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The effect of a charge-density wave transition on the transport properties of 2H-NbSe$_2$

Lin-jun Li[1], **Zhu-an Xu**[1,3], **Jing-qin Shen**[1], **Li-min Qiu**[2] **and**
Zhi-hua Gan[2]

[1] Department of Physics, Zhejiang University, Hangzhou 310027, People's Republic of China
[2] Institute of Refrigeration and Cryogenic Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

E-mail: zhuan@css.zju.edu.cn

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Abstract

Single crystals of two-dimensional 2H-NbSe$_2$, which undergoes a superconducting transition at $T_c = 7.2$ K and a charge-density wave (CDW) transition at $T_{CDW} = 30$ K, were synthesized. Measurements of the resistivity, Hall coefficient and magnetoresistance (MR) versus temperature were performed on NbSe$_2$ crystals with different resistance residual ratios (RRR $= R(300\ \mathrm{K})/R(8\ \mathrm{K})$), chosen from different batches. The superconducting transition temperature hardly changes with the RRR, while the MR and Hall coefficient are strongly dependent on the RRR values of the samples. Moreover, the temperature and field dependence of the MR violate Kohler's rule, indicating that the scattering times of the charge carriers are no longer isotropic. A steep decrease of the Hall coefficient R_H below 50 K is only observed for the high quality sample; this can be interpreted in terms of a drastic increase of the mean free path for the electron-type charge carriers. The effect of the CDW transition on the Hall coefficient is discussed using a two-band model and a sharp change in the scattering rate on an electron-like orbit below T_{CDW} is suggested.

1. Introduction

Metallic transition-metal dichalcogenides which crystallize in the trigonal prismatic 2H lamellar structure have been the subject of intensive work for many years. Among these compounds, 2H-NbSe$_2$ is well known for undergoing both a charge-density wave (CDW) transition ($T_{CDW} = 33$ K) and a superconducting transition ($T_c = 7.2$ K). Renewed interest in superconducting dichalcogenides arose from their similarity to high temperature

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[3] Author to whom any correspondence should be addressed.

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superconducting cuprates. Both are layered, highly anisotropic materials that are often described in terms of a quasi-two-dimensional (2D) Fermi surface (FS) in their normal state. The mechanism for the coexistence of the two competitive orders in $NbSe_2$ is still under debate. Possible candidates include a simple Fermi surface (FS) nesting [1] or FS nesting with strong electron–phonon coupling effects [2, 3] and a van Hove singularity or saddle point driven CDW [4]. Transport measurements can detect CDW induced electronic structure changes and it has already been found that the sample quality influences the CDW transition [5].

In this paper, we report a comparative study of transport properties of $NbSe_2$ crystals with different qualities. The temperature dependences of the resistivity (ρ) and the Hall coefficient (R_H) indicate that the sharp decrease of R_H around 50 K is closely related to CDW induced electronic structure changes while the superconducting properties are hardly influenced by these changes. The transport properties are discussed in the framework of a two-band model. A drastic change in scattering rate on an electron-like orbit accompanying the CDW transition is suggested and the relationship with the driving mechanism of the CDW instability in $NbSe_2$ is discussed.

2. Experimental details

Single crystals of 2H-$NbSe_2$ were grown by the standard iodine vapour transport method. Stoichiometric amounts of 99.9% pure Nb and 99.99% pure Se powders, together with a transport agent (iodine), were mixed and placed in one end of a quartz tube, which was then evacuated and sealed. The sealed quartz tube was heated up in a temperature gradient furnace for one week. The charge-zone and growth-zone temperatures were 800 and 725 °C respectively. The crystals obtained by this method were in the form of thin platelets with mirror-like surfaces perpendicular to the *c*-axis direction. The crystal quality may differ from batch to batch due to the slightly different growing conditions.

The structure of the 2H-$NbSe_2$ was confirmed by means of x-ray diffraction patterns. The average *c*-axis lattice constant is 12.56 Åand its variation is about 0.03 Å for the six samples checked. The in-plane resistivity was measured by the standard four-probe method and the Hall effect was measured by applying a 5 T magnetic field in a Quantum Design PPMS-9 system. The resistivity measurements found that the resistance residual ratio ($\mathrm{RRR} = R(300\ \mathrm{K})/R(8\ \mathrm{K})$) for the samples from different batches varies from 10 to 30.

