Bulk-Sensitive Photoemission Spectroscopy of TlFe$_2$Se$_2$

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Abstract. We have investigated the electronic structures of the parent compound of an iron chalcogenide superconductor TlFe$_2$Se$_2$ by bulk-sensitive photoemission spectroscopy (PES). Valence-band PES demonstrates the energy gap opening at the Fermi level due to the shift of Fe 3$d$ state to the higher binding energy side as compared to the calculated density of states, being consistent with the insulating behaviour in transport measurements.

1. Introduction

TlFe$_2$Se$_2$ has the same crystal structure as the parent compound of an Fe-based superconductor (SC), BaFe$_2$As$_2$. It is pointed out that the carrier doping makes this compound the SC. Similarly, the superconductivity was recently revealed in (Tl,K)Fe$_{2-x}$Se$_2$ [1]. Interestingly, most of parent compounds of Fe-based SCs are metals but TlFe$_2$Se$_2$ is not a metal but an insulator as well as cuprates. Therefore, it is expected that superconducting mechanism and electronic structures of the TlFe$_2$Se$_2$ system might be different from those of other Fe-based SC.

We have performed high-resolution bulk-sensitive soft-x-ray photoemission spectroscopy (PES) for the TlFe$_2$Se$_2$ to investigate bulk electronic structures.

2. Experimental

The TlFe$_2$Se$_2$ single crystal of which we performed the PES measurement was obtained under the following conditions. Powders of Tl$_2$Se (99.9%), Fe (99.9%) and Se (99.9%) were mixed in a ratio of Tl$_2$Se:Fe:Se = 1:4:4 and pressed into a pellet. The pellet was sealed in a quartz tube under $10^{-2}$ Pa of vacuum. Then, the tube was kept at 973 K and quenched to room temperature after the reaction [2]. The stoichiometric composition of grown samples (Tl : Fe : Se = 0.94:1.10 : 1.96-1.98 : 2) was determined by the x-ray fluorescence analysis with the fundamental parameter method.
Soft-x-ray PES was carried out at the undulator beamline BL-25SU in SPring-8 [3]. The highest total energy resolution $\Delta E$ (the full width at half maximum) is 100 meV evaluated by measuring the Fermi edge of Au. Clean surface of the $a$-$a$ plane is obtained by fracturing the sample in ultrahigh vacuum ($\sim 10^{-8}$ Pa) at the measurement temperature ($T=100$ K) which is below the Neel Temperature ($T_N=450$ K).

3. Results and Discussion

Figure 1 shows Tl 4$f$ core-level PES spectrum of TlFe$_2$Se$_2$. There are two peaks split by the spin-orbit interaction ($\Delta_{SO}=4.46$ eV). The peak at the higher binding energy ($E_B=122.6$ eV) is attributed to Tl 4$f_{5/2}$ component and another at the lower binding energy ($E_B=118.2$ eV) to Tl 4$f_{7/2}$ component. As compared with the Tl metal [4], these peaks shift slightly toward the lower $E_B$ side due to the chemical bonding of TlFe$_2$Se$_2$. In addition, there is no remarkable satellite peak in the spectrum even though very weak plasmon-satellite peaks are seen at $E_B$ 136.2 and 140.6 eV (not shown here). These suggest that Tl atoms are almost isolated in this system. In other words, the electronic states of the Tl atom are hardly hybridized with those of the neighboring Se atoms and the Tl valence is monovalent. This is consistent with results of the valence-band PES and the band structure calculation as shown later.

![Figure 1. Tl 4$f$ core-level PES spectrum of TlFe$_2$Se$_2$.](image1)

![Figure 2. Fe 2$p$ core-level PES spectrum of TlFe$_2$Se$_2$.](image2)
Figure 2 shows Fe 2p core-level PES spectrum of TlFe₂Se₂. There are two major components split by the spin-orbit interaction ($\Delta_{SO} = 12.9$ eV) as well as the Tl 4f core-level PES spectrum shown in Fig. 1. The peak at the higher binding energy ($E_B = 720.94$ eV) is attributed to Fe 2p$_{3/2}$ component and another at the lower $E_B$ ($E_B = 708.04$ eV) to Fe 2p$_{1/2}$ component. The remarkable satellite peak is seen on the lower $E_B$ side of the Fe 2p$_{3/2}$ main peak (indicated by an arrow). The satellite peak has two possible origins. (1) It originates from the charge transfer from mainly Se 4p ligand orbitals to screen the core-hole potential. (2) A different electronic configuration from the Fe$^{2+}$ ($|3d^6>$) state can give rise to another peak in the spectrum, which is realized by an additional electron doping from Tl atoms to conserve the charge neutrality of the crystal. In this energy region, Tl 4p$_{1/2}$ peak ($E_B = 721$ eV) should also appear. However, the photoionization cross section of Fe 2p state at $h\nu \sim 900$ eV is 8 times larger than the that of Tl 4p one. Then, the photoemission from the Fe 2p states becomes predominant and the contribution of the Tl 4p states is negligible in this spectrum.

Figure 3 shows valence-band PES spectrum of TlFe₂Se₂ and the DOSs calculated by D.J. Singh.[5]. These DOSs are obtained by the band structure calculation within the local spin-density approximation (LSDA) for the antiferromagnetic TlFe₂Se₂. The valence-band PES spectrum has some peak and shoulder structures. As compared with the calculated DOSs, it is revealed that the structures located at $E_B = 3.6$ and 5.7 eV and at $E_B = 7.4$ eV originate from Se 4p and Tl 6s electronic states, respectively. Meanwhile, Fe 3d minority- and majority-spin DOSs predominantly contribute to the spectrum near the Fermi level ($E_F$). The sharp peak just below $E_F$ in the PES spectrum should correspond to the Fe 3d minority-spin state. The peak position shifts to the higher binding energy side compared to the calculated DOS. Nevertheless, an additional new structure is not observed.
in the vicinity of $E_F$ as seen in the DOS. Instead, the spectral intensity rapidly decreases as the energy approaches $E_F$ and becomes zero at the $E_F$. These indicate the gap formation at $E_F$, which is consistent with so-far reported other experimental results [2] although the calculation predicts the ground state of TlFe$_2$Se$_2$ below $T_N$ (~450 K) is a metallic state.

4. Summary
We have carried out the high-resolution bulk-sensitive photoemission spectroscopy for the parent compound of an iron chalcogenide superconductor TlFe$_2$Se$_2$ using soft x-rays ($h\nu=600$-900 eV). The valence-band PES spectrum reproduces the overall characteristic structure of calculated DOSs. The spectral intensity, however, rapidly decreases near $E_F$ and the energy gap is formed unlike the calculated result.

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