Resistive anisotropy of candidate excitonic insulator Ta$_2$NiSe$_5$ under pressure

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Abstract. We have measured anisotropic electrical resistivity of quasi-one-dimensional Ta$_2$NiSe$_5$ single crystals under pressure. While the in-plane anisotropy is almost pressure independent, the inter-plane one greatly decreases at $P_c \sim 3$ GPa accompanied by a pressure-induced semiconductor-semimetal transition. Nevertheless, a similar anomaly in the temperature dependence of in-plane anisotropy has been observed in each phase. This anomaly in the low-pressure phase below $P_c$ is regarded as an excitonic transition, and thus both of these anomalies are suppressed with increasing pressure. These results suggest that the suppression of the excitonic binding energy with pressure is caused by the increase of free carrier densities and the inter-plane conductivity.

1. Introduction

Phase transitions involving collective electronic states, such as charge-density wave (CDW) and superconductivity, are intriguing research topics in condensed matter physics. In real materials, a CDW transition is often observed in organic conductors and transition metal chalcogenides because of the low-dimensionality of these systems. The effect of reduced dimensionality can also lead to another novel electronic instability known as an excitonic insulator, which is theoretically predicted to be formed close to the border between semiconductor with small energy gap and semimetal with small band overlap [1, 2]. An exciton is a bound pair of hole and electron through the Coulomb attraction. If the excitonic binding energy $E_b$ is larger than the energy gap $E_g$, the system undergoes an excitonic phase transition due to the spontaneous formation of excitons. Furthermore, it is known that the reduced effective dimensionality leads to an enhancement of $E_b$, which stabilizes the excitonic state [3]. In an indirect gap system, the excitonic insulator phase is characterized by a finite $\vec{q}$ periodical lattice distortion, where $\vec{q}$ is a vector connecting the top of the valence band and the bottom of the conduction band. Indeed, the possibility of excitonic gap formation has been discussed in $1T$-TiSe$_2$ and TmSe$_{1-x}$Te$_x$ with
an indirect gap [4–7], however, its experimental identification remains controversial. Since the possible excitonic transition in these compounds is accompanied by a finite \( \vec{q} \) periodical lattice distortion, it is difficult to distinguish from other scenarios such as a charge density wave and a band Jahn-Teller transition.

In recent years, a narrow direct-gap semiconductor Ta\(_2\)NiSe\(_5\) attracts much attention as a prime candidate for the excitonic insulator. Ta\(_2\)NiSe\(_5\) forms layered structures with Ni single and Ta double chains composed of corner-shared NiSe\(_4\) tetrahedra and edge-shared TaSe\(_6\) octahedra, respectively. These layers are stacked by van der Waals interaction along the \( b \) axis. At ambient pressure, Ta\(_2\)NiSe\(_5\) has a finite direct gap at \( \Gamma \) point \((\vec{q} = 0)\) with an energy gap \( E_g \sim 0.1 \) eV and exhibits a second-order semiconductor to insulator transition at \( T_c \sim 326 \) K, accompanied by a structural transition from an orthorhombic to a monoclinic structure [8–10]. Angle-resolved photoemission spectroscopy measurement reveals a flattening of the valence band at \( \Gamma \) point and has a finite direct gap \((\vec{q} = 0)\) with an energy gap \( E_g \sim 0.1 \) eV reflecting quasi-one-dimensionality has been detected and furthermore the electronic phase diagram by chemical and physical pressure tuning the energy gap is similar to theoretical prediction [13]. In particular, the excitonic transition temperature \( T_c \) and semiconducting behavior are suppressed with pressure, and the first-order structural phase transition occurs at \( P_c \sim 3 \) GPa. It is expected that application of hydrostatic pressure can lead to increase of the dimensionality of the system and may destabilize the excitonic phase. In this study, we have measured the resistivity anisotropy under pressure to investigate the influence of anisotropy change on the formation of the excitonic phase.

2. Experimental

Single crystals of Ta\(_2\)NiSe\(_5\) were grown by the chemical vapor transport method [13]. Ta\(_2\)NiSe\(_5\) single crystals were cut into rectangular pieces along the three principal axes with typical dimensions about 0.5 mm \( \times \) 0.1 mm \( \times \) 0.02 mm. Electrical resistivity was measured by the standard four-probe method by using a GM refrigerator. High-pressure resistivity measurements were performed using an opposite anvil cell [14]. Glycerin was used as a pressure transition medium. The pressure inside the pressure cell was determined by the ruby fluorescence method. In this experiment, the pressure differences between room and low temperature were at most 0.6 GPa.

