Evidence for the complicated Fermi surface in 2H- and 4H-NbSe₂

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Abstract. In this study, we have found superconducting state (SC) at 7.4 and 6.4 K and charge density wave state (CDW) at 35 and 42 K in our 2H- and 4H-NbSe₂ single crystals, respectively. Besides this, there exists a positive magneto-resistance (MR) below the CDW transition temperature on both the crystals. Therefore, we have calculated their fractional change in MR i.e., $\Delta\rho/\rho_0$ around 8 K in $H_{\perp}$ plane of NbSe₂ and $H_{\parallel}$ plane of NbSe₂ configurations. Both single crystals show anisotropic $\Delta\rho/\rho_0$, which are described by Kohler's rule, two-band model and magnetic breakdown model. In the present scenario, the magnetic breakdown model explains our anisotropic $\Delta\rho/\rho_0$ better than other two models: Kohler's and two-band model. This model also established the presence of complicated Fermi surface on both single crystals.

Keywords. Transition metal compound; low-field transport; magneto-resistance.

1. Introduction

The chemical composition of transition metal dichalcogenide compounds (TMDC) is represented by MX₂, where M = transition metal atom and X = S, Se and Te, in which M atoms are sandwiched between two X layers. The NbSe₂ is one of the group-V TMDC, which shows polymorphic phase transitions by sintering at different temperatures [1–3]. One of its polytype known as 2H-NbSe₂ with trigonal prismatic coordination shows a charge density wave (CDW) followed by a superconducting (SC) transition at low temperature [3–9]. A relation is made, to some extent, between CDW and SC by studying transport properties on 2H-NbSe₂ with and without pressure [10–15]. Besides this, the scientific community has provided lots of information regarding the formation of CDW by X-ray diffraction, neutron diffraction and nuclear magnetic resonance (NMR), which elucidate the super-lattice formation or softening of longitudinal phonon branch along the wave vector ($a/3, 0, 0$) [16–20].

In this paper, we report the low temperature conduction behaviour of 2H- and 4H-NbSe₂ in which CDW and SC states coexist. Besides this, they show directional dependence of magneto-resistance (MR) below CDW state. From this MR anisotropy, we made an attempt to understand the topology of Fermi surface. Because, the Fermi surface area depends on the concentration of electrons, whereas the shape depends on the electron-lattice interaction.

2. Experimental

Single crystals of 2H- and 4H-NbSe₂ were achieved at 750 and 950°C, respectively, in chemical vapour transport

technique same as reported earlier [3]. The room temperature X-ray diffraction on polycrystalline compound provides the information about lattice constants i.e., $a \approx 3.445$ Å and $c \approx 12.551$ Å for 2H-NbSe₂ and $a \approx 3.436$ Å and $c \approx 2 \times 12.596$ Å for 4H-NbSe₂. The MR presented here was measured by applying magnetic field parallel and perpendicular to the single crystal plane of NbSe₂ along which current flows.

3. Results and discussion

3.1 Resistance

The temperature-dependent resistance with and without magnetic field on 2H- and 4H-NbSe₂ single crystals is plotted in the temperature range of 10–55 K as shown in figure 1. It clearly shows a positive MR below CDW transition temperature, which increases in 4H-NbSe₂ and almost constant in 2H-NbSe₂ on cooling. The inset of figure 1 shows the coexistence of SC and CDW states in temperature-dependent resistivity of 2H- and 4H-NbSe₂. Here, we have noticed large MR at low temperature analogous to the reported results, which depends strongly on crystal purity as well as temperature below CDW [4,7,21]. Therefore, we have measured the resistance below 15 K under different external magnetic fields and configurations. On both the single crystals, we have obtained significant large positive MR in $H_{\perp}$ plane of NbSe₂ configuration compared to $H_{\parallel}$ plane of NbSe₂ configuration. This directional dependence of MR in an anisotropic compound such as 2H- and 4H-NbSe₂ single crystals is expected to depend strongly on the conduction mechanism of charge particles associated with its Fermi surface. Therefore, we have described in further sections

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Figure 1. Temperature-dependent resistance with and without magnetic field on 2H- and 4H-NbSe₂. Inset figure shows the normalized resistivities for 2H- and 4H-NbSe₂.

the magneto-resistance by possible models to understand the conduction mechanism in the above compounds.

