PRAMANA — journal of physics

© Indian Academy of Sciences

Vol. 76, No. 6
June 2011
pp. 957–963

Charge density wave and superconductivity in 2H- and 4H-$NbSe_2$: A revisit

I NAIK[1,*] and A K RASTOGI[2]

[1]Department of Physics, North Orissa University, Baripada 757 003, India
[2]School of Physical Sciences, Jawaharlal Nehru University, New Delhi 110 067, India
*Corresponding author. E-mail: indrajit_naik@yahoo.co.in

MS received 3 July 2010; revised 11 October 2010; accepted 29 December 2010

Abstract. Good-quality hexagonal $NbSe_2$ single crystals were prepared. In 2H-$NbSe_2$, superconducting and charge density wave (CDW) transitions were found at $T_s = 7.4$ K and $T_c = 35$ K respectively as reported previously. We have noticed that these two transitions are changed to $T_c = 42$ K and $T_s = 6.5$ K, in 4H-$NbSe_2$. Thermopower has shown clear anomaly at CDW transitions. The anisotropic upper critical field was calculated as ~3 and 6.3 for 2H- and 4H-single crystals around $t = 0.81$, where $t = T/T_s$, from resistivity and explained in terms of coherence length. From the relation, $H_{c2}(T) = H_{c2}(0)[1 - t^2]$, $H^l_{c2}(0)$ was calculated as ~8.15 T and 16.98 T at $t = 0.84$ in 2H-$NbSe_2$ and 4H-$NbSe_2$ respectively. However, $H^t_{c2}(0) = 2.68$ T for both single crystals.

Keywords. Transition metal compounds; superconductivity.

PACS Nos 72.80.Ga; 74.25.Op

1. Introduction

Group V transition metal dichalcogenide compounds (TMDC) with chemical formula MX_2, where M = V, Nb or Ta and X = S, Se and Te, have been studied extensively for layered structure, charge density wave (CDW) and superconductivity. 2H-$NbSe_2$ is a polymorph of $NbSe_2$. Its interesting point is the existence of superconductivity ($T_s = 7.4$ K) below the charge density wave (CDW) at 39 K [1,2]. Though the mechanism of these two transitions is the same, due to electron–phonon interaction, its origin is not understood till today. There are some reports which say that CDW develops because of the Fermi surface nesting [3] or the saddle points in the electronic band [4]. It is theoretically predicted that this CDW transition is frequently observed in low-dimensional (1D and 2D) metals. Its evidence in 2H-$NbSe_2$ is reported through neutron scattering [5], scanning tunnelling microscope [6], NMR [7] and X-ray diffraction [8]. This CDW transition is very sensitive to the crystal imperfection as is reported by measuring the resistivity in two different single crystals grown by CVT method [1].

The highest superconducting transition temperature reported in the group V transition metal dichalcogenides is ∼7.4 K is noticed in 2H-$NbSe_2$. Its superconducting parameters such as critical fields (H_{c1} and H_{c2}), coherence length (ξ) and penetration depth (λ) are also reported in clean single crystals [9]. The existence of two transitions (CDW and superconducting) in 2H-$NbSe_2$ is explained in terms of the density of states (DOS) in conduction band by Chu *et al* [10].

We have prepared single crystal polytypes of 2H- and 4H-$NbSe_2$ by CVT method to understand the microscopic nature of the compound. More than one polytype can be obtained in $NbSe_2$ by annealing it at different temperatures as reported by Kadjik and Jellinek [11]. Here, we report the low-temperature electrical resistivity, thermopower and upper critical field of 2H- and 4H-$NbSe_2$. We have calculated H_{c2} values of 2H-$NbSe_2$ from DC resistivity which are found to be very close to the reported results obtained from magnetization data [12].

2. Experimental details

Single crystals of 2H- and 4H-$NbSe_2$ were grown at 750 and 925°C respectively from polycrystalline compounds, made of high purity elements (Nb = 99.8% and Se = 99.999%) at 700 and 925°C, using vapour transport technique. The lattice constants (see table 1) were calculated from the room temperature powder X-ray diffraction data.

DC resistance measurements were carried out on single crystals from 2 to 320 K using the four-probe method of van der Pauw geometry [13]. The thermopower was measured with respect to Cu by reversing the temperature gradient at different temperatures and then absolute Seebeck coefficient was calculated by subtracting the thermopower of Cu.

