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Structural and Magnetic Properties of Intercalation Compounds Fe_xTiSe_2

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Neutron diffraction and magnetic studies are performed about iron-intercalated titanium diselenide, Fe_xTiSe_2, with $0<x\leq 0.5$. Neutron diffraction study shows that Fe-atoms are located in van der Waals gaps between neighboring selenium layers. Magnetic study shows that Fe_xTiSe_2 are spin glasses for $x\leq 0.22$ and antiferromagnets for $x\geq 0.25$. T-x magnetic phase diagram is determined.

KEYWORDS: Fe_xTiSe_2, metal atom location, spin glass, antiferromagnetism, T-x magnetic phase diagram

§1. Introduction

TiX_2 (X=S and Se) crystallize in a hexagonal CdI_2 crystal structure with a repetition of X-, Ti- and X-layers along the c-axis. Various atoms are intercalated in van der Waals gaps between neighboring X-layers. Recently one of the present authors (Y. T.) and his collaborators have studied magnetic properties of intercalation compounds M_xTiS_2,[1-3] where M are 3d transition metal elements ranging from V to Cu. Depending on the element M and x, spin glass and ferromagnetic phases appear. These magnetic phases are caused by RKKY interactions between the M-atoms. There have been small number of magnetic studies about M_xTiSe_2 up to now.[4,5] In the present study, structural and magnetic properties of Fe_xTiSe_2 are studied by neutron diffraction and magnetic measurements. Polycrystalline samples were prepared at 750°C succeeded by rapid quenching to room temperature.

§2. Structural Study

There are two kinds of layers into which metal atoms (M- and Ti-atoms) can enter: Ti-layers and the van der Waals gaps. We call the latter layers M-layers. One kind of metal layers can contain 1.0 mole of metal atoms. In TiX_2, Ti-atoms fill the Ti-layers and the M-layers are vacant. In the studies of M_xTiX_2, it has been supposed that the M-atoms are located only in the M-layers and the Ti-atoms fill the Ti-layers. For sulfur-compound, Kuroiwa *et al.*[6] determined the arrangements of Fe-atoms in the M-layers of Fe_xTiS_2 with x=1/4 and 1/3 by neutron diffraction experiment, verifying this supposition as a result. It is now valuable to verify this supposition for selenium compound also.

The problem is to determine what kind of metal atoms are contained in each kind of metal layers. Neutron diffraction study is suited to this problem because scattering lengths of Fe and Ti are quite different. Powder neutron diffraction pattern of $Fe_{0.2}TiSe_2$ was obtained at room temperature by the HRPD-diffractometer installed in JAERI, Tokai. Top of Fig. 1 shows the pattern, which was analyzed by model structures under following assumption about distribution of metal atoms. Depending on structure, a kind of metal layers contain one or two kinds of metal atoms, the total amount of metal atoms in this kind of metal layers being equal to or less than 1.0 mole. Since the sample was prepared by rapid quenching, it is reasonable to assume that metal atoms (and metal vacancies) are randomly distributed in each kind of metal layers.

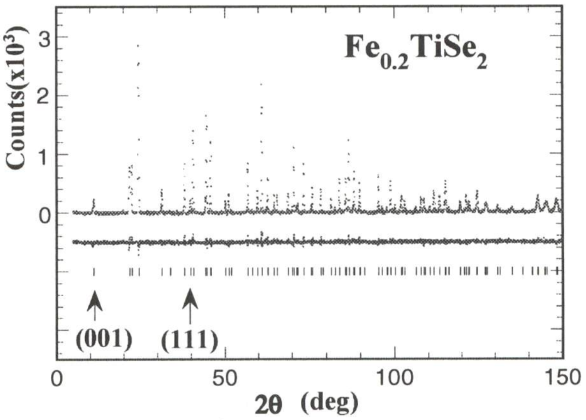

Fig. 1. Neutron diffraction pattern of $Fe_{0.2}TiSe_2$ with a wavelength of 1.1622Å and result of Rietveld analysis (see text).