3. Results and discussion

Figure 1 shows the temperature dependence of the in-plane resistivity for two typical $NbSe_2$ samples, labelled as samples B1 and B2, whose RRR values are 13.0 and 27.0 respectively. The inset of figure 1 shows an enlarged plot of ρ–T curves around $T = 30$ K. Although the RRR values vary from 10 to 30 for different samples, the superconducting transition temperatures are nearly the same. The mid-point transition temperature T_c is 7.2 K and the width of the transition is less than 0.1 K, indicating a sharp superconducting transition. However, the broad hump around 30 K in the ρ–T curve, which is believed to be caused by the hidden CDW transition, is only observed in the samples with larger RRR—for example, sample B2. Previous reports [5] have already found that such a CDW transition induced hump structure in the ρ–T curve can only be observed for high quality $NbSe_2$ crystals.

Figure 2 shows the temperature dependence of the Hall coefficient (R_H) for the typical samples B1 and B2. The inset shows the temperature dependence of the ratio of the mean free path of p-type charge carriers to that of n-type charge carriers estimated from the Hall effect

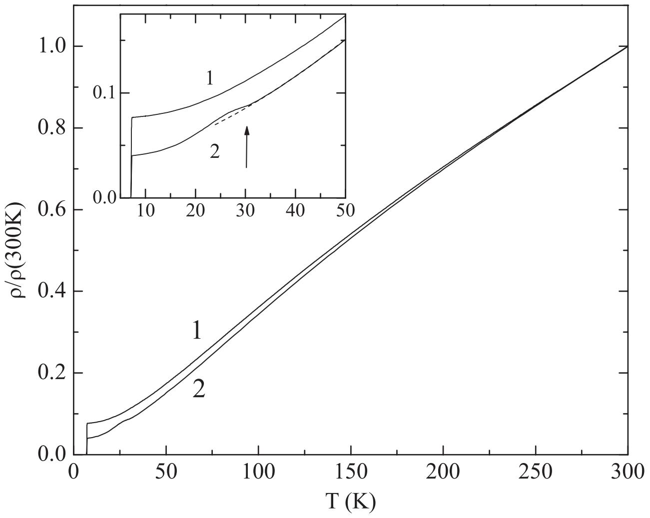

Figure 1. The temperature dependence of the resistivity for samples B1 and B2. The resistivity has been normalized to $\rho(300\text{ K})$. Inset: an enlarged plot of the ρ–T curves around $T \sim 30$ K. The arrow indicates the onset of the hump induced by CDW transition. The numbers 1 and 2 denote samples B1 and B2 respectively.

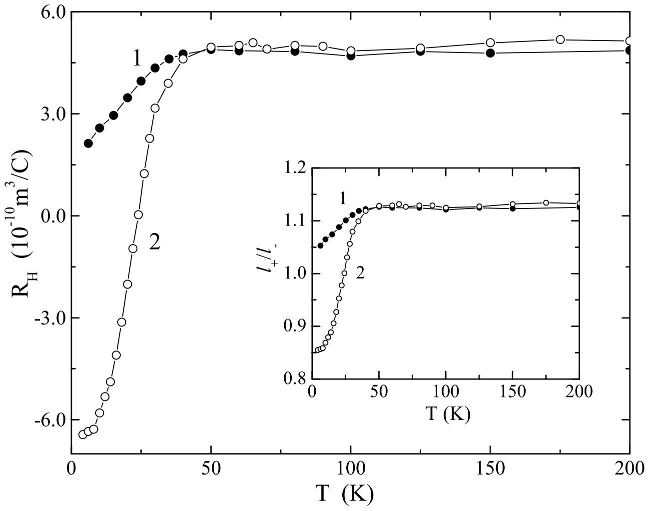

Figure 2. The temperature dependence of the Hall coefficient (R_H) for samples B1 and B2. The inset shows the temperature dependence of the ratio of the mean free path of the hole-type charge carriers to that of the electron-type charge carriers, l_+/l_-, estimated using equation (3). The numbers 1 and 2 denote samples B1 and B2 respectively.

data, which will be discussed later. Above 50 K, R_H for both samples is positive (p type) and almost independent of the temperature, like that for a typical conventional metal. Assuming a simple isotropic FS, the p-type charge carrier density estimated from the Hall coefficient ($R_H \sim 4.8 \times 10^{-10}$ m^3 C^{-1} at 100 K) is about 1.3×10^{22} cm^{-3}, consistent with previous reports [6, 7]. R_H starts to decrease when $T < 50$ K, but two samples exhibit a big difference in the dependence of R_H on T. R_H for sample B2 decreases rapidly and changes sign from