3.1a Kohler's rule: Kohler's rule is based on the idea of the presence of universal mean free path. Although, this rule is derived only for the isotropic model of closed Fermi surface, it describes the experimental data very well. Then, non-linear behaviour of $\Delta\rho/\rho_0$ in metallic compounds is described by the following expression,

$$\frac{\Delta\rho}{\rho_0} = f(H/\rho_0). \quad (1)$$

Suppose, if p is the exponent of the applied magnetic field H , then, depending on the value of p , metals are divided into two groups: group-1 if $2 \geq p \geq 1$ and group-2 if $p < 1$. In group-1, the $\Delta\rho/\rho_0$ rises to infinity with H/ρ_0 because of the movement of charge particle in a constant energy surface between the zones known as open orbit and saturation of $\Delta\rho/\rho_0$ at finite value of H/ρ_0 is due to the movement of charge particle within the single zone known as closed orbit.

To know the field dependence of MR, here, we have plotted $\Delta\rho/\rho_0$ around 8 K with respect to H/ρ_0 in a log-log scale known as Kohler's plot for 2H- and 4H-NbSe₂ single crystals as shown in figure 2. It shows straight-line behaviour within our applied magnetic field of 6 T. From the above plot, the exponent of H/ρ_0 is found as ~ 1.6 on both the compounds in $(\Delta\rho/\rho_0)_\perp$ i.e., $H_\perp$ plane of NbSe₂ irrespective of their magnitude in H/ρ_0 . But in $(\Delta\rho/\rho_0)_\parallel$ i.e., $H_\parallel$ plane of NbSe₂, the $\log(\Delta\rho/\rho_0) \sim \log(H/\rho_0)$ is well fitted by equation (1) above 2 T field with $p \sim 1.2$ and 0.2 in 2H- and 4H-NbSe₂, respectively (see figure 2). From these exponents, it is expected that the charge particles follow the path of open orbit in 2H-NbSe₂ independent of field configuration. But, as the stacking order increases along the c-axis in

Figure 2. The log-log plots of Kohler's law $\Delta\rho/\rho_0$ vs. H/ρ_0 at 8 K for 2H- and 4H-NbSe₂.

4H-NbSe₂, however, the constant Fermi surfaces between the zones get separated along that direction. As a result, charge particles follow the path of close orbit without much disorder in other directions. As the anisotropy plays a significant role in these compounds, we have adopted other methods to explain MR.

3.1b Two-band model: In this model, we have assumed two types of charge carriers having n_1 electron concentration and n_2 hole concentration, which gives rise to σ_{01} and σ_{02} conductivities, respectively. Then, the fractional change in MR, $\Delta\rho/\rho_0$, is represented as

$$\begin{aligned} \frac{\Delta\rho}{\rho_0} &= \frac{\rho - \rho_0}{\rho_0} = \frac{\sigma_0 - \sigma}{\sigma} \\ &= \frac{\left(\frac{H}{ec}\right)^2 \left(\frac{\sigma_{01}}{n_1} + \frac{\sigma_{02}}{n_2}\right)^2 \frac{\sigma_{01}\sigma_{02}}{(\sigma_{01} + \sigma_{02})^2}}{1 + \left(\frac{H}{ec}\right)^2 \left(\frac{n_1 - n_2}{n_1 n_2}\right)^2 \frac{(\sigma_{01}\sigma_{02})^2}{(\sigma_{01} + \sigma_{02})^2}}. \end{aligned} \quad (2)$$

