24BG005, 25BG038 BL-1, BL-7, BL-9A, BL-14

Electronic structure of Fe_xTiS_2 ($x = 0 \leq x \leq 0.33$) studied by ARPES and XAS

K. Kimura[a], Y. Nakashima[a], Y. Tanimoto[a], Y. Murakami[b], H. Sato[c], M. Arita[c], S. Ideta[c], K. Shimada[c], M. Sawada[c], T. Bizen[d], M. Miyata[d], M. Koyano[d]

[a]*Graduate School of Advanced Science and Engineering, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*
[b]*Faculty of Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*
[c]*Hiroshima Research Institute for Synchrotron Radiation Science, Hiroshima University, Higashi-Hiroshima 739-0046, Japan*
[d]*School of Materials Science, Japan Advanced Institute of Science and Technology, Nomi 923-1292, Japan*

Keywords: intercalation, superlattice, angle resolved photoemission spectroscopy

1*T*-TiS_2 is non-magnetic layered material with 1*T*-CdI_2-type crystal structure. The hexagonal layer of Ti ions is sandwiched between the two hexagonal layers of S ions and the Ti ion is octahedrally coordinated with six S ions. The S-Ti-S triple layers are covalently bonded and these TiS_2 triple layers are weakly coupled with van der Waals (vdW) force. In the vdW gap located between the TiS_2 layers, the other 3*d* transition-metal *M* can be intercalated as M_xTiS_2. Among them, Fe_xTiS_2 exhibits a wide variety of magnetic properties [1]. With increasing the Fe concentration from $x = 0$, the cluster spin grass (CG) state with the Ising spins is found for $x < 0.20$. After exhibiting the antiferromagnetic (AFM) state from $x = 0.20$ to 0.28, the CG state is again realized for $0.28 < x < 0.38$ and the AFM state for $0.38 < x < 0.50$. Above $x = 0.50$, the ferrimagnetic behavior is observed. On the other hand, the Fe ions intercalated in the vdW gap between the TiS_2 layers occupy the octahedral site surrounded by six S ions. X-ray studies reveal the Fe random distribution for $x < 0.20$, while the formation of $2\sqrt{3}a \times 2a \times 2c$ superlattices due to the Fe ordering for $x = 0.25$ and $\sqrt{3}a \times \sqrt{3}a \times 2c$ superlattice for $x = 0.33$. The rich magnetic states of Fe_xTiS_2 are expected to link to the change in electronic band structure due to the Fe intercalation. In this study, we carried out angle-resolved photoemission spectroscopy (ARPES) and soft X-ray absorption spectroscopy (XAS) at the Ti 2*p* edge to investigate the electronic structure of Fe_xTiS_2 ($0 \leq x \leq 0.33$) at beamlines BL-1, BL-7 and BL-9A, and BL-14 of HiSOR, respectively.

Figures 1(a) and 1(b) show the ARPES spectra along the *Γ*-*M* direction for TiS_2 and $Fe_{0.33}TiS_2$, respectively, measured at 20 K using *p*-polarized light with a photon energy of $h\nu = 66$ eV. In TiS_2, an upward-dispersing band derived from S 3*p* orbitals is observed around the *Γ* point, while an electron pocket originating from Ti 3*d* orbitals appears around the *M* point. The Ti 3*d* electron pocket exhibits significantly reduced intensity under *s*-polarized light, indicating that it predominantly consists of the Ti $3d_{z^2}$ orbital component. In $Fe_{0.33}TiS_2$, both the S 3*p* and Ti 3*d* bands shift toward higher binding energies, demonstrating electron doping into the TiS_2 layers induced by Fe intercalation. From the observed Fermi surface volume, the electron doping level is estimated to be approximately 0.54 electrons per intercalated Fe ion. In addition, a dispersive Fe 3*d*-derived band emerges in the 0.2 - 0.8 eV binding energy range. This band exhibits band folding approximately at 0.6 k_M as well as at the *M* point, reflecting the formation of an in-plane $\sqrt{3}a \times \sqrt{3}a$ superlattice structure between the TiS_2 layers. Photon-energy-dependent ARPES measurements further reveal that both the Fe 3*d* and S 3*p* bands disperse along the *Γ*-*A* (k_z) direction. Notably, the Fe 3*d* band shows a periodicity half that of the S 3*p* band, consistent with the formation of a 2*c* superlattice structure along the out-of-plane direction.

