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STEM Study of Structure and Local Short-Range Orders in the $Fe_{5-x}GeTe_2$ Crystals with Ferromagnetism Near Room Temperature

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Van der Waals (vdW) bonded materials have historically attracted intense attention, due to their promise for advanced electronic and optical functionalities. Recently, magnetically-active vdW materials have been recognized as an important class of materials for realizing new physics and functionalities. Of the magnetic vdW materials, ferromagnetic Fe_3GeTe_2 has garnered significant attention for its high Curie temperature T_C ~230 K [1]. Recently, a $Fe_{5-x}GeTe_2$ compound with thicker Fe-Ge slabs and stronger magnetism has been successfully obtained [2-4]. As viewed by bulk diffraction, the material has a relatively large unit cell and contains intrinsic disorder. The nature of the local structure is anticipated to impact the Curie temperature, which ranges from 270–310K depending on processing conditions. As such, an atomic-scale probe of the local structures and compositions is essential for understanding the intrinsic magnetism in this vdW material.

STEM imaging and spectroscopy were firstly used for the investigation of the average crystal structure of $Fe_{5-x}GeTe_2$ starting with bulk single crystals. Quantitative analysis of high-angle annual dark-field (HAADF) images provided the initial lattice parameters (a = 4.04(2) Å, c = 29.19(3) Å) and positions of the atomic sites. Electron-energy loss spectroscopy (EELS) mapping provided the chemical information of these sites. Using this initial structure model, x-ray diffraction data was then analysed to identify the average structure (space group R-3m) and these data also revealed a split site nature of the Ge position as well as electron density at Fe(1). The structure schematics in the [100] projection is displayed in Figure 1a. Finally, the average structure was used for HAADF image simulation, and this indicated good agreement between the model and average local structures.

Importantly, STEM imaging also reveals local stacking faults and different types of short-range order (SRO). A typical HAADF image in Figure 1b reveals the occurrence of stacking faults without obvious ordering along c. Figure 1c, Left panel shows one type of SRO, induced by an ordered Fe(1) layer being up (or down) in a given Fe_5GeTe_2 slab. This SRO tends to occur in adjacent Fe_5GeTe_2 layers, namely, up/down pairs couple across the vdW gap. Results from a quantitative analysis for this HAADF image in Right panel of Figure 1c indicate no change of the width of the vdW gap associated with this SRO. However, the slab thickness is enhanced and asymmetric Ge-Te distances are observed when Fe(1) preferentially occupies the up or down layer in a given slab. The HAADF image along [1-10] in Figure 1d shows another type of SRO, which is caused by Fe(1) occupying an “up-down-down” pattern within a layer. This SRO can also be revealed by superstructure reflections in its fast Fourier transform (FFT) pattern (inset of Figure 1d). By masking the superstructure reflections in this FFT pattern and performing an inverse-FFT, the regions in Figure 1d with such SRO are highlighted, as revealed in Figure 1e. This supercell corresponds to a $\sqrt{3}a\times\sqrt{3}a$ increase in cell dimension.

This work not only demonstrates the strong capability for STEM to assist in obtaining a crystal structure model for layer compounds with large unit cells, but also indicates local stacking faults and short-range

orders may dramatically influence the magnetic properties of vdW materials [4]. Further work will be needed to link the types of SRO observed here with the physical properties of $Fe_{5-x}GeTe_2$, but these results clearly demonstrate that this material contains disorder and complex local structures that may be important for understanding the bulk properties.

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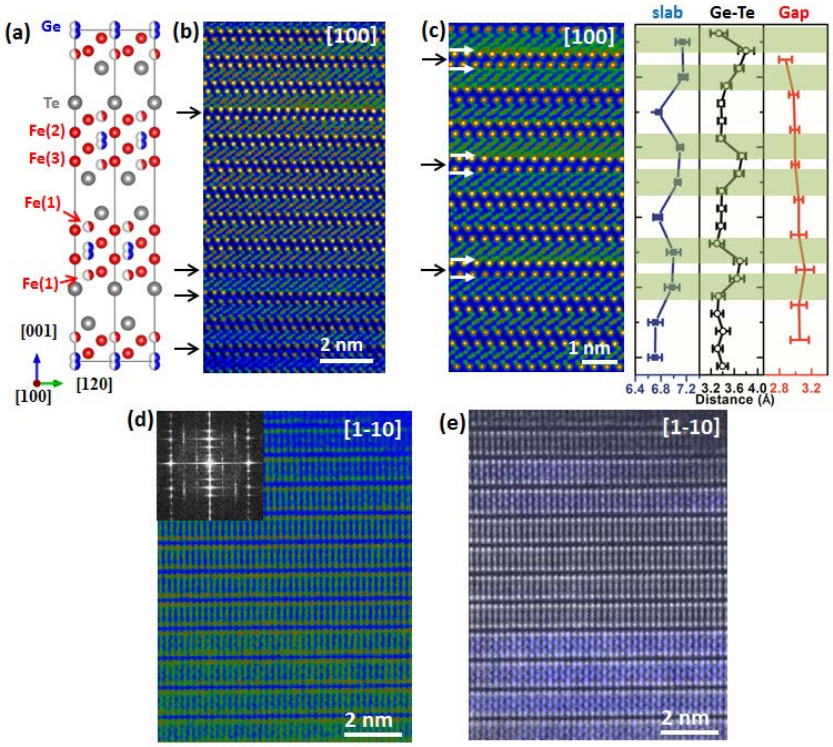

Figure 1. (a) Crystal structure of $Fe_{5-x}GeTe_2$ in the projection of [100]. (b) A HAADF image along [100] for a region with stacking faults; the layers with stacking faults are marked by black arrows. (c) Left panel: A HAADF image along [100] shows a region with the ordered Fe(1) layers, which are marked by white arrows; the black arrows indicate the stacking faults; Right panel: quantitative analysis for this HAADF image, including slab thickness, and Ge-Te and Gap distances. (d) A HAADF image along [1-10] shows another type of short-range order, as indicated by the superstructure reflections in its FFT pattern (inset). By masking the superstructure reflections in this FFT pattern and performing inverse FFT, the composite image of inverse-FFT superimposed on raw HAADF image is given in (e). The colored regions in (e) highlight the layers in (d) with such short-range order.

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