Observation of weak interlayer interaction in layered 2D material TiS_2

The nature of the weak interlayer interaction that holds together two-dimensional (2D) materials is decisive for realizing layered materials with unique properties. 2D materials and their layered materials such as graphene and transition metal dichalcogenides (TMDs) are attracting much attention owing to their many energy applications, such as electrode materials for ion batteries, as well as their physically interesting properties such as topological insulators. It is commonly assumed that the layers are held together by the van der Waals (vdW) force, which is caused by fluctuations in electron clouds. Since the vdW force is not described in ground states, it is very difficult for current theory to describe the weak interlayer interaction in layered 2D materials [1]. In addition, an unexpectedly strong interlayer interaction in layered PtS_2 was reported using spectroscopy [2].

The structure of the archetypal layered 2D material 1*T*-TiS_2, where 1*T* represents a trigonal phase, is shown in Fig. 1. The TiS_2 slabs are constructed by covalent Ti–S interactions, which should be accurately described by current theory. The slabs are stacked by weak interlayer interactions. Observation of the electron distribution in TiS_2 enables us to investigate the intralayer and interlayer interactions simultaneously. We have accurately observed the electron distribution using high-resolution diffraction data [3,4].

We observed the distribution of electrons between layers in TiS_2 with high resolution using synchrotron X-rays [5]. The electron density in TiS_2 was determined by Hansen-Coppens multipole modeling of the experimental and theoretical structure factors with a resolution of $d > 0.3$ Å. To obtain the experimental structure factors, we measured single-crystal diffraction data at 20 K using an imaging plate detector at SPring-8 **BL02B1**. The wavelength of the X-rays was 0.248 Å. To obtain the theoretical structure factors, we carried out density functional theory (DFT) calculations. The experimental lattice parameters and atomic positions were used for the calculations. The SCAN, LDA and PBE functionals coupled with several vdW functionals including rVV10, rev-vdW-DF2, vdW-DF2 and optB86b-vdW were used for the calculations. The theoretical structure factors were obtained by Fourier transform of the DFT electron densities.

Figure 2 shows the static deformation density in the intralayer of TiS_2. The deformation density was obtained by subtracting the independent atom model (IAM) electron density from the true electron density. Thus, the deformation density enhances interaction features that are unclear in electron density maps. Good agreement is observed between the experimental and theoretical deformation densities. The covalent nature of the Ti-S bond is confirmed from the electron accumulation. The quantitative agreement between the experimental and theoretical electron densities for the intralayer Ti–S interactions mutually validates both the experimental and theoretical approaches.

Figure 3 shows the static deformation density in the interlayer of TiS_2. The experimental interlayer S···S deformation density is significantly higher than the theoretical one. This indicates that a stronger interlayer interaction is observed in the experiment than that according to the theory at this DFT level. The discrepancy in the interlayer interaction is quantitatively evaluated by the dipole moment of the

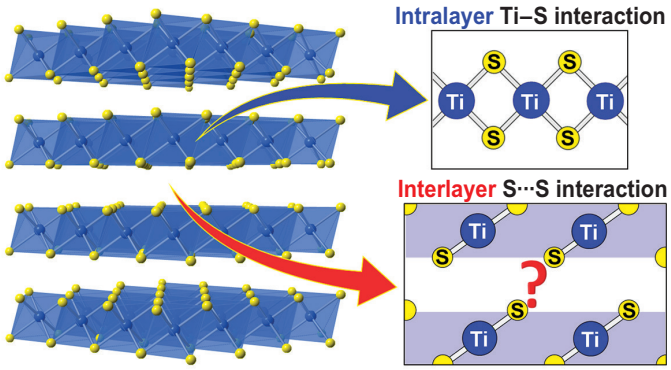

Fig. 1. Structure of 1*T*-TiS_2.