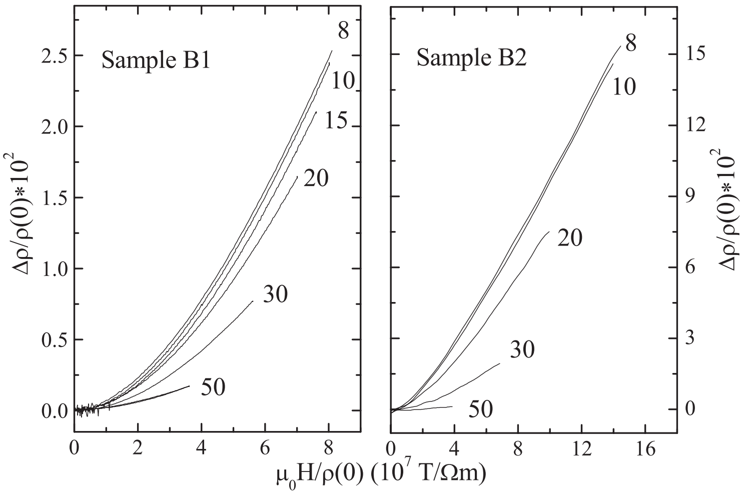

Figure 3. The Kohler plot of the magnetoresistance for samples B1 and B2. The numbers beside the curves denote the temperatures in units of K.

p type to n type at about 25 K. Meanwhile, R_H for sample B1 decreases slowly and remains positive even at $T = 8$ K. Recalling that the CDW transition induced hump structure in the ρ–T curve was only observed for the samples with larger RRR, we know that the sign reversal of R_H should also be closely related to the CDW transition.

The magnetoresistance (MR) of samples B1 and B2 was also measured for the temperature range between 8 and 100 K. Above 100 K, the MR is too small to detect. The MR for both samples B1 and B2 increases quickly with decreasing temperature. But compared to that of sample B2, the MR of sample B1 is generally small. Even at $H = 8$ T, the MR is only about 2.7% at $T = 8$ K. This is probably due to the small RRR value. It is well know that semiclassical transport theory predicts Kohler's rule to hold if there is a single type of charger carrier and the scattering time is isotropic on the FS [8]. Kohler's rule is expressed as

$$\frac{\Delta\rho(H,T)}{\rho(0,T)} = F(\omega_c\tau) = f\left(\frac{H}{\rho(0,T)}\right) \tag{1}$$

where ω_c is the cyclotron frequency, τ the scattering time, $\rho(0,T)$ the zero-field resistivity and $\Delta\rho(H,T) \equiv \rho(H,T) - \rho(0,T)$. The corresponding plots are known as Kohler plots. Figures 3(a) and (b) show the Kohler plots of the MR for samples B1 and B2. It is obvious from figure 3 that $\frac{\Delta\rho(H,T)}{\rho(0,T)}$ versus $\frac{H}{\rho(0,T)}$ cannot be scaled to a universal curve, which means that Kohler's rule is violated for $NbSe_2$. Both the temperature dependent Hall coefficient and the violation of Kohler's rule could be related to the complicated FS of $NbSe_2$.

Band calculations [9, 10] have predicted a complex FS for $NbSe_2$ which consists of a small hole-like closed pocket, two hole-like cylinders and two electron-like cylinders. Recent angle resolved photoemission spectroscopy (ARPES) studies have led to the detection of all portions of the predicted FS [10, 11]. Since $NbSe_2$ is a multi-band metal, let us assume that there are two FS sheets with dominant carriers of opposite signs. Following Ong's geometrical picture of two-dimensional Hall conductivity [12], the Hall coefficient of $NbSe_2$ in a weak magnetic field can be expressed as

$$R_H = \frac{2\pi d(l_+^2 - l_-^2)}{e[(k_F^+ l_+)^2 + (k_F^- l_-)^2]} \tag{2}$$

where $k_F^{\pm}$ and $l_{\pm}$ are the Fermi vector and the mean free path for electrons and holes; d is the space between conducting layers. Here, $l_{\pm}$ is assumed to be isotropic for each band. From equation (2), it can be readily concluded that a drastic increase in l_- below T_{CDW} could lead to a sign reversal of R_H without any modification in the FS. Our result is consistent with this scenario. Sample B2, with a higher RRR value, has a much larger enhancement of the negative Hall signal and an obvious hump in its ρ–T curve around 30 K, suggesting that the sample quality, as indicated by the mean free path of the charge carriers, plays an essential role in determining the transport properties at low temperature. Bel *et al* [7] observed a large quasi-particle contribution to the Nernst effect in the normal state for NbSe$_2$ and considered that this is the consequence of this scenario for the thermoelectric coefficients.