Figure 2 presents Ti 2*p* XAS spectra of Fe_xTiS_2 ($0 \leq x \leq 0.33$) measured at 300 K. The spectral line shape evolves continuously with increasing Fe concentration. For $x = 0$ (TiS_2), the Ti $2p_{3/2}$ absorption region exhibits two peaks at 456.4 and 458.6 eV. As the Fe content increases, the lower-energy peak intensity decreases and becomes a shoulder at $x = 0.33$. In the Ti $2p_{1/2}$ region, two peaks at 462.2 and 464.3 eV for $x = 0$ gradually merge into a single peak at $x = 0.33$ due to enhanced spectral weight between them. The spectral shape at $x = 0$ closely resembles that of $CaTiO_3$ (Ti^{4+}) [2], indicating that Ti is nearly tetravalent in TiS_2. In contrast, the spectrum at $x = 0.33$ is similar to that reported for mixed-valent $Y_{0.61}Ca_{0.39}TiO_3$ [2], suggesting the coexistence of Ti^{3+} and Ti^{4+} states. These results indicate that the Ti valence evolves from predominantly Ti^{4+} toward Ti^{3+} with increasing Fe intercalation, in good agreement with the electron-doping behavior inferred from ARPES measurements.

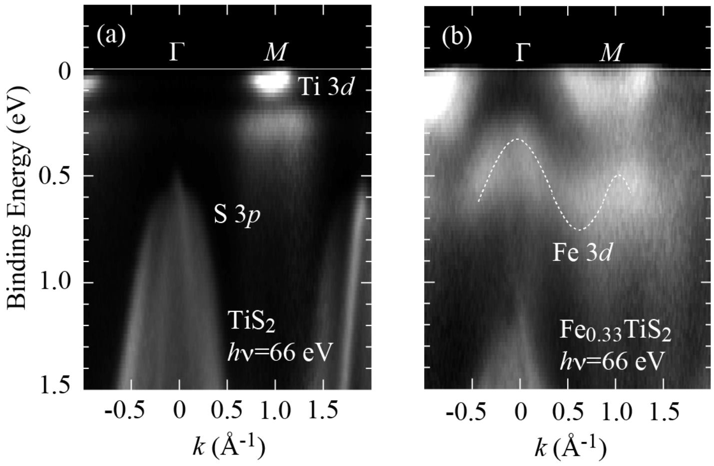

FIGURE 1. ARPES intensity plots of (a) TiS_2 and (b) $Fe_{0.33}TiS_2$ measured at $h\nu = 66$ eV and $T = 20$ K along the Γ-M direction. Dashed line in (b) is guide for the eye for the Fe 3d band.

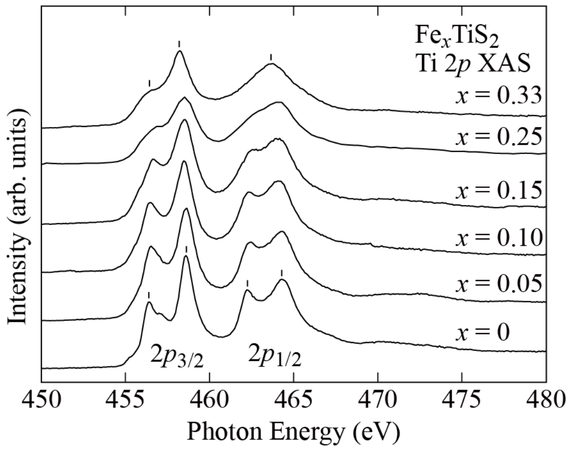

FIGURE 2. Ti 2p XAS spectra of Fe_xTiS_2 ($0 \leq x \leq 0.33$) measured at 300 K.

REFERENCES

1. N. V. Selezneva, E. M. Sherokalova, A. Podlesnyak, M. Frontzek and N. V. Baranov, Phys. Rev. Mater. **7**, 014401 (2023).
2. M. Arita, H. Sato, M. Higashi, K. Yoshikawa, K. Shimada, M. Sawada, Y. Ueda, H. Namatame, M. Taniguchi, S.-i. Fujiomori, Y. Saitoh, M. Tsubota, F. Iga and T. Takabatake, J. Phys. Soc. Jpn. **76**, 074720 (2007).