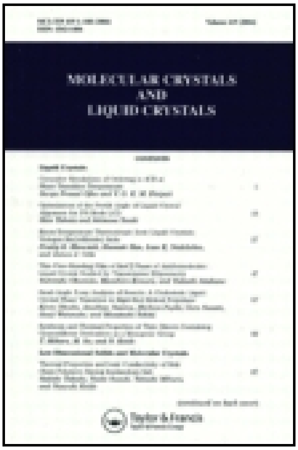

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Structural and Magnetic Properties of Fe^xTiSe^2 Intercalation Compounds

Masakatsu Shintomi [a], Yuuichi Tazuke [a] & Haruyuki Takahashi [a]

[a] Faculty of Engineering, Ibaraki University, Hitachi, Ibaraki, 316-8511, Japan

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Structural and Magnetic Properties of Fe_xTiSe_2 Intercalation Compounds

MASAKATSU SHINTOMI, YUUICHI TAZUKE
and HARUYUKI TAKAHASHI

Faculty of Engineering, Ibaraki University, Hitachi, Ibaraki 316–8511, Japan

Magnetic and neutron studies are done about iron-intercalated titanium diselenide, Fe_xTiSe_2 with $0<x\leq0.5$. A neutron diffraction measurement shows that Fe-atoms are located between neighboring selenium layers. Magnetic measurements show that Fe_xTiSe_2 are spin glasses for $0.15\leq x\leq0.22$ and antiferromagnets for $0.25\leq x\leq0.5$. T-x magnetic phase diagram is determined. This diagram is slightly different from that determined by Huntley et al. The difference may be caused by a formation of Fe-clusters in their samples. The x-dependence of the parameters of paramagnetic susceptibilities is determined.

Keywords: Fe_xTiSe_2; metal atom location; spin glass; antiferromagnetism; T-x magnetic phase diagram

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 the layers between the neighboring X-layers. We call such layers as M-layers. Recently one of the present authors (Y. T.) and his collaborators have studied various magnetic properties of 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. Between the TiS_2-band and M-atoms occur hybridizations, whose magnitudes depend on the element M. There have been small numbers 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.

STRUCTURAL STUDY

$Fe_{0.1}TiSe_2$ showed paramagnetic behavior in our previous study[4], whereas it showed spin glass behavior in a study by Huntley et al.[5] Since this discrepancy might be due to a difference in crystal structure caused by a difference in sample preparation, structural study is necessary. Three experiments were done in order to determine locations of Fe- and Ti-atoms in two kinds of metal layers: M- and Ti-layers. In the first experiment susceptibilities were measured about $Fe_{0.1}TiSe_2$ samples prepared from two kinds of starting materials: a mixture of Fe- and $TiSe_2$-powders as in Ref.-4, and a mixture of Fe-, Ti- and Se-powders as in Ref.-5. After heat-treatment at 750°C the two samples were rapidly quenched to room temperature. No difference was found between the susceptibilities in $4.2\ K \leq T \leq 300\ K$. This result shows that the difference in the starting material makes no difference. Therefore, hereafter, the samples were prepared from mixtures of Fe-, Ti- and Se-powders at 750°C.

In usual studies about M_xTiX_2 intercalation compounds, it has been assumed that the M-atoms are located in the M-layers and not located in the Ti-layers. It is now valuable, as the second experiment, to directly prove this structure by a structural analysis. Fig. 1 shows powder neutron diffraction spectrum of $Fe_{0.2}TiSe_2$ obtained at room temperature by the HRPD-spectrometer installed in JAERI, Tokai. Since the sample was prepared by a rapid quenching, it is

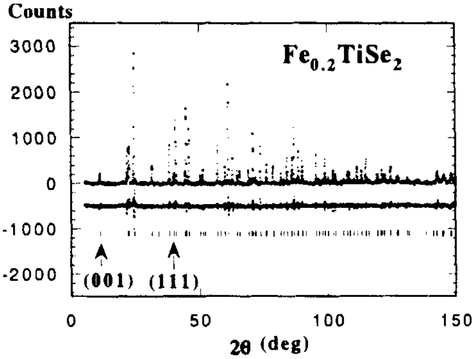

FIGURE 1 Neutron diffraction spectrum of $Fe_{0.2}TiSe_2$ at room temperature with λ=0.11624 nm, and result of a Rietveld analysis.

