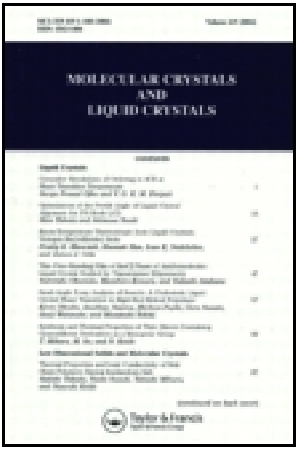

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Neutron Magnetic Scattering of Intercalation Compounds Fe_xTiS_2

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Neutron magnetic scattering of intercalation compounds Fe_xTiS_2 has been measured systematically as a function of Fe concentration x. In the $x = 0.15$ and 1/4 samples, so-called small-angle scattering was observed associated with a spin-glass transition. In the $x = 1/2$ sample, clear magnetic Bragg reflections were observed. The position of the magnetic peak with the smallest Q number was not commensurate with the nuclear lattice-unit. The magnetic structure of $Fe_{1/2}TiS_2$ was found not to be a simple ferromagnetic structure as was ever suggested but a long-period magnetic structure. In the $x = 1/3$ sample, broad magnetic diffuse peak whose Q number was also not commensurate with the nuclear lattice-unit was observed. The origin of the magnetism of $Fe_{1/3}TiS_2$, what is called a cluster-glass, seems the short-range ordered magnetic-clusters with a long-period magnetic structure.

Keywords: Fe_xTiS_2; intercalation; spin-glass; cluster-glass; neutron magnetic scattering; long-period magnetic structure

INTRODUCTION

When iron(Fe) atoms are intercalated into a layered compound titanium disulfide(TiS_2), the intercalation compounds Fe_xTiS_2 show variety of physical and chemical properties[1].

On the magnetic properties of Fe_xTiS_2, a phase diagram in which three magnetic ordered phases are shown is proposed by means of magnetization measurements[1]. Similar phase diagrams are proposed by other groups for the

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low-concentration region[2, 3]. On the basis of Ref. [1.], a ferromagnetic (FM) phase is established at low temperatures in the high-concentration region($0.4 \leq x \leq 1$). In the low-concentration region($0 \leq x \leq 0.2$), a spin-glass (SG) phase appears. In the intermediate region($0.2 \leq x \leq 0.4$), a so-called cluster-glass (CG) phase appears. In addition, different magnetic behaviors are recently reported[4] between $x = 1/4$ and $x = 1/3$ although they are found in the phase diagram as the compounds which transform into the same CG phase. From the anisotropy in the AC susceptibility of a single crystalline $Fe_{1/4}TiS_2$, Ising nature of the magnetic spins aligning preferentially along the c-axis is suggested[5].

Systematic studies on the crystal structures have been performed by our group[6, 7]. In the low-concentration region, $0 \leq x \leq 0.2$, the arrangement of Fe atoms is almost at random. However, X-ray diffuse scattering reveals that the correlation of Fe atoms is of short-range order and the local structure of Fe atoms is a $2a \times 2a \times 2c$ structure, where a and c are lattice parameters of the host lattice TiS_2($a^* = 2.13$ Å^{-1}, $c^* = 1.10$ Å^{-1}). In the region of $x \geq 0.2$, the correlation of Fe atoms is of long-range order. Fe atoms form several types of superlattices depending on the Fe concentration x. In the narrow region near $x = 1/4$, the $2\sqrt{3}a \times 2a \times 2c$ superlattice is observed. In the region near $x = 1/3$ up to $x = 0.4$, the $\sqrt{3}a \times \sqrt{3}a \times 2c$ superlattice is observed. Furthermore, in a higher Fe-concentration region, for instance in $x = 1/2$, the $\sqrt{3}a \times a \times 2c$ superlattice is formed[8]. As summarized in Fig. 1, the magnetic phase boundaries well coincide with the boundaries of structural changes[9]. Accordingly, it

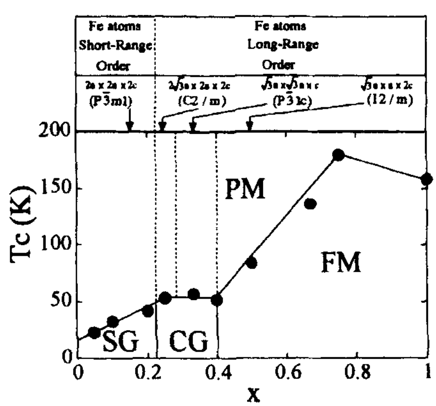

FIGURE 1 Phase diagram of Fe_xTiS_2[1, 9].

is suggested that the magnetism in Fe_xTiS_2 strongly depends on the crystal structure.