Table 1. Room temperature lattice constants, resistivity, thermopower and superconducting and charge density wave transition temperature for different polytypes of $NbSe_2$.

Compound name	$NbSe_2$[a]	$NbSe_2$[a]
Symmetry (300 K)	4H	2H
Latice constant (a)	3.436 Å[b]	3.445 Å[b]
(c)	2 × 12.596 Å[b]	12.551 Å[b]
RRR value	21.0	66.7
ρ_{300} (Ω-cm) × 10^{-4}	11.4	0.68
T_s (K)	6.5	7.4
S_{300} ($\mu V/K$)	−9.16	−4.08
T_c (K)	42	35

[a] For single crystal.
[b] For polycrystalline compound.
T_s(K): Superconducting transition temperature.
T_c(K): CDW transition temperature.

3. Results and discussion

3.1 *Resistivity*

The temperature dependence of resistivity for 2H-$NbSe_2$ and 4H-$NbSe_2$ is shown in figure 1. For superconducting compounds, the residual resistance ratio (RRR) is defined as ρ_{300}/ρ_{T_s}, where ρ_{T_s} is the resistivity at superconducting transition temperature T_s and we have calculated ∼66.7 for 2H-$NbSe_2$. 2H-$NbSe_2$ exhibits superconductor and CDW transitions at 7.4 and 35 K respectively and the values are the same as in the previous result. We have found its room temperature resistivity to be $\sim 6.8 \times 10^{-5}$ Ω-cm.

For 4H-$NbSe_2$, we have calculated the RRR value as ∼21. This is smaller than the value of 67 obtained for 2H-$NbSe_2$. In 4H-$NbSe_2$, the superconducting and CDW transitions are noticed at 6.5 and 42 K respectively. The correlation of these two transitions observed in our two single crystals is consistent with the pressure effect on 2H-$NbSe_2$ [10]. Room temperature resistivity of 4H-$NbSe_2$ is found to be 11.4×10^{-4} Ω-cm. This is ∼15 times larger than that of 2H-$NbSe_2$. According to the free-electron model, this can be interpreted in terms of the mean free path length of charge carriers which is less in 4H-phase. From the mean free path length and the pressure effect on CDW, it is suggested that the electron density in the conduction band of 4H-$NbSe_2$ is more compared to 2H-$NbSe_2$ irrespective of their structure.

The resistivity is very high in our metallic compounds. This is quite common in transition metals and arises due to the inter-band scattering of electrons in two-band model. We believe a similar mechanism may be responsible in our case. Our resistivity data follow nearly T^3 dependence below CDW transition similar to the reported result [2].

3.2 *Seebeck coefficient*

In figure 2, we have plotted the temperature dependence of absolute Seebeck coefficient S for 2H- and 4H-$NbSe_2$. Around room temperature, the negative value of S in 4H-$NbSe_2$ is

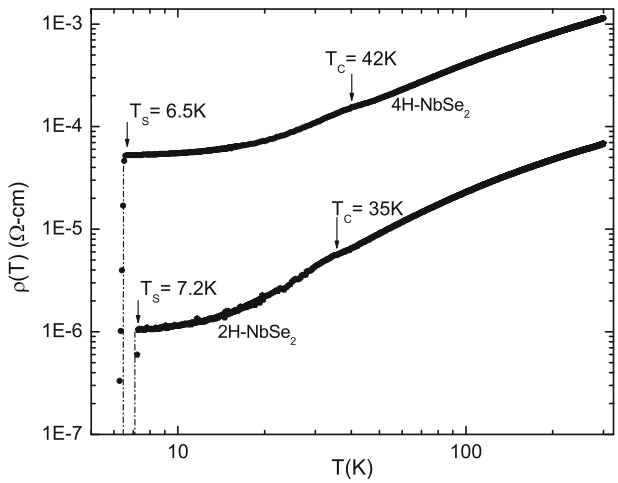

Figure 1. Resistivity vs. temperature on 2H- and 4H-$NbSe_2$.