For the present scenario of small external magnetic field, here, we have assumed equal density of states in both bands i.e., $n_1 = n_2 = n$, which implies that $\sigma_{01} = \sigma_{02} = \sigma_0/2$. Then, the above equation (2) can be simplified in SI unit as,

$$\frac{\Delta\rho}{\rho_0} = \frac{\sigma_0^2}{(2ne)^2} H^2 = \left(\frac{e\tau_0}{2m}\right)^2 H^2 = B H^2. \quad (3)$$

Here, $B = (e\tau_0/2m)^2$, which provides the intrinsic scattering time (τ_0) of the charge carriers because of zero intercept constant as seen from equation (3), is independent of the orientation of magnetic field H . Therefore, equation (3) is valid only for isotropic materials. Then, anisotropic effect

Figure 3. The $\Delta\rho/\rho_0$ vs. H^2 plot at 8 K for 2H- and 4H-NbSe₂ with $H_\perp$ plane of NbSe₂ i.e., $(\Delta\rho/\rho_0)_\perp$ and $H_\parallel$ plane of NbSe₂ i.e., $(\Delta\rho/\rho_0)_\parallel$. Inset figure shows $(\Delta\rho/\rho_0)_\parallel$ for both the single crystals.

on $\Delta\rho/\rho_0$ can be understood by considering $B_\perp$ and $B_\parallel$ with adjustable parameters a and b , respectively, as given below,

$$B_\perp = \frac{a\sigma_0^2}{(ne)^2} \quad \text{and} \quad B_\parallel = \frac{b\sigma_0^2}{(ne)^2}. \quad (4)$$

In figure 3, the $\Delta\rho/\rho_0$ is plotted with respect to H^2 . It clearly shows that $(\Delta\rho/\rho_0)_\parallel$ almost saturates above 3 T and $(\Delta\rho/\rho_0)_\perp$ increases continuously with magnetic field for both the single crystals which can be seen from the inset of figure 3. The saturation in $\Delta\rho/\rho_0$ indicates the unequal density of states in two bands i.e., $n_1 \neq n_2$ at high fields, which makes equation (2) independent of H^2 . On the other hand, for non-zero value of $B_\parallel$, the anisotropic effect is found to be ~ 9.89 at $H = 3$ T which increases with the fields. Though, the intercept constant has non-zero value in $\Delta\rho/\rho_0$ vs. H^2 plot, however, we have calculated same $\tau_0 \sim 1.48 \times 10^{-12}$ s in $(\Delta\rho/\rho_0)_\perp$ from $B_\perp$ for both single crystals. But from $B_\parallel$ of $(\Delta\rho/\rho_0)_\parallel$, τ_0 is found to be $\sim 5.11 \times 10^{-13}$ and 2.01×10^{-13} s below 3 T and $\sim 2.53 \times 10^{-13}$ and 1.38×10^{-13} s above 3 T in 2H- and 4H-NbSe₂, respectively. This variation in τ_0 with fields and non-zero intercept constant in $\Delta\rho/\rho_0$ vs. H^2 for $H_\parallel$ plane of NbSe₂ configuration can be understood better from the magnetic breakdown model as discussed in subsection 3.1c.

3.1c Magnetic breakdown model: In this model, the electron effectively undergoes an additional scattering due to complete neglect of small gaps when external magnetic field is increased. These gaps are appeared in the degenerate energy levels of conduction electrons by a peculiar charge ordering under the periodic lattice distortion called CDW in these compounds [22,23]. Then, the effective scattering time τ_{eff} of the electron is given by,

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_0} + \frac{1}{\tau_m}. \quad (5)$$

Here, τ_0 and τ_m are the scattering times for intrinsic and due to magnetic breakdown, respectively. Then the MR in SI unit can be stated as follows,

$$\begin{aligned} \frac{\rho}{\rho_0} - 1 &= \frac{m \{1 + (\omega_c \tau_{\text{eff}})^2\} / ne^2 \tau_{\text{eff}}}{m/ne^2 \tau_0} - 1, \\ &= \left(\frac{\tau_0}{\tau_{\text{eff}}} - 1 \right) + \left(\frac{e^2 \tau_0 \tau_{\text{eff}}}{4m^2} \right) H^2. \end{aligned} \quad (6)$$