In the present paper, we measure neutron magnetic scattering in Fe_xTiS_2 (x = 1/2, 1/3, 1/4 and 0.15) and discuss the magnetic structures against the crystal structures and magnetic properties that are already reported.

EXPERIMENTAL

Powder samples of Fe_xTiS_2 with volume of approximately 2.5 cc for each concentration were synthesized.

Neutron magnetic scattering measurements were performed on the triple-axis spectrometers TAS(4G) and HETAS(C1-1) installed in a reactor hall and in a cold neutron guide hall, respectively, of the JRR-3M reactor in JAERI Tokai. Bent PG(002) crystals were used both for a monochromator and an analyzer. The cryostat employed was a He gas closed-cycle-type cryogenic refrigerator(CTI) down to 8K. Magnetic scattering was investigated in the region of 0.05 $Å^{-1} \le Q \le 3$ $Å^{-1}$. In this paper, we will show the preliminary results on the HETAS(C1-1). The fixed wavenumber of the incident neutron 1.55 $Å^{-1}$ (5meV) was used with a Be-filter. Collimations selected after the PG monochromator were 20'-80'-80' on the HETAS(C1-1).

RESULTS

Temperature dependence of magnetic scattering profiles observed at a small Q region(0.05 $Å^{-1} \le Q \le 0.4$ $Å^{-1}$) is shown in Fig. 2.

$Fe_{1/2}TiS_2$

$Fe_{1/2}TiS_2$ was considered in former experiments to transform into a ferromagnetic phase at 80K as shown in the phase diagram in Fig. 1. In the present neutron-scattering measurements, clear magnetic Bragg peaks were observed below 140K in the $Fe_{1/2}TiS_2$ sample. The widths of the peaks at 8K were the same compared with the (002) nuclear Bragg reflection of the host lattice. The profile with the smallest Q-value at 0.295 $Å^{-1}$ is shown in Fig. 2(a). Comparing the Q-value of the magnetic peak with the nuclear reciprocal-lattice unit, the magnetic structure of $Fe_{1/2}TiS_2$ was found not to be a simple ferromagnetic

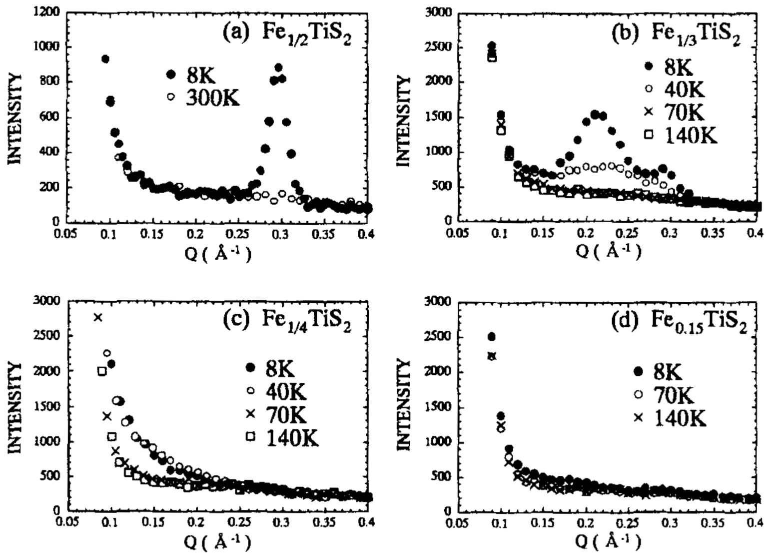

FIGURE 2 Temperature dependence of neutron magnetic scattering.

ordered structure as was commensurate with the nuclear lattice-unit but a long-period structure with long-range ordering.

$Fe_{1/3}TiS_2$

Both $Fe_{1/3}TiS_2$ and $Fe_{1/4}TiS_2$ were considered to transform into a cluster-glass phase at 50K as shown in Fig. 1. In the present study on the $Fe_{1/3}TiS_2$ sample, diffuse scattering which showed a peak at Q = 0.21 $Å^{-1}$ was observed at low temperatures as shown in Fig. 2(b). The diffuse peak at 8K was 3.5 times as broad as the (002) nuclear Bragg reflection of the host lattice. Any peaks except this one were not observed in higher Q region. The peak intensity of the diffuse scattering increased below 80K little by little and increased extremely below 50K. The position of the diffuse peak was not commensurate with the nuclear lattice-unit as well as $Fe_{1/2}TiS_2$. A long-period magnetic structure corresponding to Q = 0.21 $Å^{-1}$ was found in $Fe_{1/3}TiS_2$, and the correlation was of short-range.

