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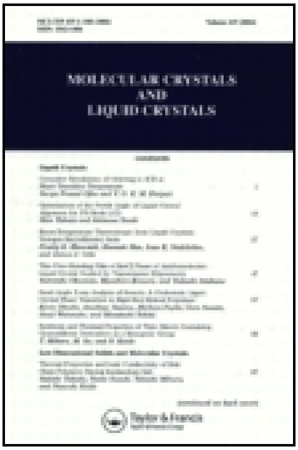

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Magnetic Order in Iron Intercalated Misfit Layer Compounds $(LaS)_{1.19}[Fe_{0.33}(TiS_2)_2]$ and $(CeS)_{1.19}[Fe_{0.33}(TiS_2)_2]$

Kazuya Suzuki [a] & Osamu Nakamura [a]

[a] Graduate School of Engineering, Yokohama National University, Hodogayaku, Yokohama, 240, Japan

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Magnetic Order in Iron Intercalated Misfit Layer Compounds $(LaS)_{1.19}[Fe_{0.33}(TiS_2)_2]$ and $(CeS)_{1.19}[Fe_{0.33}(TiS_2)_2]$

KAZUYA SUZUKI and OSAMU NAKAMURA
Graduate School of Engineering, Yokohama National University, Hodogaya-ku, Yokohama 240, Japan

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We synthesized the Fe intercalated misfit layer compounds $(LaS)_{1.19}[Fe_{0.33}(TiS_2)_2]$ and $(CeS)_{1.19}[Fe_{0.33}(TiS_2)_2]$, and investigated their structure and magnetism. It was found by electron diffraction study that the intercalated Fe atoms form the $\sqrt{3}\times\sqrt{3}$ superstructure to the TiS_2 lattice. The Fe atoms order ferromagnetically bellow 45 K. The long interlayer distance of Fe indicates that the quasi two-dimensional itinerant ferromagnetism of Fe is formed in these compounds. The magnetization curve of $(CeS)_{1.19}[Fe_{0.33}(TiS_2)_2]$ below T_N=2.7 K of the antiferromagnetic transition temperature of Ce is formed of the superposition of the hysteresis curve of ferromagnetic Fe layer and the metamagnetic curve of Ce layer occurring at 0.15 T. This suggests that nine different magnetic states can be attained below 0.2T by different field cooling process.

Keywords: misfit layer compounds; intercalation;magnetic order;

INTRODUCTION

Incommensurate misfit layer compounds $(RX)_x(TX_2)_n$ (R=rare earth metal, Pb, Sn, Bi, T=Ti, V, Cr, Nb, Ta, X=S, Se, x=1.08-1.25 and n=1,2) are now well known low dimensional electronic systems in which the structure consists of alternate stacking of hexagonal transition metal dichalcogenides (TX_2) layers and tetragonal metal monochalcogenide (RX) *bi*-layers[1]. The lattice symmetries of these two kinds of layers are mutually different, $(RX)_x(TX_2)_n$ cannot have the same crystalline lattice any longer, resulting in forming mutually incommensurate lattices. Considering their alternate stacking structure, the incommensurate misfit layer compounds are regarded as a novel class of intercalation compounds. In addition, $(RX)_x(TX_2)_n$ shows the "staging" structure denoted by a stage index n. In the case n=2, there exist the Van der Waals gaps between the adjacent TX_2 layers and one can intercalate some kinds of atoms or molecules in the TX_2 interlayer. This indicates the possibility to yield highly designed magnetic materials by intercalation magnetic species[2].

Based on this notion, we have synthesized the iron intercalated compounds in $(LaS)_{1.19}(TiS_2)_2$ and $(CeS)_{1.19}(TiS_2)_2$ and investigated their structure and magnetism.

EXPERIMENTS

Crystals of these compounds were grown by chemical transport method. Element powders of each constituent element were mixed in chemical composition ratio, and were enclosed with iodine in a quartz tube in vacuum. Using two-zone furnace, the crystals were grown by heat-treating the mixture of powders at 950 and 850 degrees for about one week. The lattice constant of the stacking direction was measured by X-ray powder diffraction and the in-plane structure was examined by electron diffraction. The chemical composition of the crystals was semi-quantitatively estimated by X-ray fluorescence analysis. Crystals different in chemical composition grew up in the same reaction tube so that we made X-ray powder diffraction and X-ray fluorescence analysis for *each* crystal used for magnetization measurements. The magnetic susceptibility of the characterized crystals was measured in the range of 1.8 to 300K both under filed cooling and zero filed cooling process, and the magnetization curve was measured up to 5 T at 1.8 and 5K.