reasonable that the metal atoms are randomly distributed in the two kinds of metal layers. The purpose of the experiment is to determine which of three possible structures is realized. A-structure: Ti- and Fe-atoms are located in the Ti- and M-layers, respectively. B-structure: all the metal-atoms are randomly distributed in both kinds of metal-layers, where Ti- and M-layers contain 1.0 and 0.2 moles of metal atoms, respectively. C-structure: the M-layers contain 0.2 moles of Ti-atoms and the remaining metal atoms are randomly distributed in the Ti-layers. The reason for selecting the composition of x=0.2 rather than 0.1 is that we can easily distinguish the A-structure from the B- and C-structures in the case of x=0.2: for the A-structure (001), (111) and several other diffraction lines are expected to be strong, whereas they are expected to be feeble for the B- and C-structures. The spectrum shows strong (001) and (111) diffraction lines. Rietveld analyses were done for the three structures. The A-structure reproduces the spectrum with reliability factors R_p=0.09 and R_{wp}=0.12, and reasonable values of thermal parameters are obtained. Fig. 1 shows also the result of a fitting by the A-structure. The B- and C-structures do not reproduce (001) and (111) lines, and values of thermal parameters are not reasonable.

The results of the above two experiments lead to a conclusion that the Fe-atoms are located in the M-layers regardless of the starting mixture, at least for samples prepared by a rapid quenching. Since a Ti-atom can become tetravalent easily while an Fe-atom cannot, it is reasonable to assume that this conclusion does not depend on the method of cooling the sample to room temperature. However, distribution of Fe-atoms within an M-layer may depend on the method of cooling. As the third experiment, effect of the method of cooling on the magnetic property of $Fe_{0.1}TiSe_2$ was studied. For this purpose a sample was prepared by cooling it to room temperature at a rate of 10°C/hour after heat-treatment at 750°C. This sample showed susceptibility maximum around T_m=10 K, contrary to the quenched sample which showed no susceptibility maximum. This result suggests that in the slowly cooled sample the Fe-atoms are not randomly distributed in the M-layers. Rather, they form clusters, in which the effective composition is higher than the nominal composition. These clusters give the susceptibility maximum. Since T_m of 10 K of our slowly cooled sample is much lower than that, 24 K, of the sample of Huntley et al.[5], it is probable that the degree of clustering is weaker in our slowly cooled sample than that in the sample of Huntley et al.

MAGNETIC PROPERTIES

Magnetizations were measured for rapidly quenched samples with $0.1 \leq x \leq 0.5$ in $4.2\ \mathrm{K} \leq T \leq 300\ \mathrm{K}$. According to the conclusion in the structural study, the Fe-atoms are randomly distributed in the M-layers. Since it was found after publishing Ref.-4 that the samples are easily oxidized in air, cautions were paid to prevent oxidation. For $0.15 \leq x \leq 0.5$ a maximum was observed at T_m in the temperature dependence of the magnetization. For $0.15 \leq x \leq 0.22$ the forms of the maximum are rounded and magnetizations are time-dependent below T_m. Clear differences were observed between field-cooled (FC) and zero-field-cooled (ZFC) magnetizations for $0.15 \leq x \leq 0.22$. Fig. 2 shows an example for $x=0.2$. These data show that the magnetic state for $T \leq T_m$ are spin glasses. For $0.25 \leq$

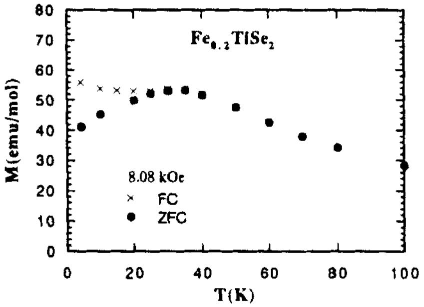

FIGURE 2 M-T dependence of $Fe_{0.2}TiSe_2$ at 8.08 kOe.

