

# Photoemission study on electronic structure of $\text{TiSe}_2$

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## Abstract

We have examined core-level photoemission spectra of 1T- $\text{TiSe}_2$  and 1T- $\text{TaS}_2$  to study chemical shifts associated with unusual superlattice formation. While large temperature-dependent core-level splitting was observed for  $\text{TaS}_2$ , temperature-dependent chemical shift was not observed for  $\text{TiSe}_2$ . On the other hand, angle-resolved valence-band photoemission spectra of  $\text{TiSe}_2$  showed appearance of a new branch (band-folding) at the L points in the ordered phase at 50 K. These results suggest smaller lattice distortion in  $\text{TiSe}_2$  than that in  $\text{TaS}_2$ .

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$\text{TiSe}_2$ , one of the transition-metal dichalcogenides with 1T- $\text{CdI}_2$  type layered structure, shows an electrical phase transition at  $T_c \sim 200$  K from the metallic phase (normal phase) to the semimetallic phase (ordered phase) on cooling, which is associated with a  $2a \times 2a \times 2c$  superlattice (SL) structure formation [1]. Although there exist many arguments on the mechanism of this phase transition, such as charge density wave (CDW) formation [1], band Jahn-Teller distortion [2] and excitonic insulator mechanism [3], its origin has not been fully elucidated yet [4, 5].  $\text{TaS}_2$  with the 1T structure in the normal phase, on the other hand, has three kinds of CDW phases, two of them have the in-plane  $\sqrt{13}a \times \sqrt{13}a$  SL consisting of so-called “Star of David” cluster [6].

In the present paper, we will examine chemical shifts of the core-levels of  $\text{TiSe}_2$  and  $\text{TaS}_2$  associated with the SL formation. In the case of  $\text{TiSe}_2$ , 2 Ti and 4 Se atoms occupy geometrically two distinct sites with ratios of 3 : 1 in the ordered phase [1]. On the other hand, the SL in  $\text{TaS}_2$  involves 13 Ta atoms that are classified into three distinct sites with ratio of 6 : 6 : 1

[6]. We will also examine the valence-band band structure in the ordered phase of  $\text{TiSe}_2$  by means of angle-resolved photoemission (ARPES) spectroscopy.

$\text{TiSe}_2$  and  $\text{TaS}_2$  single crystals were grown by a chemical vapor transport technique [1, 7]. Core-level and valence-band photoemission spectra were measured at the beamline BL-7 and BL-1 of a compact electron-storage ring (HiSOR) at Hiroshima Synchrotron Radiation Center (HSRC) with a high-resolution hemispherical electron-energy analyzer (SES100 and SES200, GAMMADATA-SCIENTA). We set total energy resolution at  $\Delta E = 50$  meV and 20 meV for core-level and valence-band experiments, respectively.

Figs. 1(a) and (b) show Se 3d and Ti 3p core-level spectra of  $\text{TiSe}_2$  at 16 K (ordered phase) and 300 K (normal phase). We cannot clearly observe chemical shifts and core-level splitting for these spectra, in contrast to a large splitting in the case of  $\text{TaS}_2$  (Fig. 2). In the  $\text{TaS}_2$  case, each of the double peaks of Ta 4f spectra at 360 K (incommensurate CDW phase) splits slightly at 340 K (nearly commensurate CDW phase),

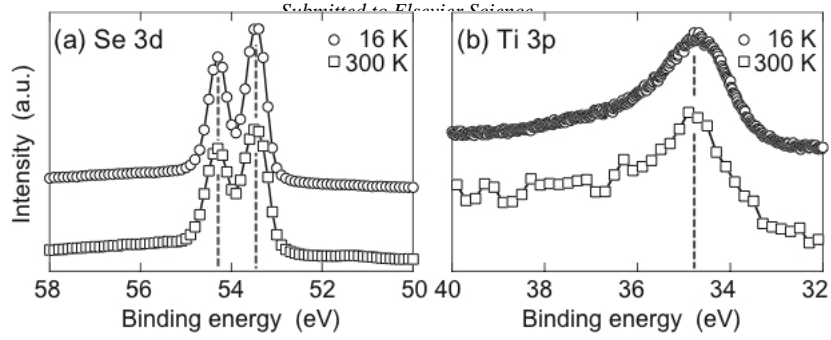


Fig. 1. Core-level spectra of  $\text{TiSe}_2$  at  $T=16$  and  $300$  K. (a) Se 3d and (b) Ti 3p.

