Electronic structure of $\text{Ta}_2\text{NiSe}_5$ as a candidate for excitonic insulators

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Abstract. We make the electronic structure calculations of $\text{Ta}_2\text{NiSe}_5$, known as a candidate for excitonic insulators where the semiconducting or semi-metallic ground state becomes unstable against the coherent formation of excitons. We use the generalized gradient approximation (GGA) in the density functional theory, where the Hubbard-type repulsive interaction $U$ is taken into account (GGA+$U$). We find that the material has a very simple quasi-one-dimensional (1D) electronic structure which relates to the formation of excitons. From the calculated partial density of states, band dispersion and spatial distribution of charge densities, we find in the first approximation that the conduction band is configured by the Ta 1D chain and the valence band is configured by the Ni-Se 1D chain.

1. Introduction

The idea of excitonic insulator was proposed about half a century ago [1]. The formation of excitons is driven by the Coulomb attraction between conduction-band electrons and valence-band holes. Condensed state of excitons (composite bosons) is called excitonic insulator.

$\text{Ta}_2\text{NiSe}_5$ is a new candidate for excitonic insulator, which has a layered structure stacked loosely by a weak van der Waals interaction. In each layer, Ni single chains and Ta double chains are running along the $a$ axis and the layers are aligned alternately along the $c$ axis. Se ions are coordinated around the Ni ions tetrahedrally and around the Ta ions octahedrally [2]. The resistivity shows a metal-like behavior above 550 K, while it becomes semiconductor-like below 500 K with an anomaly at 328K which is accompanied by a structural phase transition. Magnetic susceptibility exhibits diamagnetism with an anomaly at the same temperature (328K) found in resistivity [3]. The tight-binding band calculation suggests that the system is a semiconductor and has a direct gap at the $\Gamma$ point of the Brillouin zone [4]. X-ray photoemission spectroscopy (XPS) and cluster-model calculation for $\text{Ta}_2\text{NiSe}_5$ [5] indicate that the Ni site has the $d^9\text{L}$ character, where $\text{L}$ is a Se 4p hole. The flatness of the valence-band top observed by the angle-resolved photoemission spectroscopy (ARPES) experiment [5] suggests that the excitonic-insulator ground state is realized in $\text{Ta}_2\text{NiSe}_5$, where the excitons are formed by the Ni 3d-Se 4p holes and the Ta 5d electrons [5].

In this paper, motivated by such development in the field, we make the electronic structure calculations employing the WIEN2k code [6], where we use the generalized gradient approximation (GGA) in the density function theory, taking into account the Hubbard-type repulsive interaction (GGA+$U$) [7, 8]. Thereby, we make careful examination of the electronic structure of this material.
We will show from our calculations that the valence-band top and the conduction-band bottom are made by a very simple quasi-one-dimensional (1D) structure, despite its structural and band-dispersion complexity. The conduction band has a cosine-like 1D band, which is formed by the 1D Ta $5d_{xy}$ chains. The valence band top is formed by a hybrid Ni $3d_{zx}$ and Se(3) $4p_y$ orbitals, which are arranged alternately to form the 1D chain. The Ni-Se chain which connects with the neighboring two Ta 1D chains is effective to the formation of excitons. This simple quasi-1D electronic structure may give us a hint for the mechanism of the occurrence of the excitonic insulator.

2. Results of calculation

We use the experimental crystal structure of Ta$_2$NiSe$_5$ observed at room temperature, where the lattice constants are $a = 3.496$, $b = 12.829$ and $c = 15.641$ Å [2]. The symmetry of the lattice is monoclinic (space groups $C2/c$). The primitive unit cell contains four Ta ions, two Ni ions, and ten Se ions. All the Ta sites and Ni sites are crystallographically equivalent but there are three inequivalent Se sites, Se(1), Se(2) and Se(3) (see Fig. 1). In the self-consistent calculations, we use 506 $k$ points in the irreducible part of the Brillouin zone with an anisotropic sampling to achieve better convergence. Muffin-tin radii ($R_{MT}$) of 2.5, 2.33 and 2.06 Bohr are used for Ta, Ni and Se, respectively, and we assume the plane-wave cutoff of $K_{\text{max}} = 7/R_{MT}$. To improve the description for electron correlations in Ta $5d$ and Ni $3d$ orbitals, we use the rotationally invariant version of the GGA+$U$ method [7, 8], where we apply the same value of $U$ to Ta $5d$ and Ni $3d$ orbitals. We use the codes VESTA [9] and XCrySDen [10] for graphical purposes.

![Figure 1](image_url). The crystal structure of Ta$_2$NiSe$_5$. Thin solid line indicates the conventional unit cell.

