Clarification of Fe ordering in Fe_xTiS_2 structure using transmission electron microscopy

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Iron-intercalated titanium disulfide (Fe_xTiS_2) is a material where Fe guest atoms are introduced into the van der Waals gaps of TiS_2 nanosheets, thereby changing its atomic bonding and band structure, causing a deviation to its bulk properties. The physical properties of Fe_xTiS_2 were reported to be influenced by the distribution of Fe atoms in the van der Waals gap between TiS_2 layers. However, the in-plane and inter-plane orders of Fe atoms are still open to dispute [1,2,3]. In this study, we managed to clarify the arrangements of Fe atoms in Fe_xTiS_2 crystals through scanning transmission electron microscope (STEM) and transmission electron diffraction (TED) observation three dimensionally from the orientations of [100], [110] and [001] and created full atomic models for Fe_xTiS_2 for x = 0.33 and 0.25. We also found that the low Fe concentration (x = 0.15) had dominant short range ordering of $\sqrt{3}a$. The Fe_xTiS_2 crystals of x = 0.33, 0.25 and 0.15 were synthesized by chemical vapor transport technique with iodine as transport agent. The STEM observation was achieved at the accelerating voltage of 120 kV to avoid serious radiation damage. During the in-plane observation in [001] direction, it is particularly important for sample thickness to be sufficiently thin, especially for the case of x = 0.15, to distinguish the atoms originated from in-plane or inter-plane. $\sqrt{3}a \times \sqrt{3}a \times 2c$ superlattice for x = 0.33 and $2a \times 2a \times 2c$ superlattice for x = 0.25 were observed clearly and indicated in Fig. 1(a) and (b) which matches the simulated atomic models in the insets. Due to the $2c$ periodicities in the structures, a shift in the unit cell was observed between planes, as indicated by the red and yellow parallelograms showing the unit cells at z = ¼ and ¾. The overlapping of these layers created hexagonal patterns for x = 0.33 and parallel lines for x = 0.25 in [001] direction. For x = 0.15, Fe atoms were found to arrange with the short-range orders of $\sqrt{3}a$ or $2a$ in the STEM image viewed from the [001] direction [Fig. 1(c)]. Quantitatively, the number of $\sqrt{3}a$ order was measured to be larger than the one of $2a$ order.

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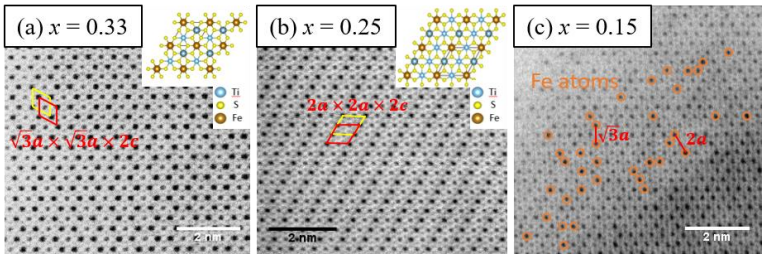

Fig. 1 [001] direction STEM images of Fe_xTiS_2 of (a) x = 0.33, (b) x = 0.25 and (c) x = 0.15. The insets show the atomic structures and the parallelograms show the $\sqrt{3}a \times \sqrt{3}a$ and $2a \times 2a$ unit cells at two different layers due to the $2c$ periodicities.