In constructing model structures, it is reasonable to restrict to the case in which Ti- and M-layers contain 1.0 and 0.2 moles of metal atoms, respectively. Within this restriction, we constructed three structures which differ with each other in the locations of the Fe- and Ti-atoms. The A-structure is the supposed structure: Ti- and Fe-atoms are located in the Ti- and M-layers, respectively. In this structure a M-layer contains 20% of Fe-atoms and 80% of vacancies. In the B-structure Ti- and Fe-atoms are not distinguished as to the location: each kind of metal layers contain Ti- and Fe-atoms in a ratio of 1.0 : 0.2. In the C-structure Fe-atoms preferentially enter the Ti-layers: the Ti-layers contain 0.8 moles of Ti-atoms and 0.2 moles of Fe-atoms, and the M-layers contain 0.2 moles of Ti-atoms. The reason for selecting the composition of x=0.2 is that we can easily distinguish the A-structure from the B- and C-structures for x=0.2: under the above assumption of random distribution of metal atoms and vacancies, (001), (111) and several other diffraction lines are expected to be strong for the A-structure, whereas they are expected to be feeble for the B- and C-structures. The diffraction pattern shows strong (001) and (111) diffraction lines, favoring the A-structure. Rietveld analyses were performed for the three structures by a program kindly offered from Dr. F. Izumi. Table I lists reliability factors: R_p, R_F, and thermal parameters of Se, metal(s) in the Ti-layer and metal(s) in the M-layer: B(Se), B(Ti-layer), B(M-layer), for the A-, B- and C-structures. Parameters for $TiSe_2$ are also listed for comparison. The reliability factors of B- and C-structures are larger than those of the A-structure, and the thermal parameters of B- and C-structures are not reasonable, favoring the A-structure. Middle of Fig. 1 shows the difference between the observed intensity and the theoretical intensity calculated by the A-structure. Very small differences are found at (001) and (111) diffraction lines in Fig. 1, whereas corresponding differences are large for B- and C-structures.

The result of the neutron diffraction experiment leads to a conclusion that the Fe-atoms are located and randomly distributed in the M-layers.

Table I. Parameters of Rietveld analysis.

Structure	R_p (%)	R_F (%)	B(Se) (Å^2)	B(Ti-layer) (Å^2)	B(M-layer) (Å^2)
A	7.52	3.37	0.495	0.800	0.929
B	8.25	4.79	0.590	0.360	6212
C	8.35	4.97	0.590	-0.459	16.7
$TiSe_2$	7.46	2.42	0.565	0.751	

§3. Magnetic Properties

Since it was found after publishing ref. 4 that the samples were easily oxidized in air, cautions were paid to prevent oxidation. Magnetization(M)-field(H) variations were measured in a temperature range of 4.2 K$\leq T \leq$300 K. For all the samples a maximum was observed at T_m in the M-T variation. Susceptibilities in $T > T_m$ are analyzed by a Curie-Weiss term plus a constant term: $\chi = C/(T-\theta)+\chi_0$. Figure 2 shows x-variations of χ_0, θ and paramagnetic effective moment μ_{eff} of all the samples. Some of the data are different from those of the previous study$^{4)}$ due to the reason stated above about sample oxidation.

Below T_m each sample must be in an ordered state. The nature of the ordered state was investigated by various methods. Magnetic data for x=0.10, 0.20, 0.25 and 0.45 are shown in Fig. 3, where magnetization data were taken at 8.08 kOe. For all the samples with $x \leq 0.22$ the forms of the M-T maximum are rounded, and below T_m time-dependent magnetization was observed at fixed field. Clear differences were observed between field-cooled magnetization (M_{FC}) and zero-field-cooled magnetization (M_{ZFC}). Data of ac-susceptibility showed a sharp maximum at T_g. Examples of this behavior are shown for x=0.10 and 0.20 in Fig. 3. These data demonstrate that the magnetic state in $T < T_g$ for $x \leq 0.22$ is a spin glass state. For all the samples with $x \geq 0.25$, the forms of the M-T maximum are sharp at finite field and M-H dependence is linear at all temperatures except near 4.2 K. Time-dependent magnetization was not observed except near 4.2 K. For x=0.25, M_{FC} and M_{ZFC} were measured. No difference between them was detected except near 4.2 K, as shown in Fig. 3. These data demonstrate that the dominating state in $T < T_m$ is not a spin glass state, but an antiferromagnetic state for x=0.25. This conclusion may be true for x>0.25 also. Investigation of the spin glass like behavior, or reentrant spin glass like behavior, near 4.2 K is a future problem.