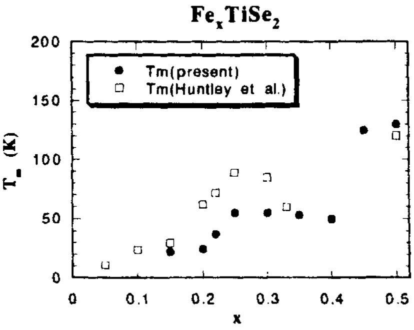

FIGURE 3 T-x magnetic phase diagram of Fe_xTiSe_2.

$x \leq 0.5$ the forms of the maximum are sharp and no time-dependent magnetization was observed. Generally, the average of exchange interactions increases with increasing composition of magnetic atoms, and a ferromagnetic or antiferromagnetic phase appears.[6,7] Then the maximum for $0.25 \leq x \leq 0.5$ may be due to an antiferromagnetic transition. For $x=0.1$ magnetization is nearly temperature independent for $T \leq 10$ K. $Fe_{0.1}TiSe_2$ may be a spin glass with a very low transition temperature. Fig. 3 shows x-dependence of T_m determined at 8.08 kOe. The fact that T_m-values in the present study are smaller for $x \leq 0.3$ than those of Huntley et al. determined at 10.85 kOe can be explained by the above conclusion about the Fe-clustering. Determination of spin glass transition temperatures at a low field is a future theme.

Above 10 K for $x=0.1$ and above T_m for $0.15 \leq x \leq 0.5$, paramagnetic behavior was observed. The susceptibilities χ are analyzed by a Curie-Weiss term plus a constant term: $\chi = C/(T-\theta)+\chi_0$. Fig. 4 shows x-dependence of paramagnetic effective moment μ_{eff}, χ_0 and θ. Some of the data are different from those of the previous study[4] due to the reason stated above about sample oxidation. In the following we discuss about the behavior of these parameters. If the Fe-atom is in a divalent ionic state with a high-spin and $g=2$, the paramagnetic effective moment $\mu_{eff}^{ion}=4.90\ \mu_B$. Since μ_{eff} is smaller than μ_{eff}^{ion} by a small amount, the Fe-atom is in a high-spin state and has covalent character by a small amount.[8] The degree of covalency slightly increases with increasing x because μ_{eff} slightly decreases with increasing x.

Finally we discuss about the behavior of χ_0 and θ. Both χ_0 and θ show a small variation for $x \leq 0.3$ and a remarkable variation for $x \geq 0.3$. Huntley et al. also observed this behavior.[5] The correlation in the x-dependence of χ_0 and θ

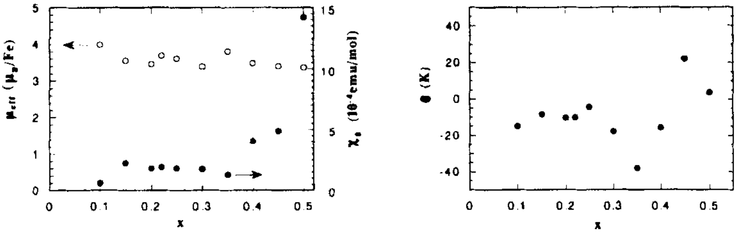

FIGURE 4 x-dependence of the parameters of paramagnetic susceptibility, μ_{eff}, χ_0 and θ with $\chi = C/(T-\theta)+\chi_0$.

is explained as follows. The constant paramagnetism χ_0 is related to a conduction electron density n and a band structure. Since the Fe-atoms supply the conduction electrons, n is proportional to x and χ_0 is an increasing function of x in the first approximation, as is realized approximately. The non-linear χ_0-x dependence suggests that the band structure changes with x. The remarkable increase of χ_0 suggests a remarkable change of the band structure for $x \geq 0.3$. The θ-value is a measure of the average of exchange interactions. In the case of M_xTiS_2 the origin of the exchange interactions is the RKKY interaction.[9] It is reasonable that in M_xTiSe_2 also the origin of the exchange interactions is the RKKY interaction. The magnitude of the RKKY interaction is dependent on n and a band structure. So explained the correlation between the behavior of χ_0 and θ. There is a difference, however. The functional dependence of χ_0 on x is very different from that of θ on x. The RKKY interaction constant J_{RKKY} is a complicated function of n through the Fermi wave number k_F, while χ_0 is proportional to n in the first approximation. Then the complicated θ-x dependence may be a manifestation of the complicated J_{RKKY}-n dependence.[1]

Acknowledgments

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