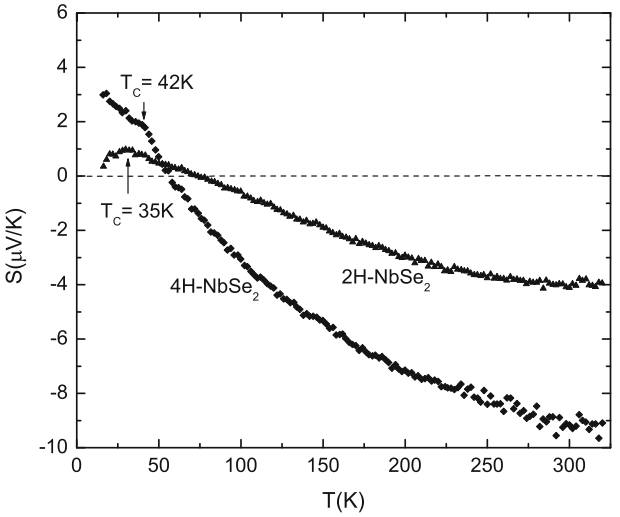

Figure 2. Temperature dependence of absolute Seebeck coefficient on 2H- and 4H-$NbSe_2$.

almost doubled compared to 2H-$NbSe_2$. As stated previously, the large value of S in 4H-$NbSe_2$ is due to the increase in the number density of charge carriers (electrons). As the temperature decreases, S of 2H-$NbSe_2$ increases slowly and changes sign from negative to positive around 75 K followed by a perceptible decrease at the onset of CDW transition on cooling. We have reported this in terms of the increase of electron mean free path length $l(\varepsilon)$ in two-band model [14]. But for 4H-$NbSe_2$, S rapidly increases with decreasing temperature and changes sign from negative to positive around 60 K followed by an anomaly, where S starts decreasing on cooling, at 42 K. We suggest that, this is due to the competition between the two average carriers in the presence of imperfections as we observed that the drop in S at CDW is large for larger RRR values.

3.3 *2H- and 4H-Polytype of $NbSe_2$*

Polymorphic phase transitions are possible in group V transition metal dichalcogenides by varying the preparative conditions. We have obtained two polytypes of $NbSe_2$, 2H with trigonal prismatic coordination and 4H with alternatively octahedral and trigonal prismatic coordinations of Nb atom (see figure 3). Figure 3 shows some possible models of 2H and 4H symmetry of $NbSe_2$. In these two polytypes, a CDW transition is followed by a superconducting transition at low temperature. Increase of resistivity and thermopower in 4H-$NbSe_2$ compared to 2H-$NbSe_2$ as explained earlier indicates that, the hexagonal polytypic between 2H and 4H does not affect the size of the conduction band much but the density of states is more in 4H-$NbSe_2$ and its CDW transition temperature is increased compared to 2H-$NbSe_2$. Moreover, the suppression of T_s in 4H-$NbSe_2$ is ascribed to be due to the increase of CDW transition.

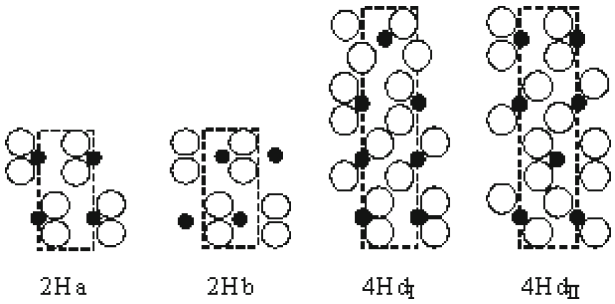

Figure 3. $1\,1\,\bar{2}\,0$ section diagram of 2Ha- and 2Hb-$NbSe_2$ and two possible models for 4Hd-$NbSe_2$. Transition-metal atom and selenium atom are represented by small solid circles and big open circles respectively.

3.4 *Upper critical field, H_{c2}*

$NbSe_2$ is a type-II superconductor and its upper critical field $H_{c2}(T)$ is determined from DC resistivity using the standard procedure. The $H_{c2}(T)$ values obtained from single crystals are quite different between the parallel and perpendicular to the layer as expected in large anisotropic compounds. The anisotropy of the upper critical field is calculated as $\sim$3 and 6.3 around $t = 0.81$, where $t = T/T_s$, in 2H- and 4H-$NbSe_2$ single crystals respectively. As can be seen in figure 4, the in-plane critical field H^l_{c2} has an unusual linear dependence on temperature and it increases rapidly in 4H-$NbSe_2$ compared to 2H-$NbSe_2$ single crystal. This linear dependence has been widely explained in the bulk type-II superconductor by Helfand and Werthamer [15]. We have obtained $H^l_{c2}(0) \sim 8.15$ T and 16.98 T from the empirical formula $H_{c2}(T) = H_{c2}(0)[1-t^2]$ at $t = 0.84$ for 2H- and 4H-$NbSe_2$ respectively.