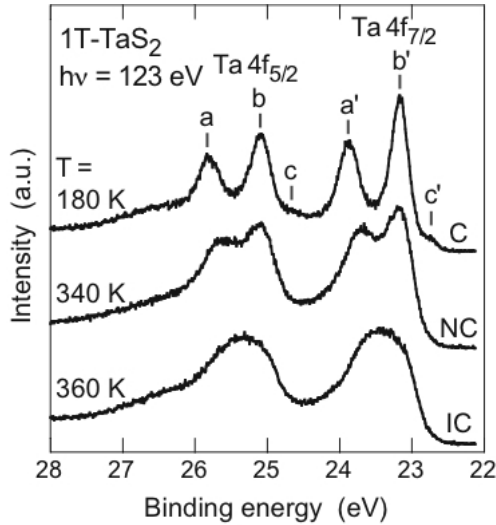


Fig. 2. Ta 4f core-level spectra of  $\text{TaS}_2$  at  $T = 180$  (commensurate CDW phase),  $340$  (nearly commensurate CDW phase) and  $360$  K (incommensurate CDW phase).

and splits completely at  $180$  K (commensurate CDW phase) into three components with intensity ratio,  $6 : 6 : 1$  (spectral feature  $a(a')$ ,  $b(b')$  and  $c(c')$  in Fig. 2). Previous ARPES measurements report that the energy-band dispersion of  $\text{TaS}_2$  in the ordered phase exhibits energy gaps at new Brillouin-zone boundaries derived from the  $\sqrt{13}a \times \sqrt{13}a$  SL formation [8].

In order to see the SL formation effects in  $\text{TiSe}_2$ , we have measured ARPES spectra in the  $\Gamma$ AML plane of the BZ using  $h\nu = 21.2$  eV in the ordered phase ( $50$  K). Figure 3 (a) and (b) show energy-distribution curves and an intensity plot, respectively. A hole pocket lies near the  $\Gamma$  point and an electron one near the L point, in agreement with the calculated results and previous ARPES experiments [4, 5, 9]. In the ordered phase, one can clearly recognize new branches or band folding exist around the L point (Fig.

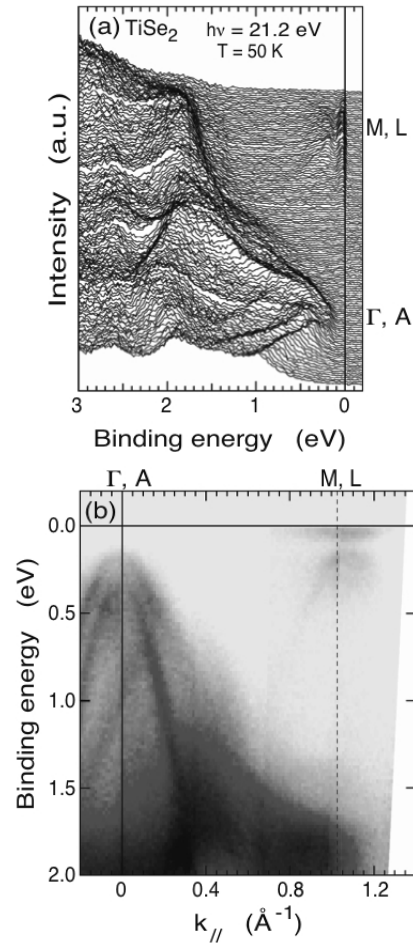


Fig. 3. ARPES results of  $\text{TiSe}_2$  with  $h\nu = 21.2$  eV at  $T = 50$  K. (a) EDC curves and (b) Intensity plot.

3(a) and (b)), which is absent in the normal phase. The modification of the energy bands in  $\text{TiSe}_2$  is, however, much less significant compared with that in  $\text{TaS}_2$  [8].

Our results indicate that distortions of Ti and/or Se atoms in the  $2a \times 2a \times 2c$  SL does not significantly

modify the chemical environment of Ti and Se valence electrons. On the other hand, in the case of TaS<sub>2</sub> in  $\sqrt{13a} \times \sqrt{13a}$  SL, the displacement of Ta atoms is much larger, which leads to large band modification and chemical shifts in Ta 4f states.

In summary, we investigated chemical shifts associated with the SL formation by core-level photoemission spectra of TiSe<sub>2</sub> and TaS<sub>2</sub>. While the chemical shift of TaS<sub>2</sub> was clearly observed, that of TiSe<sub>2</sub> was not observed. The valence-band ARPES of TiSe<sub>2</sub> exhibited band-folding due to the SL formation. Our results indicate that the displacement of atoms in the SL of TiSe<sub>2</sub> is much smaller than that of TaS<sub>2</sub>.

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