been paid to the resistivity measurements with high temperature and high pressure on single crystals of $NbSe_2$ grown by a chemical vapour transport technique. The layered compounds are indeed anisotropic and there is a great variation in the anisotropy ratio amongst them. Measurements of c-axis resistivity of $NbSe_2$ in the temperature range 313K – 423K have also been undertaken. The determination of anisotropy ratios and their variation in the temperature 313K – 423K have been carried out and the results have been presented and discussed.

2. Experimental

The single crystals of Niobium Diselenide ($NbSe_2$) were grown by the chemical vapour transport (CVT) technique using iodine as a transporting agent. For the measurements of resistivity perpendicular to growth axis () in the temperature range of 303 K to 423 K, the high temperature resistivity set up manufactured by Scientific Equipments, Roorkee was used.

The experimental set up for the measurements of resistivity normal to the basal plane was prepared by USIC, Sardar Patel University. The sample is mounted on the sample holder, which is then very carefully inserted into the sample chamber and then closed from the top. The sample chamber assembly is introduced into a vertical single zone furnace and then the temperature is raised. The temperature at the sample is measured with the help of Cr-Al thermocouple kept in vicinity of the sample. Starting from room temperature (303 *K*), the temperature of the sample is increased slowly to 503*K*, in steps of 10 *K* and at each step the corresponding value of the resistivity of the sample is evaluated. To avoid excessive heating of the sample chamber, cold water is circulated around it with the help of copper tubing, which cools it. The resistance parallel to growth axis was measured at an interval of 10 *K* temperature with the help of a digital multimeter.

In order to achieve higher pressure, Bridgman suggested the use of two opposed anvil [26]. In the basic design of the anvil, the truncated anvils of tungsten carbide are supported by steel binding rings with an interference-fit to apply inward acting redial stresses. This design uses Bridgman's principle of "massive support". Bridgman anvil can be readily used up to about 10 GPa [27]. The sample is in the form of a thin disk surrounded by a gasket, normally of pyrophyllite material [28] with talc as a pressure transmitting medium. A four probe method was used to measure the resistance of the zirconium sulphoselenide single crystals up to 8 GPa pressure.

Results & Discussion

The graph of log versus 1000/*T* are shown in **Figure 1.** As shown in the **Figure 1**, the resistivity decreases with increase in the temperature. From the slope of the straight-line portion of the graphs of **Figure 1**, the activation energies of the charge carriers were calculated using the formula:

$$E_a = 2.303 \times k_B \times slope \qquad (1)$$

where $k_B = 8.602 \times 10^{-5}\ eV/K$

The resistivity at each temperature was determined. The results obtained from the above data are shown in **Figure 2** in form of a graph of log $_{\parallel}$ versus 1000/*T*. From these graphs, it is learnt that in the temperature range 303 *K* to 423 *K*, as the temperature increases, the resistivity decreases. Beyond 423 K the resistance increase with increasing temperature which indicates it's conducting behaviour. As release the temperature it comes again in normal condition. We repeated this experiment for many times, the results remain same. A careful study of the best fit in **Figure 1** and **Figure 2** shows that in comparison to the resistivity along the basal plane, the resistivity is considerably high in a direction normal to the basal plane. From the slope of the straight-line portion of the graph of log$_{\parallel}$ versus 1000/*T*, the values of activation energy were calculated using equation (1).

The value activation energy for normal to the basal plane is 0.054 eV and along the basal plane is 0.241 eV. The values of the activation energies obtained confirm that $NbSe_2$ single crystals behave as extrinsic semiconductors in the temperature range of 303 *K* to 423 *K*.

For the single crystals belonging to the layered structure family, the anisotropy of the transport properties is an interesting phenomenon. The single crystals of the layered materials behave extremely two-dimensional as far as their mechanism is concerned. They are very difficult to handle because planes slide easily along the layers held together by the very weak Van der Walls bonding. Intuitively and inquisitively enough one might also expect similar anisotropies in the electrical properties i.e. conductivities or mobilities.

Although layered compounds are indeed anisotropic, there is a great variation in the anisotropy ratio among them. In some cases, anisotropy factors up to 10^6 have been reported. The measurements of resistivity along the basal plane ⊥ρ and normal to the basal plane ||ρ in the temperature range 303 K to 423 K were used to determine the anisotropy ratio for the single crystal of $NbSe_2$.

The anisotropy ratio can be defined as,

$$\gamma = \frac{\rho_{\parallel}}{\rho_{\perp}} \qquad (2)$$

The dependence of g on the reciprocal of temperature is shown in Figure 3. It is seen from the graph that the anisotropy ratio g depends on temperature for all the crystals.