Note that the magnetic-scattering peak at Q = 0.295 $Å^{-1}$ in Fig. 2(b) is not intrinsic for the original crystal-structure of the x = 1/3 sample. The actual concentration of the $Fe_{1/3}TiS_2$ sample used was $x = 0.35$, so that it is supposed that the composite fluctuation occurred and the same crystal structure as $Fe_{1/2}TiS_2$ was produced partially in the powder sample of $Fe_{1/3}TiS_2$. Indeed, the Q-value of 0.295 $Å^{-1}$ was the same as $x = 1/2$, as found in Fig. 2(a). The magnetic scattering at $Q = 0.21$ $Å^{-1}$ and $Q = 0.295$ $Å^{-1}$ is characteristic scattering for the crystal structures with $\sqrt{3}a \times \sqrt{3}a \times 2c$ superlattice of $x = 1/3$ and $\sqrt{3}a \times a \times 2c$ superlattice of $x = 1/2$, respectively.

<u>$Fe_{1/4}TiS_2$</u>

In the $Fe_{1/4}TiS_2$ sample, any peaks of magnetic scattering were not observed in the region of $Q \leq 3$ $Å^{-1}$ even at 8K. The entire powder-diffraction pattern at 8K was essentially unchanged compared with that at 300K. However, as shown in Fig. 2(c), what is called small-angle scattering whose peak was probably at $Q =$ 0 $Å^{-1}$ was observed, which seemed to be caused by the condensation of magnetic spins associated with the spin-glass transition. The intensity of the magnetic scattering began to increase below 80K and saturated at 40K.

<u>$Fe_{0.15}TiS_2$</u>

The $Fe_{0.15}TiS_2$ sample, which was considered to transform into the spin-glass phase at 40K in Fig. 1, showed a similar feature to that in $Fe_{1/4}TiS_2$. The difference was that the intensity of the small-angle scattering was so much weak compared with that in $Fe_{1/4}TiS_2$. The intensity of the magnetic scattering increased below 70K, but it did not saturate even at 8K.

DISCUSSION

We measured neutron magnetic scattering using powder samples of Fe_xTiS_2 as a function of Fe concentration x. In $x = 0.15$ and $x = 1/4$, so-called small-angle scattering was observed associated with the spin-glass transition. In $x = 1/3$ and $x = 1/2$, a magnetic peak that can give evidence on a long-period magnetic ordering was observed. Accordingly, the magnetic structure of $x = 1/2$ was found not to be a simple ferromagnetic structure as was ever suggested. The particular magnetic-structure is not clear at the present stage because we have just measured a few peaks in the powder sample. In case of $x = 1/3$ and $x = 1/2$, observed magnetic peaks may suggest the appearance of a long-period antiferromagnetic ordering with ferromagnetic components such as fan or cone structure. The magnetic correlation is of short-range and long-range for $x = 1/3$ and $x = 1/2$, respectively.

Based on our preliminary structure-analysis for $Fe_{1/2}TiS_2$, Fe atoms fully occupy the 2a site in the space group I2/m. Another site on the Fe-layer is vacant. On the other hand, Fe atoms in $Fe_{1/3}TiS_2$ occupy the 2a and 2c sites in the space group $P\bar{3}1c$[7]. Most of Fe atoms occupy the 2c site. However, certain Fe atoms fractionally occupy the 2a site and the occupancy number is definitely not zero. It is supposed that this imperfection on the Fe occupancy involving the arrangement of Fe atoms is one of the reasons why the magnetic scattering in $Fe_{1/3}TiS_2$ is diffuse compared with that in $Fe_{1/2}TiS_2$. The imperfection on the Fe occupancy becomes greater in the case of $Fe_{1/4}TiS_2$ to affect the appearance of spin-glass[7].

Recently we measured neutron magnetic scattering in $Fe_{1/3}TiS_2$ using a single crystal. The shape of the magnetic scattering was found to be a ring at the particular Q position. The details will be published elsewhere.

Acknowledgments

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