3. Results and discussion

Figure 1(a) shows the temperature dependence of the electrical resistivity of Ta\(_2\)NiSe\(_5\) at ambient pressure. Here the resistivities with current along the \( a \), \( b \) and \( c \) axes are denoted as \( \rho_a \), \( \rho_b \) and \( \rho_c \), respectively. For all directions, \( \rho \) shows a semiconducting behavior. A clear anomaly is observed at \( T_c \) in \( \rho_a \) and \( \rho_b \) while the anomaly in \( \rho_c \) is less visible, which is consistent with previous reports [13, 15]. Reflecting the quasi-one-dimensional structure of Ta\(_2\)NiSe\(_5\), the temperature dependence of \( \rho \) is anisotropic at high temperature (see also Fig.2), however, this anisotropy of resistivity becomes weaker below \( T_c \). As we will discuss later, this was suggested to be the characteristic of the excitonic transition [13]. To estimate an activation energy \( E_g \), we use the Arrhenius equation \( \rho = \rho_0 \exp(E_g/2k_B T) \), where \( k_B \) is the Boltzmann constant. \( E_g \) derived from the slopes of the dashed lines in the inset of Fig.1(a) yields \( \sim 0.1 \) eV within the temperature range above \( T_c \), which is independent of the direction of current flow. At temperatures below \( \sim 80 \) K, the temperature dependence of \( \rho \) does not follow the activation behavior, but is dominated by a variable-range hopping. In this regime, resistivity is characterized by \( \rho = \rho_0 \exp(T_0/T)^{\alpha} \), where \( \alpha \equiv 1/(d + 1) \) is a parameter depending on the spatial dimension \( d \). As shown in Figs. 1(b) and 1(c), this model gives a better description of the low temperature resistivity even though the space dimensionality is virtually indistinguishable.
Figure 1. (a) Temperature dependence of electrical resistivity with current along \(a\) (circles), \(b\) (squares) and \(c\) (triangles) axes. The inset shows Arrhenius plot \(\ln \rho\) versus \(1000/T\). The dashed line represents the linear fits of the data above \(T_C\). \(\ln \rho\) versus (b) \(1/T - \frac{1}{3}\) and (c) \(1/T - \frac{1}{4}\) in a temperature range of 20-200 K.

Next, we focus on the pressure dependence of electrical resistivity at room temperature. As shown in the upper panel of Fig. 2, the normalized resistivity is first suppressed continuously through the application of pressure and then shows discontinuous change at \(P_c \sim 3\) GPa. While the inter-plane resistivity (\(\rho_b\)) largely decreases at \(P_c\), the in-plane resistivity (\(\rho_a\) and \(\rho_c\)) increases slightly. As a result, the inter-plane anisotropy \(\rho_b/\rho_a\) becomes half of that at ambient pressure at \(P_c\), on the other hand, in-plane anisotropy \(\rho_c/\rho_a\) is almost pressure independent. It is worth noting that the structural transition at \(P_c\) leads a decrease in the \(b\) axis lattice constant by 6% and an increase in the \(a\) and \(c\) axes lattice constant by \(\sim 1\%\) [10]. Therefore, the shrinkage of the interlayer distance causes an increase of interlayer conductivity, which may give rise to a dimensional change in this system.

The temperature dependences of the resistivity for each pressure are shown in Fig. 3. At 2.3 GPa, the resistivities along all the axes show semiconducting behavior. With lowering temperature from \(T_c\), the resistivity anisotropy becomes weak, but apparent again particularly below \(\sim 100\) K, where the system enters the variable range hopping regime (see Fig. 3(a)). All these features are similar to those observed at ambient pressure. At pressures above \(P_c\), the temperature dependences of \(\rho_a\), \(\rho_b\) and \(\rho_c\) are quite different from those of below \(P_c\) (see Figs. 3(b), 3(c) and 3(d)). The resistivity along the \(a\) axis exhibits an upward anomaly at \(T^* \sim 175\) K at 3.9 GPa. In contrast, the resistivities along the \(b\) and \(c\) axes shows a downward anomaly at \(T^*\). With further increasing pressure, the overall resistivities at all axes decrease in magnitude.
Figure 2. Pressure dependence of (a) normalized resistivity $\rho(P)/\rho(0 \text{ GPa})$ and (b) anisotropy ratio at room temperature. $\rho_b/\rho_a$ and $\rho_c/\rho_a$ denote in-plane and inter-plane anisotropy, respectively. Solid lines are a guide to the eyes.

Figure 3. Temperature dependence of the electrical resistivity at various pressures with current along the three principal axes for (a) $P < P_c$ and (b)-(d) $P > P_c$. Vertical arrows indicate the transition temperature $T_C$ and $T^*$. The pressure noted here is an average of the pressure determined at room temperature and at the lowest temperature.

and change to a metallic behavior. In this pressure region, $T^*$ shifts to lower temperature and becomes less pronounced and is finally no longer discernible.

At a glance, the temperature dependence of $\rho$ is quite different beyond $P_c$, including the pressure-induced change from semiconductor to semimetal. However, the phase transition at $T^*$
represents similarities with that at $T_c$. First, in-plane anisotropy, which corresponds to $\rho_c/\rho_a \sim 6$ above the transition temperature, starts to decrease with lowering temperature as shown in Fig.4 (a). Second, as summarized in Fig.4 (b), negative pressure coefficients for both $T_c$ and $T^*$. These results suggest that $T^*$ is of the same origin as $T_c$, even though the occurrence of the first-order phase transition at $P_c$. Remembering that the excitonic phase is realized below $T_c$, we suggest that the suppression of both $T_c$ and $T^*$ upon application of pressure results from the combined effects of the increase of free carrier densities and inter-plane conductivity.

4. Conclusion
We have measured high-pressure anisotropic electrical resistivity of a candidate material for excitonic insulator Ta$_2$NiSe$_5$. The semiconducting behavior and the excitonic transition temperature $T_c$ are suppressed with increasing pressure. The inter-plane anisotropy reflecting the quasi-one-dimensional structure becomes comparable to in-plane anisotropy across a critical pressure $P_c \sim 3$ GPa. However, the anomaly detected at $T^*$ above $P_c$ has a close resemblance to that at $T_c$, suggesting the spontaneous formation of excitons even in the high-pressure phase. These results deserve further high-pressure study to complete the phase diagram on Ta$_2$NiSe$_5$.

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