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Low Dimensional Triangular Magnetic Systems in Transition Metal Intercalates of Misfit Layer Compounds

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Low dimensional triangle magnetism was studied for transition metal intercalates of incommensurate misfit layer compounds $(RS)_x[M_{0.33}(NbS_2)_2]$ (R = La, Ce, M = Fe, Mn). Magnetization measurements for the single crystals of the Fe intercalated compounds $(RS)_x[Fe_{0.33}(NbS_2)_2]$ show the successive magnetic transition at 14 K and 22 K. The strong frustration appears between two transition temperatures as quasi two-dimensional antiferromagnetic triangular Ising spin system. In contrast, the Mn compounds $(RS)_x[Mn_{0.33}(NbS_2)_2]$ has very low transition temperature of 3.0 K due to the nature of quasi two-dimensional Heisenberg spin system.

Keywords: misfit layer compounds; rare earth metal; low dimensional magnetism; spin frustration

INTRODUCTION

In order to investigate low-dimensional electrical conduction or magnetism, layered compounds and their intercalation compounds are useful materials since various parameters such as inter-layer distances, conduction carrier densities or stacking sequence of magnetic layers can be varied by intercalation technique. Incommensurate misfit layer compounds $(RX)_x(TX_2)_n$ (M=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 good model compounds. The structure consists of alternate stacking of hexagonal transition metal dichalcogenides (TX_2) layers and tetragonal metal monochalcogenide (RX) *bi*-layers[1]. We have studied the synthesis and properties of Fe intercalated $(RS)_{1.19}(TiS_2)_2$ in the past years, and found that in $(CeS)_{1.19}[Fe_{0.33}(TiS_2)_2]$

magnetic order of Ce and intercalated Fe both developed in the different temperature, antiferromagnetic for Ce and *triangular* ferromagnetic for Fe, respectively. The magnetization curve of $(CeS)_{1.19}[Fe_{0.33}(TiS_2)_2]$ indicates that nine different magnetic states can be attained within the external field of 0.3 T, where the magnetic states are formed of the combination of the metamagnetic states of Ce and ferromagnetic states of Fe[2,3]. In this paper, we focused on novel compounds $(RS)_x[M_{0.33}(NbS_2)_2]$ (R = La, Ce, M = Fe, Mn). It is expected in the compound of T = Nb that the antiferromagnetic interaction works among intercalated Fe atoms that form triangle arrangement within the layer. The magnetic moments align in the stacking direction so that the very strong frustration may be well appear. We have investigated the synthesis of single crystal and electrical, magnetic and thermal properties of these compounds.

EXPERIMENTAL

Crystals of these compounds were grown by chemical transport method. Each constituent element in powder form was mixed in the chemical composition ratio and 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 a week. The lattice constant of the stacking direction was measured by X-ray powder diffraction, and in-plane structure was investigated by Laue photographs using imaging plate. The electrical resistivity was measured by conventional four-probe method between 8 K and 300 K. The magnetic susceptibility was measured by SQUID magnetometer between 1.8 K and 300 K both under field cooling (FC) and zero field cooling (ZFC) process, and the magnetization curves were measured up to 5 T at 2 K and 5 K.

RESULTS AND DISCUSSION

Figure 1 is a X-ray Laue photograph of $(LaS)_{1.14}[Mn_{0.33}(NbS_2)_2]$. The photograph contains diffraction spots from the pseudo-tetragonal sublattice of LaS, the pseudo-hexagonal sublattice of NbS_2 and the pseudo-hexagonal superlattice of intercalated Fe. As for $(RS)_x[Fe_{0.33}(NbS_2)_2]$ (R=La,Ce), similar photographs were obtained[4] and single crystal X-ray analysis was carried out[5]. These compounds have a stacking structure similar to $(CeS)_{1.19}[Fe_{0.33}(TiS_2)_2]$[3], where

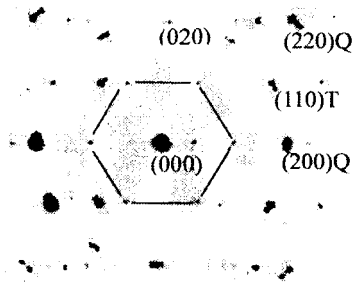

FIGURE 1 X-ray Laue photograph of $(LaS)_{1.14}[Mn_{0.33}NbS_2]$. Q: pseudo tetragonal LaS, T: pseudo hexagonal NbS_2. The hexagon shows the diffraction from the Mn superlattice.

