ABSTRACT

A Study on Ordering of Fe Atoms in Fe_xTiS_2 Structures and Their Magnetic Properties

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Two dimensional transition metal dichalcogenide (TMDC) structures have received much interest due to the emergence of unique physical or chemical properties by being intercalated with various guest atoms or molecules. Thus, extensive studies have been performed to synthesize such intercalated layered structures for various applications such as superconductors, thermal conductors and magnetic materials. Iron-intercalated titanium disulfide (Fe_xTiS_2) structure, which is one of such materials, had been reported to show various magnetic or thermoelectric properties that varied depending on the concentration of Fe atoms in the van der Waals gaps of the TiS_2 host structure. So, to fully understand the physical properties of Fe_xTiS_2, it is important to first know the arrangement of Fe atoms. Experimental and theoretical calculations had been performed to identify the ordering of Fe atoms in Fe_xTiS_2 at different concentrations but no conclusive results could be obtained since some showed contradictory results. So, it is worth investigating these samples with transmission electron microscopy (TEM) since they could provide more in depth information on the local ordering of Fe atoms in the van der gaps of the host structures. In this study, we have investigated the Fe_xTiS_2 structures with various Fe concentrations systematically to clarify the arrangement of intercalated Fe atoms in the TiS_2 structure by transmission electron diffraction (TED) and scanning transmission electron microscopy (STEM) observation. Especially since atomic resolved STEM image is a powerful tool in identifying individual Fe atoms, it can be used to find the short range ordering of Fe atoms at low intercalation concentrations.

STEM observations of the crystals three-dimensionally revealed short-range in-plane ordering of $\sqrt{3}a$ and $2a$ at $x \leq 0.15$, with a higher ratio of atoms with $\sqrt{3}a$ distances. $x = 0.20$ showed the onset of three-dimensional ordering of Fe atoms within the planes and along the *c*-axis, forming short-range ordering of $2a \times 2a \times 2c$. As more Fe atoms were intercalated, long-range ordering of $2a \times 2a \times 2c$ at $x = 0.25$ and $\sqrt{3}a \times \sqrt{3}a \times 2c$ at $x = 0.33$ were observed. The ordering of the Fe atoms could be attributed to the Fe interatomic interactions. At low Fe concentrations ($x \leq 0.15$), Fe atoms would only interact with one another within the plane and thus the main interaction was repulsive forces, creating preferential atomic pairs at $\sqrt{3}a$ distances. Whereas at higher Fe concentrations ($x \geq 0.20$), there were more Fe atoms between the TiS_2 layers and thus the interaction of Fe atoms between the layers would influence the atomic arrangement of Fe atoms in the layers as well, thus creating 3D superstructures.

TED analysis using Patterson method revealed some unprecedented superstructures of $\sqrt{7}a \times \sqrt{7}a$, $\sqrt{31}a \times \sqrt{31}a$ and $\sqrt{43}a \times \sqrt{43}a$, which is equivalent to Fe concentrations of 0.14, 0.29 and 0.26, respectively. In these superstructures, the Fe atoms were separated almost equidistant, suggesting that the Fe atoms would always try to distance themselves equally apart and thus, they did not only occupy octahedral sites as previously reported, but at tetrahedral sites as well. The occupancy of Fe atoms at tetrahedral sites was confirmed by STEM imaging which showed some darker contrasts at S site, which is also known as the tetrahedral sites.

Lastly, the magnetic measurements showed that the crystals switched from spin glass behavior at $x \leq 0.15$ to ferromagnetic behavior at $x \geq 0.20$. The onset of ferromagnetic behavior at $x = 0.20$ was a match to the onset of 3D Fe ordering at $x = 0.20$ in the STEM observation. So, the magnetic properties displayed by these crystals could be a result of whether the crystal had 2D Fe ordering or 3D Fe ordering. The short-range in-plane ordering at low concentrations indicated smaller exchange interactions of the spins and thus led to spin glass behavior. Whereas at higher concentrations, the 3D Fe ordering meant stronger exchange interactions of the spins, which allowed the spins to align easier to the magnetic field and thus display ferromagnetic behavior.

Keywords: Fe_xTiS_2, superstructure, atomic ordering, electron diffraction, scanning transmission electron microscopy