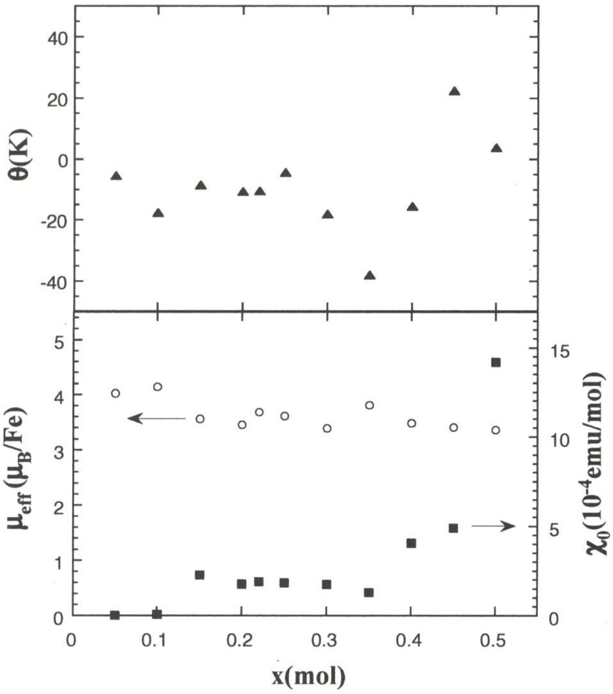

Fig. 2. x-variations of parameters of paramagnetic susceptibility.

Figure 4 shows T-x magnetic phase diagram determined in the present study. Values of T_m were determined at 8.08 kOe. It has been shown theoretically and experimentally$^{7,8)}$ that, as the average of exchange interactions increases with increasing composition (x) of magnetic atoms, a ferromagnetic or antiferromagnetic phase appears for large x. Then the present result is in accordance with previous results, and therefore the above conclusion, which states that the dominant state in $T \leq T_m$ is an antiferromagnetic state for x>0.25, is supported. A striking feature of the present result is strong x-variation of the antiferromagnetic transition temperature (T_m) for x>0.4.

§4. Discussion

In the case of M_xTiS_2 the origin of the exchange interactions is the RKKY interaction.$^{10)}$ In M_xTiSe_2 also the origin of the exchange interactions is the RKKY interaction, as follows. Since spin glass phase does not appear in a two-dimensional magnetic system,$^{8)}$ there must be exchange interaction between Fe-atoms belonging to different M-layers. According to the crystal structure verified in §2, two neighboring M-layers are separated by three layers: Se-, Ti- and Se-layers. It is not probable that superexchange interaction occurs over such a long distance, and the origin is the RKKY interaction.

Next, discussion is given about the x-variations of parameters of paramagnetic susceptibility. If the Fe-atom is in a divalent ionic state with a high-spin and g=2, the paramagnetic effective moment $\mu_{\rm eff}{}^{\rm ion}$=4.90 $\mu_{\rm B}$. Since $\mu_{\rm eff}$ is smaller than $\mu_{\rm eff}{}^{\rm ion}$ by a small amount, the Fe-atom is in a high-spin state and has covalent character by a small amount.[9] The degree of covalency slightly increases with increasing x because $\mu_{\rm eff}$ slightly decreases with increasing x.