RESULTS AND DISCUSSION

Crystal Structure

In this synthesis, crystals of $(LaS)_{1.19}[Fe_x(TiS_2)_2]$ or $(CeS)_{1.19}[Fe_x(TiS_2)_2]$ and Fe_xTiS_2 were simultaneously obtained. Because these two kinds of crystal are different in the lattice constant in the stacking direction, they can be distinguished by X-ray powder diffraction. The lattice constant in the stacking direction little changes by the insertion of 3d transition metal into $(RS)_{1.19}(TiS_2)_2$. This result is quite similar in the case of Fe_xTiS_2[3] where the iron atoms are intercalated between the Van der Waals gap of TiS_2. Electron diffraction patterns of $(LaS)_{1.19}(TiS_2)_2$ and $(LaS)_{1.19}[Fe_{0.33}(TiS_2)_2]$ are shown in Fig. 1. The diffraction patterns of these compounds are made of the diffraction spots from quasi tetragonal lattice and quasi hexagonal lattices, corresponding

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to the diffraction from the LaS layer and the TiS_2 layer, respectively. Some satellite spots were found in the incommensurate direction (a^* direction). The origin of the satellite spots was interpreted in terms of the result of mutual lattice modulation. More complicated diffraction pattern was found in the iron intercalated compound. The additional diffraction spot arises from the $\sqrt{3}\times\sqrt{3}$ superstructure formed of the intercalated Fe atoms for the quasi hexagonal TiS_2 lattice. These results suggest that the Fe atoms are certainly inserted in the TiS_2 interlayer and the chemical composition ratio x of Fe to $(TiS_2)_2$ is 0.33. On the other hand, there exist the crystals whose diffraction pattern is quite similar to that of unintercalated $(LaS)_{1.19}(TiS_2)_2$, although the crystals have nearly same amount ($x\sim0.33$) of Fe ascertained by X-ray fluorescence analysis. This fact suggests the presence of the crystals different in the order of Fe site occupation. It is clear that physical properties of $(LaS)_{1.19}[Fe_{0.33}(TiS_2)_2]$ and $(CeS)_{1.19}[Fe_{0.33}(TiS_2)_2]$ strongly depend on degree of order of Fe site occupation, as will be mentioned in the following section.

Magnetic Properties

Unintercalated compounds $(LaS)_{1.19}(TiS_2)_2$ consist of nonmagnetic chemical elements and shows Pauli paramagnetism, while $(CeS)_{1.19}(TiS_2)_2$ having localized 4f electron of Ce shows antiferromagnetism below $T_N = 2.7$ K. Because the CeS layer is separated about 17 Å by two TiS_2 layers, $(CeS)_{1.19}(TiS_2)_2$ is regarded as a quasi two-dimensional magnet[3-5]. By intercalation of Fe into the TiS_2 interlayer of $(LaS)_{1.19}(TiS_2)_2$ and $(CeS)_{1.19}(TiS_2)_2$, the magnetic order of Fe is formed below about 45 K[6].

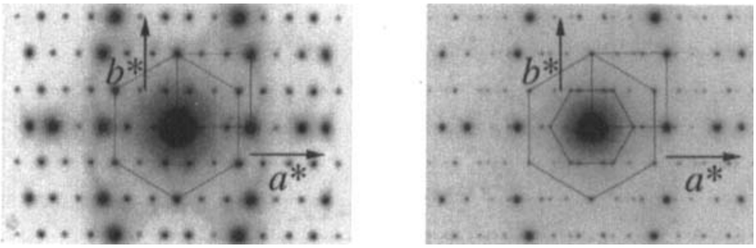

FIGURE 1. Electron diffraction patterns of $(LaS)_{1.19}(TiS_2)_2$ (left) and $(LaS)_{1.19}[Fe_{0.33}(TiS_2)_2]$ (right). The inner hexagon in the right figure is drawn by the segments among the spots from the superlattice of Fe.

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Temperature dependence of the magnetization (logarithmic scale) of $(LaS)_{1.19}[Fe_{0.33}(TiS_2)_2]$ under each condition of field cooling (FC) and zero field cooling (ZFC) is shown in Fig. 2. In the crystal where the intercalated Fe atoms form the √3x√3 superlattice, the magnetization almost diverges near by 50 K and the differences of those in FC and ZFC processes become apparent below the temperature. This suggests the transition to ferromagnetic or cluster glass states[7]. On the other hand, as for the crystals where Fe does not form the superlattice, the magnetization is quite small and shows very weak dependence on field cooling processes. This looks like the spin-glass behavior[7].