Here $\omega_c = eH/2m$ is the cyclotron frequency. This is analogous to two-band model with $n_1 = n_2$ at $(\tau_0/\tau_{\text{eff}}) = 1$. The existence of $(\tau_0/\tau_{\text{eff}}) - 1$ in equation (6) provides the relative change in scattering time with fields. In $(\Delta\rho/\rho_0)_\perp$, τ_{eff} is found to be approximately same with τ_0 because $\tau_0/\tau_{\text{eff}} \approx 1.031$ for both single crystals, whereas τ_{eff} is affected significantly by the magnetic field above 3 T in $(\Delta\rho/\rho_0)_\parallel$. Though $\tau_0/\tau_{\text{eff}} \approx 1.002$ and 1.015 below 3 T and ≈ 1.016 and 1.016 above 3 T in 2H- and 4H-NbSe₂, respectively, the τ_{eff} is found to be same as τ_0 as presented in previous subsection. If we assume τ_{eff} below 3 T field is equal to τ_0 , then the reduction in τ_{eff} above 3 T field establishes the additional scattering points because the percentage of increase in $(\tau_0/\tau_{\text{eff}}) - 1$ is 700 and 7 in 2H- and 4H-NbSe₂, respectively. Conversely, the velocity of charge particles u_0 around 8 K is calculated as $\sim 1.9 \times 10^4$ m s⁻¹ from the classical equipartition of energy. As the mean free path relates with scattering time as $l = u_0 \tau$, the l is found to be $\sim 2.8 \times 10^2$ Å in $(\Delta\rho/\rho_0)_\perp$. But in $(\Delta\rho/\rho_0)_\parallel$, l is calculated as $\sim 9.7 \times 10$ Å and 3.8×10 Å below 3 T, which reduces to $\sim 4.7 \times 10$ Å and 2.6×10 Å above 3 T due to the appearance of new scattering points in 2H- and 4H-NbSe₂, respectively. This additional scattering time relates with the breakdown probability as $\tau_m = 1/\omega_c f(P)$, where the function f depends on the shape of the Fermi surface and Brillouin zone. Further, it can be realized that the appearance of different τ_{eff} or l along different directions at the same field is affected significantly only in $(\Delta\rho/\rho_0)_\parallel$ above 3 T, which implies the presence of complicated Fermi surface.

4. Conclusion

Here, we have adopted three methods: Kohler's rule, two-band model and magnetic breakdown model to explain the anisotropic behaviour of MR on 2H- and 4H-NbSe₂, respectively. Though, the Kohler's rule gives a qualitative idea about the conduction mechanism, it is not accepted because of the anisotropic nature of the compounds. Therefore, two-band model is used in which the anisotropic behaviour is understood, but fails to provide the clear picture about the saturation in $(\Delta\rho/\rho_0)_\parallel$ above 3 T magnetic field. Finally, we have used the magnetic breakdown model and able to get the origin for the anisotropic MR in our single crystals. This model has provided same τ_{eff} or l on both the single crystals within 6 T magnetic field in $H_\perp$ plane of NbSe₂ configuration because the dimension of ab-plane per formula unit was

approximately equal for both compounds. But in $H_{||}$ plane of NbSe₂ configuration, the τ_{eff} or l reduces significantly compared to other configuration with strong dependence on the stacking order along c-axis. However, this τ_{eff} or l is influenced greatly on 2H-NbSe₂ than 4H-NbSe₂ by the field above 3 T due to the additional scattering points. Therefore, the appearance of $\tau_m = 1/\omega_c f(P)$ in $H_{||}$ plane of NbSe₂ configuration and absence in $H_{\perp}$ plane of NbSe₂ configuration within 6 T magnetic field along with unequal scattering times between them indicate the existence of complicated Fermi surface on both the single crystals.

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