The values of activation energy are low. This shows that the conduction in this temperature ranges is due to transformation from its impurity levels lying within the band gap of these materials to be conduction band.

The graph of Resistance vs. Pressure for as grown single crystals using Bridgman anvils is shown in **Figure 4.** As shown in Figure 4, resistance decreases continuously as pressure increases. No phase transition is occurring in as grown crystals up to 8 GPa. However the samples are becoming more conducting in nature at higher pressure.

The electrical resistance decreases by an order of magnitude in going from atmospheric pressure to 8 GPa pressure. The conductivity obey Arrhenius law at all pressure:

$R = R_0 \exp(-E_g / 2k_BT)$ and $R' = R_0 \exp(-E'_g / 2k_BT)$ where R = resistance at high zpressure and E'_g = the band gap at high pressure. Accordingly

$\ln(R'/R) = [(E'_g - E_g)/2k_BT]$ and from the Arrhenius law, the band gap of as grown crystal is found decreases with increase in the pressure, which indicate the semiconducting nature. The value of band gap at atmospheric pressure is 1.43 eV and at 8 GPa pressure this value is 1.32 eV. The decrease in band gap with increasing the pressure, the reason is the change in interatomic distance within layers that affect the value of band gap.

Conclusion

- The electrical resistivity perpendicular to c-axis as well as parallel to c-axis decreases with increasing temperature for NbSe2 single crystal suggesting their semiconducting nature in the temperature range 303 - 423 K.
- The anisotropy ratio decreases with increase temperature in the range 303 - 403 K for this crystal.
- Measurement of electrical resistance up to 8 GPa does not indicate the occurrence of any structural transition in them. The samples become more conducting as pressure increases.

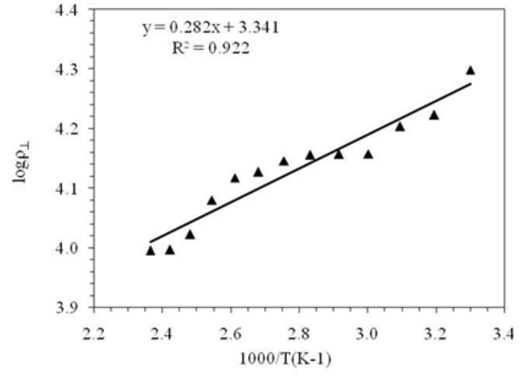

Figure 1: The graph of logρ⊥ vs 1000/T for NbSe2 single crystal.

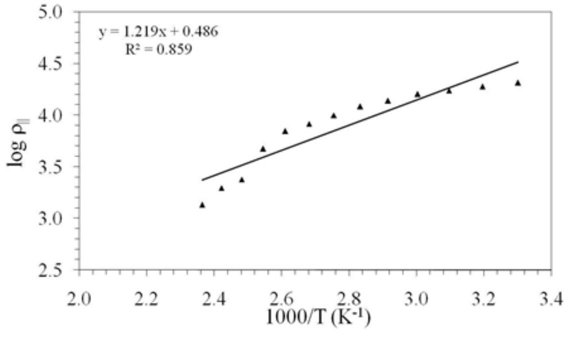

Figure 2: The graph of resistivity ll vs 1000/T for NbSe2 single crystal.

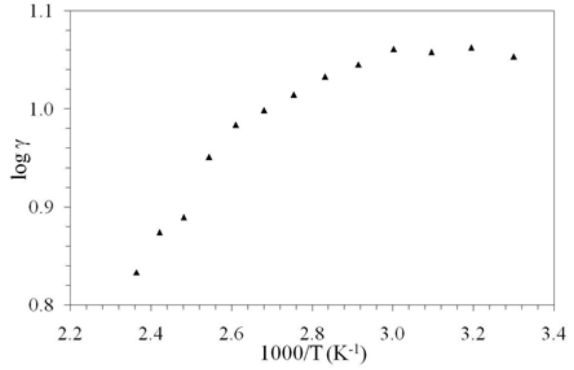

Figure 3: The graph of anisotropy ratio (γ) vs 1000/T for NbSe2 single crystal.

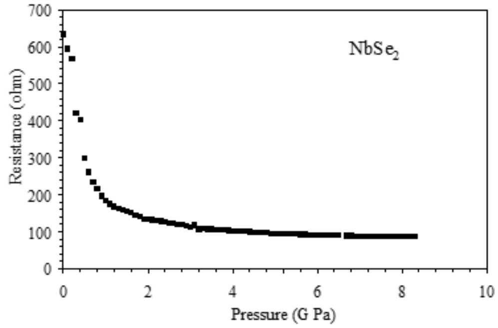

Figure 4: The graph of resistance vs pressure for NbSe2 single crystal.

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