When the site randomness of Fe is introduced in $(LaS)_{1.19}[Fe_{0.33}(TiS_2)_2]$, remarkable changes may occur in the strength of the exchange interaction and in its electronic states. It is known that the exchange interactions among intercalated Fe atoms in Fe_xTiS_2 are mainly mediated by RKKY (Rudermann-Kittel-Kasuya-Yoshida) interaction and the intercalated Fe atoms show itinerant magnetism. This is also expected for $(LaS)_{1.19}[Fe_{0.33}(TiS_2)_2]$ since the chemical environments around Fe are very similar in these compounds. The sign (ferro- or antiferromagnetic) and strength of the RKKY interaction varies depending on the distance of the magnetic atoms. Therefore the site randomness of Fe results in many different interatomic distances among Fe atoms, and it may cause the coexistence and competition of ferro- and

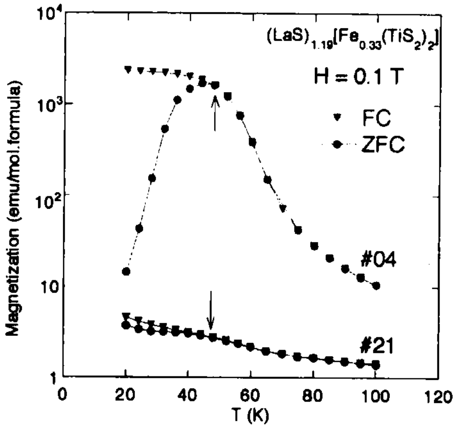

FIGURE 2. Temperature dependence of the magnetization of two different crystals of $(LaS)_{1.19}[Fe_{0.33}(TiS_2)_2]$ measured after FC and ZFC process.

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antiferromagnetic interaction. Thus, by the introduction of the site randomness, the magnetic system changes from the cluster glass state to the spin glass state because of the competition of exchange interaction. Another effect of the site randomness is that the electronic states come into localized states. The site randomness of Fe appends random potentials to the electronic structure of the host compounds. It causes the discrete energy levels in the conduction bands and impedes the band splitting associated with the ferromagnetic ordering. These two effects decrease the ordered magnetic moments as found in Fig. 2.

Figure 3 is the magnetization curve of Fe site ordered $(CeS)_{1.19}[Fe_{0.33}(TiS_2)_2]$ at 1.8 K and up to 5 T, where the magnetic field is applied along the *c*-axis (stacking direction). The magnetization curve is rather complicated, having many plateaus. The occurrence of such magnetization curve is explained as follows. It is known that the magnetic structure of $(CeS)_{1.19}(TiS_2)_2$ consists of ferromagnetic Ce layers combined antiferromagnetically within the CeS *bi*-layer. Due to the weak antiferromagnetic coupling within the CeS *bi*-layer, $(CeS)_{1.19}(TiS_2)_2$ exhibits a metamagnetic transition at the magnetic field of 0.15 T[2,8]. In $(CeS)_{1.19}[Fe_{0.33}(TiS_2)_2]$, when the crystal is cooled below T_N in the zero magnetic field, the Fe layer forms ferromagnetic domain structures. Thus, the initial magnetization is nearly zero below T_N. With increasing the magnetic field, at first the metamagnetic transition within the CeS *bi*-layer occurs so that the magnetization changes stepwisely to show nearly full

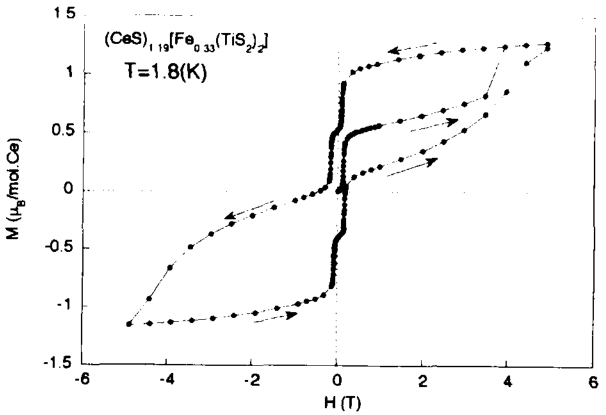

FIGURE 3. Magnetization curve of $(CeS)_{1.19}[Fe_{0.33}(TiS_2)_2]$ at 1.8 K.

magnetic moment of Ce. Then, the magnetic domain in the Fe layer is gradually broken with magnetic field to be nearly saturated at 5 T. In turns the magnetic field is lowered from 5 T to zero, the metamagnetic transition occurs in the CeS layer to be anftiferromagnetically coupled Ce moments, holding the Fe layer ferromagnetic. When magnetic field is decreased to zero, there still resides the remnant magnetization of Fe. Then the polarity of the magnetic field is reversed and increased, the metamagnetic transition occurs in the CeS *bi*-layer. At the case, the magnetic field is not large enough to reverse the direction of the magnetization of the ferromagnetic Fe layer so the magnetic moment of Ce is parallel to the magnetic field, on one hand that of Fe is antiparallel. By applying the magnetic field in this way between -5 T and 5 T, we can attain nine different magnetic states in $(CeS)_{1.19}[Fe_{0.33}(TiS_2)_2]$.

The results of the magnetization curve suggest that the magnetic order occurs independently in the Ce and Fe layer. This fact is due to very weak interactions between these two layers, and due to strong Ising nature of both Ce and Fe in the present compound[2].

The magnetization process gives a possibility that we can make a nanometer scale magnet having many magnetization plateaus by piling up metamagnetic layers and ferromagnetic layers in turns, with very weak magnetic interaction.

Acknowledgments

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