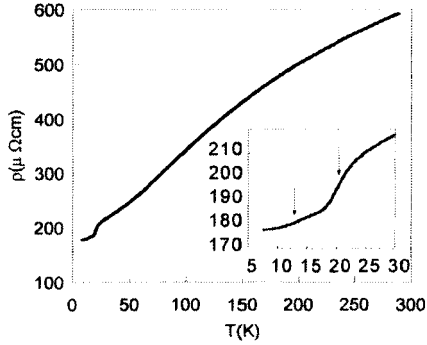

FIGURE 2 Temperature dependence of the resistivity of $(CeS)_{1.16}[Fe_{0.33}(NbS_2)_2]$. The anomalies indicated by arrows in the inset indicate magnetic phase transitions.

one RS layer and two NbS_2 layers stack alternately, and M atoms are intercalated in the gallery of adjacent NbS_2 layers.

Figure 2 shows the temperature dependence of the resistivity of $(CeS)_{1.16}[Fe_{0.33}(NbS_2)_2]$. The room temperature resistivity is 600 μΩcm and it shows the metallic behavior down to 8 K, in contrast to the resistivity of $(RS)_{1.19}[Fe_{0.33}(TiS_2)_2]$, which increases at lower temperatures due to the electron correlation effect[3]. Below about 22 K the resistivity of $(CeS)_{1.16}[Fe_{0.33}(NbS_2)_2]$ decreases steeply with temperature, suggesting a magnetic transition. One can see another small change in the resisitivity at 14 K indicated by an arrow in the Figure, which indicates an additional magnetic transition. The resistivity

decrease is due to the formation of the coherent potential of Fe moments associated with the magnetic transition. Such decrease of resistivity was also found in $Fe_{0.33}NbS_2$ at 47 K[6].

Figures 3(a) and 3(b) are the magnetic susceptibility of $(LaS)_{1.14}[Fe_{0.33}(NbS_2)_2]$ and $Fe_{0.33}NbS_2$, respectively where magnetic field is applied along the stacking direction (H//c). Since the La is nonmagnetic, the magnetism in $(LaS)_{1.14}[Fe_{0.33}(NbS_2)_2]$ arises from the magnetic moments of Fe intercalated between the NbS_2 layers. The temperature dependence of the susceptibility follows the Curie-Weiss law above 50 K, where the effective magnetic moments and the Weiss temperatures are μ_{eff} = 5.35 μ_B and θ = +11.0 K for H || c and μ_{eff} = 4.58 μ_B and θ = -32.4 K for H || a, respectively. When the magnetic field is applied within the layer, the magnetic susceptibility is nearly 1/5 compared to that at H || c. Since the anisotropy arises from the contribution of the orbital angular momentum of the 3d electron, the ionic state of Fe can be considered as Fe^{2+}. The difference in the effective moments from the ideal value of free Fe^{2+} (4.90 μ_B) is due to the crystal field effect.