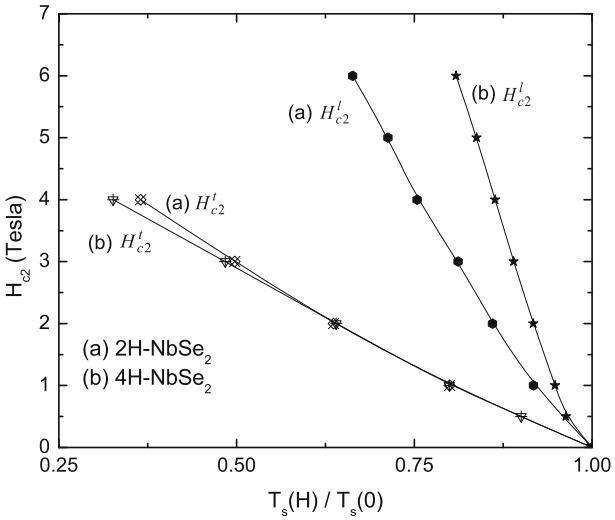

Figure 4. H_{c2} vs. $T_s(H)/T_s(0)$ for 2H- and 4H-$NbSe_2$.

However, H_{c2}^{t} is identical in two single crystals and its value is ~2.68 T at $t = 0.84$. Here, we have analysed our upper critical field data in terms of coherence length.

$NbSe_2$ is a layered compound belonging to the anisotropic type-II superconductor. Therefore, the relation between upper critical field (H_{c2}) and coherence length (ξ) is expressed as in eq. (1) for a uniaxial symmetry at the vicinity of T_s [16].

$$H_{c2} = \frac{\Phi_0}{2\pi\xi_t^2}(\cos^2\theta + \varepsilon^2 \sin^2\theta)^{-1/2}, \tag{1}$$

where θ is the angle between the unit vector normal to the conducting layer (or $\perp$ to MX_2 layer) and the applied magnetic field. But ε is the ratio between the two coherence length, i.e.,

$$\varepsilon = \sqrt{\frac{m_t}{m_l}} = \frac{\xi_l}{\xi_t}, \tag{2}$$

where

$$\xi_l = \frac{\hbar}{\sqrt{4m_l\alpha\,|\tau|}} \quad \text{and} \quad \xi_t = \frac{\hbar}{\sqrt{4m_t\alpha\,|\tau|}}.$$

Here ξ_l and ξ_t are the coherence length along parallel and perpendicular directions to the $NbSe_2$-layer. For layered structure, $\varepsilon \ll 1$ (i.e. $\xi_l \ll \xi_t$). In this case the electrons rarely jump between the layers. Therefore, the field normal to the layer is easily screened compared to other direction. When the magnetic field is applied perpendicular or parallel to the layer, eq. (1) reduces to

$$H_{c2}^{t} = \frac{\Phi_0}{2\pi\xi_t^2} \quad \text{and} \quad H_{c2}^{l} = \frac{\Phi_0}{2\pi\xi_l\xi_t}. \tag{3}$$

This clearly indicates that $H_{c2}^{l} \gg H_{c2}^{t}$ in layered structure and its coherence length decreases with the increase of H_{c2} below T_s. This is strongly agreed with our experimental data on single crystals. Therefore, we suggest that, the rapid increase of H_{c2}^{l} in 4H-$NbSe_2$ single crystal is due to the reduction of coherence length along c-axis.

4. Conclusion

Here we have observed two transitions at 7.4 and 35 K for superconductivity and CDW in 2H-$NbSe_2$. These two transitions were significantly shifted from their original positions in 4H-$NbSe_2$. A similar change is reported in 2H-$NbSe_2$ under pressure. Therefore we suggest that similar kind of mechanism, that the suppression of T_s and enhancement of CDW transition is related to the increase of density of states (DOS) in its narrow d-band, is responsible in our case.

The upper critical field H_{c2} was also calculated in these compounds below the zero-field superconducting transition temperature and explained in terms of the superconducting

coherence length. The reduction of coherence length along c-axis in 4H-$NbSe_2$ is because of the increase of H^l_{c2} below T_s. Our calculated values of $H^l_{c2}(0)$ and $H^t_{c2}(0)$ for 2H-$NbSe_2$ are quite similar to the results of Banerjee *et al* [9].

Acknowledgement

One of the authors (I Naik) acknowledges Council of Scientific and Industrial Research for the financial support during this work at Jawaharlal Nehru University, New Delhi, India.

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