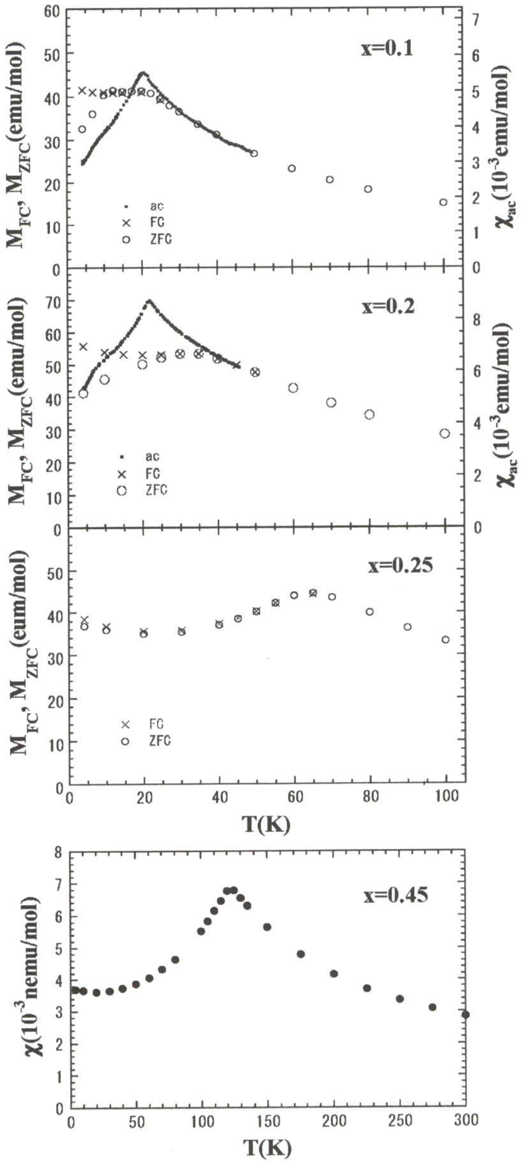

Fig. 3. Magnetic data for x=0.1, 0.2, 0.25 and 0.45.

Both χ_0 and θ show a small variation for x<0.3 and a remarkable variation for x>0.3. The correlation in the x-variations of χ_0 and θ is explained as follows. The constant paramagnetism χ_0 is proportional to a density of states at Fermi energy, $D(\epsilon_{\rm F})$, which is related to a band structure. The θ-value is a measure of the average of exchange interactions. Since the origin of the exchange interactions is the RKKY interaction, the parameter θ depends on the band structure. Then χ_0 and θ are qualitatively correlated, and the experimental x-variations suggest that the band structure changes remarkably for x>0.3. There is a quantitative difference between the x-variations of χ_0 and θ, however. The difference is due to different band structure dependence of the two parameters. While χ_0 is proportional to $D(\epsilon_{\rm F})$, θ is an average of the RKKY interaction constants ($J_{\rm RKKY}$'s) which are complicated functions of the Fermi wave number $k_{\rm F}$. The complicated θ-x variation may be a manifestation of the complicated $J_{\rm RKKY}$-$k_{\rm F}$ variations.[1]

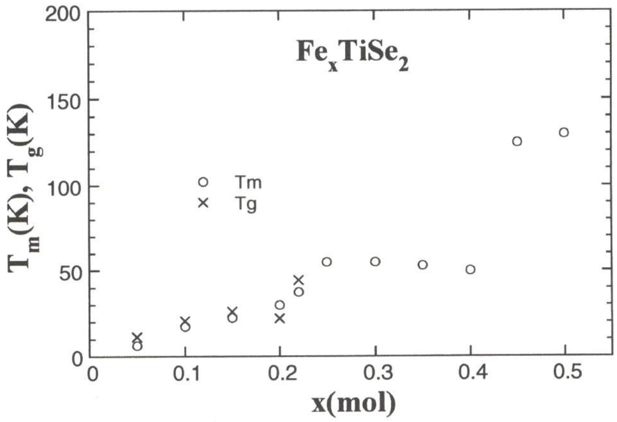

Fig. 4. T-x magnetic phase diagram.

Finally, discussion is given about x-variations of the transition temperatures $T_{\rm g}$ and $T_{\rm m}$. Theoretically the spin glass transition temperature $T_{\rm g}$ is proportional to the variance of exchange interaction constants.[8] Since the relative increase in x is large in the spin glass region (for small x), the increase in the number of exchange paths may play a major role and $T_{\rm g}$ is expected to be an increasing function of x. This expectation was realized in the present case, as well as in many examples.[7,8] The antiferromagnetic transition temperature $T_{\rm m}$ is a linear function of $J_{\rm RKKY}$'s. Since the relative increase in x is small in the antiferromagnetic region (for large x), the $J_{\rm RKKY}$-x variations may play a major role and $T_{\rm m}$ is expected to reflect the band structure change with x. The strong $T_{\rm m}$-x variation may be a manifestation of the complicated $J_{\rm RKKY}$-x variations.

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