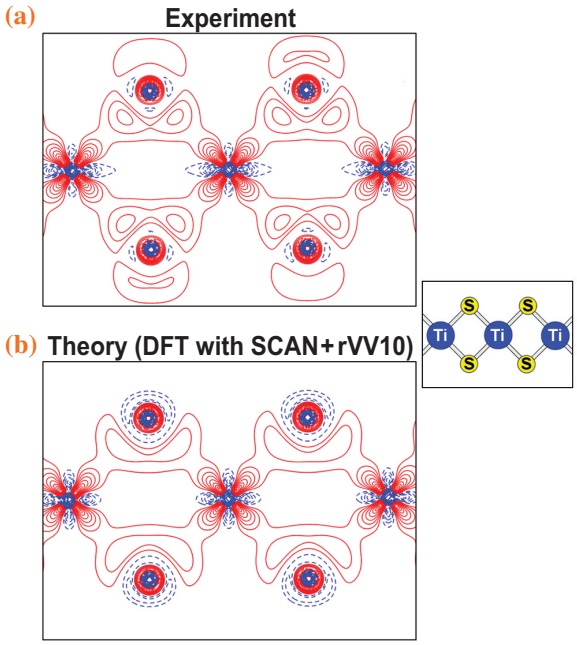

Fig. 2. Static deformation density for intralayer Ti–S interaction. Static deformation map from multipole modeling of **(a)** experimental and **(b)** theoretical structure factors. The contour interval is 0.05 eÅ^{-3}, with positive and negative contours drawn as solid red and dotted blue lines, respectively.

S atom. The magnitude of the atomic dipole moment of S obtained experimentally, μ = 0.03 *e*Å, is 1/10 of the value obtained theoretically, μ = 0.34 *e*Å. This difference is consistent with the electron density distribution in the interlayer, which is more pronounced in the experiment. This indicates that more attractive interlayer forces are observed in the experiment. While the DFT electron density is purely ground state, the experimental electron density is inherently time-averaged even when the thermal vibration is deconvoluted. This makes the experimental static electron density reflect all the chemical interactions, including the vdW forces. Therefore, it is reasonable to conclude that the observed difference between the experimental and theoretical electron distributions emerges from the existence of vdW interactions in the layered 2D material TiS_2.

Our X-ray electron density study revealed the nature of the weak interlayer interaction that holds together 2D materials. The high quality of the observation was confirmed by the quantitative agreement between the experiment and theory in the description of the intralayer Ti–S interaction. We observed substantial differences in the interlayer S···S interaction between the experiment and theory. This is attributed to the significant vdW interactions, which are poorly modeled by DFT using conventional functionals. Thus, the observed distribution of electrons provides a useful benchmark for theory in developing methods that accurately describe vdW interactions. The proper description of the weak interlayer interactions in layered materials is very important not only for science but also for the future engineering of layered 2D materials.

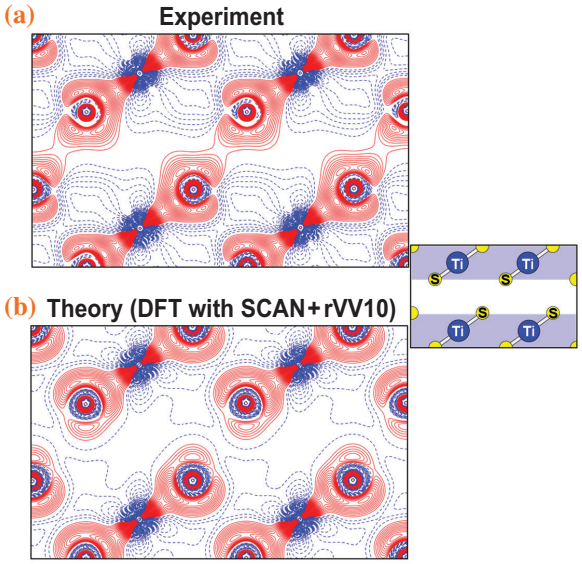

Fig. 3. Static deformation density for interlayer S···S interaction. Static deformation map from multipole modeling of **(a)** experimental and **(b)** theoretical structure factors. The contour interval is 0.01 eÅ^{-3}, with positive and negative contours drawn as solid red and dotted blue lines, respectively.

Hidetaka Kasai[a,*], Eiji Nishibori[a] and Bo B. Iversen[b]

[a] Faculty of Pure and Applied Sciences and Tsukuba Research Center for Energy Materials Science (TREMS), University of Tsukuba
[b] CMC, Dept. of Chemistry and Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Denmark

*Email: kasai.hidetaka.fw@u.tsukuba.ac.jp

References

[1] L. Shulenburger *et al.*: Nano Lett. **15** (2015) 8170.
[2] Y. Zhao *et al.*: Adv. Mater. **28** (2016) 2399.
[3] H. Kasai and E. Nishibori: Phys. Scr. **91** (2016) 043009.
[4] H. Kasai and E. Nishibori: Sci. Rep. **7** (2017) 41375.
[5] *H. Kasai, K. Tolborg, M. Sist, J. Zhang, V.R. Hathwar, M.Ø. Filsø, S. Cenedese, K. Sugimoto, J. Overgaard, E. Nishibori and B.B. Iversen: Nat. Mater.* ***17*** *(2018) 249.*