2.1. Density of states

We calculate the density of states (DOS) and find that the system is a metal at $U = 0$ eV, but with increasing $U$, the band gap opens above $U \approx 2$ eV, making the system an insulator. From the partial DOS, we find that the Ta $5d$ band is located mainly above the Fermi level, while the Ni $3d$ and Se $4p$ bands are located mainly below the Fermi level, although some hybridization exists between the Ta $5d$, Ni $3d$ and Se $4p$ orbitals. We also calculate the orbital-decomposed partial DOS. We find that Ta $5d_{xy}$ orbital has much higher DOS than the other Ta $5d$ orbitals near the Fermi level. From the partial DOS of the Ni $3d$ orbitals, we find that Ni $3d_{zx}$ orbital has the highest DOS at the Fermi level. From the orbital-decomposed partial DOS of Se(1), Se(2) and Se(3), we find that Se(3) has much higher DOS than Se(1) and Se(2) near the Fermi level. Among the $4p$ orbitals of Se(3), we find that the $p_y$ orbital has the highest DOS near the Fermi level.
2.2. Band dispersion

The calculated band dispersion at $U = 3$ eV is shown in Fig. 2. We find that in contrast to the tight-binding calculation [4] the band structure of the GGA+$U$ has a smaller gap and the minimum of the gap occurs away from the $\Gamma$ point of the Brillouin zone. In Fig. 2(a), we compare our result with the result of the ARPES experiment [5]. We find that our result agrees reasonably well with ARPES near the X point. However, our result does not fit very well with ARPES near the $\Gamma$ point; in particular, the valence-band top of ARPES looks flatter than our GGA+$U$ result. The difference in the flatness of the band near the $\Gamma$ point may possibly be caused by the effects of exciton condensation, as was suggested in Ref. [5].

We also examine the weight of the orbitals on each of the band dispersions; a part of the results is shown in Fig. 2 (b) and (c). We find in Fig. 2(b) that the Ta 5$d_{xy}$ orbitals arranged along the $a$ axis form a 1D cosine-like band dispersion, which extends from the top of the conduction band at the X point to the bottom of the conduction band near the $\Gamma$ point of the Brillouin zone. On the other hand, we find in Fig. 2(c) that the Ni 3$d_{zx}$ orbital has the largest component in the valence band near the Fermi level. Moreover, by analyzing the 4$p$ components of the Se(1), Se(2) and Se(3) ions, we find that valence band top is mainly formed by the Se(3) 4$p_y$ orbital. We therefore conclude that the hybrid Ni 3$d_{zx}$ and Se(3) 4$p_y$ orbitals are the main components forming the top of the valence band of this material.

2.3. Charge density distribution

We calculate the spatial distribution of electronic charge densities near the Fermi level and find that the Ta 5$d_{xy}$, Ni 3$d_{zx}$ and Se(3) 4$p_y$ orbitals have a large density of electrons, implying that the Ta 5$d_{xy}$ orbitals to form the two 1D chains and the Ni 3$d_{zx}$ and Se(3) 4$p_y$ arranged alternately to form the 1D chain in-between (see Fig. 3) are the essential structural unit for the low-energy electronic states of the present system. These results are consistent with the results obtained from the analyses of the DOS and band dispersion. Thus, we may conclude that the crystal structure of Ta$_2$NiSe$_5$ responsible for the formation of excitons is a very simple quasi-1D
structure shown in Fig. 3. This 1D structure may give us an effective model for explaining the mechanism of the formation of the excitonic insulator in the present material. The analysis of the effective model obtained will be presented elsewhere \[11\].

**Figure 3.** The simplified crystal structure of Ta$_2$NiSe$_5$ responsible for the electronic states near the Fermi level, where the two Ta 5$d_{xy}$ 1D chains (red dashed line) and a Ni 3$d_{zx}$-Se 4$p_y$ chain (green dashed line) are essential.

3. Summary
The electronic structure of Ta$_2$NiSe$_5$ as a candidate for excitonic insulators has been calculated using GGA+$U$ method. We have found that the system is a metal at weak correlation $U$, but it becomes an insulator above $U \approx 2$ eV. The band dispersion is reasonably consistent with the ARPES results. The difference between our GGA+$U$ and ARPES results possibly can be caused by the condensation of excitons. From the partial DOS, band dispersion and spatial distribution of charge densities, we have found that the conduction band bottom is configured by the 1D Ta 5$d_{xy}$ chain, and the valence band top is configured by the hybrid Ni 3$d_{zx}$ and Se(3) 4$p_y$ 1D chain. This simple 1D structure is important to the formation of excitons and may give us an effective model which can be used to explain the mechanism of the excitonic insulator. Further details of our calculations, including the DOS, Fermi surfaces, and the pressure effects, will be published elsewhere \[11\].

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