From equation (2), the ratio of the mean free path of holes to that of electrons can be estimated from the measured Hall coefficient data. The average c-axis lattice constant for samples B1 and B2 is 12.56 Å. So let $d = 12.56$ Å and assume that $2k_F^+ = 2k_F^- = 0.69$ Å^{-1} [13]; then we have

$$\frac{l_+}{l_-} = \sqrt{\frac{1 + 2.42 \times 10^8 \times R_H}{1 - 2.42 \times 10^8 \times R_H}}. \tag{3}$$

From the $R_H(T)$ data for the two samples, we can get the dependence of l_+/l_- on the temperature. The inset of figure 2 shows l_+/l_- versus T for samples B1 and B2. At high temperature ($T > 60$ K), the values of $l_{\pm}$ for samples B1 and B2 are similar, so the values of R_H are also very close to each other. At low temperature, the increase in mean free path length is usually limited by the impurity scattering. The lower RRR value of sample B1 means that there are more defects or impurities in sample B1, so the drastic increase in l_- below T_{CDW} is limited. This could explain why the decrease of R_H in sample B1 is much less drastic below T_{CDW} than that in sample B2. It may be concluded that the CDW transition is accompanied with a sharp change in the scattering rate on an electron-like orbit. This result provides new input for understanding the driving mechanism of the CDW instability in NbSe$_2$. A drastic change in scattering rate is naturally expected in the model proposed by Rice and Scott in which the existence of saddle points close to the Fermi surface drives the formation of the CDW [4]. The scattering rate is reduced by removing electrons from the vicinity of the saddle points where in the normal phase they are strongly scattered. It should also be noted that Rossnagel *et al* concluded from their ARPES study [10] that CDW formation seems not to be due to saddle points. The driving mechanism of the CDW instability in NbSe$_2$ merits further study.

In conclusion, the resistivity, Hall effect and magnetoresistance of two NbSe$_2$ samples with different RRR values show that the superconducting properties hardly change with the RRR, but the hump structure in the ρ–T curve around 30 K and the sign reversal of R_H are only observed for the high quality sample. The MR is larger for the sample with the higher RRR value, but the temperature and field dependence of the MR violate Kohler's rule despite the sample quality. The influence of the CDW transition on the resistivity and Hall effect is discussed in a two-band model. The strong temperature dependence of the Hall coefficient R_H below 60 K and the sign reversal of R_H at 25 K can be explained in terms of a drastic increase of l_- induced by the CDW transition, which is consistent with the model of a saddle point driven CDW [4].

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References

[1] Wilson J A 1977 *Phys. Rev.* B **15** 5748
[2] Doran N J *et al* 1978 *J. Phys. C: Solid State Phys.* **11** 699
[3] Nishio Y *et al* 1994 *J. Phys. Soc. Japan* **63** 156
[4] Rice T M and Scott G K 1975 *Phys. Rev. Lett.* **35** 120
[5] Iwaya K *et al* 2003 *Physica* B **329–333** 1598
[6] Lee H N S *et al* 1969 *J. Appl. Phys.* **40** 602
[7] Bel R, Behnia K and Berger H 2003 *Phys. Rev. Lett.* **91** 066602
[8] See, e.g., Ziman J M 1963 *Electrons and Phonons* (London: Clarendon) p 490
[9] Corcoran R *et al* 1994 *J. Phys.: Condens. Matter* **6** 4479
[10] Rossnagel K *et al* 2001 *Phys. Rev.* B **64** 235119
[11] Yokoya T *et al* 2001 *Science* **294** 2518
[12] Ong N P 1991 *Phys. Rev.* B **43** 193
[13] See, e.g., Tonjes W C *et al* 2001 *Phys. Rev.* B **63** 235101