The susceptibility has a peak at around 22 K, and the magnetization induced by magnetic field shows a cooling-process dependence below 14 K as seen in Figure 3(a). The latter feature is very resemble to the behavior of the susceptibility of $Fe_{0.33}NbS_2$ below 37 K as seen in Fig. 3(b). These two anomalies at 14 K and 22 K are coincident with the result of resistivity measurements. In $(RS)_x[Fe_{0.33}(NbS_2)_2]$, the magnetic Fe layers are separated by

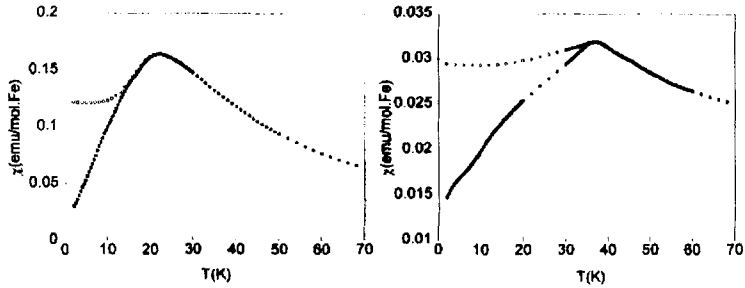

FIGURE 3 Temperature dependence of the susceptibility of $(LaS)_{1.14}[Fe_{0.33}(NbS_2)_2]$ (a) and Fe_xNbS_2 (x~0.33) (b). Magnetic field is applied parallel to the c-axis. Filled circle: after zero field cooling process and open circle: after field cooling process.

about 17.5 Å with each other and they become quasi two-dimensional, so the peak of the susceptibility at 22 K can be assigned to be due to the short range order effect. However, the resistivity clearly indicates the presence of a phase transition at 22 K, thus these two anomalies in the susceptibility suggest the successive magnetic phase transition.

The magnetic structure of the NbS_2-Fe-NbS_2 unit is known for $Fe_{0.33}NbS_2$[6], where the Fe atoms form a triangular magnetic lattice with the magnetic moments in the stacking direction. It is also known that the Fe spins have strong Ising nature so that we expect the strong spin frustration in $Fe_{0.33}NbS_2$. Because of the remarkable strength of the magnetic interaction in the stacking direction, the magnetic structure becomes a stable antiferromagnic one with ferrimagnteic layers coupling antiferromagnetically. In the actual compounds, magnetic moments in each ferrimagnetic layer cannot be neglected in a crystal so that there remain very small spontaneous magnetizations as seen in Fig. 3(b).

In the two-dimensional limit, it is known that the triangle Ising magnetic system with antiferromagnetic interaction and the moments normal to the layer shows strong spin frustration. Magnetic ordering in such system occurs when the next nearest neighbor ferromagnetic interaction is present[7]. The ordering of the moment is in the way that the honeycomb part of the triangle lattice forms the antiferromagnetic lattice with the moment in the middle of the honeycomb being paramagnetic. Then the moment orders ferrimagnetically at a lower temperature due to the interlayer magnetic interaction.

The magnetic state below 14 K in $(RS)_x[Fe_{0.33}(NbS_2)_2]$ is considered to be similar one to that in $Fe_{0.33}NbS_2$ as a three dimensional magnetic ordering. The lower transition temperature than in $Fe_{0.33}NbS_2$ is due to the decrease in the interlayer interaction because of the insertion of the RS layer. Between 14 K and 22 K, we consider that the magnetic state of this compound is the partially ordered state as mentioned above, because both antiferro- and ferromagnetic interaction can expect in $(RS)_x[Fe_{0.33}(NbS_2)_2]$ through the RKKY interaction and significantly reduced interlayer interaction. This is the first observation of the partially ordered state in layered compounds.

In $(CeS)_{1.16}[Fe_{0.33}(NbS_2)_2]$, the magnetism of Ce appears in addition to that of Fe. The magnetic susceptibility is a superposition of the Curie-Weiss like

susceptibility of Ce and that of Fe in $(LaS)_{1.14}[Fe_{0.33}(NbS_2)_2]$. The susceptibility shows a maximum at 3 K, which is due to the antiferromagnetic transition in the Ce layer. Thus, magnetic transitions of Ce and Fe occur independently as found in $(CeS)_{1.19}[Fe_{0.33}(TiS_2)_2]$.

Magnetic properties of a Mn intercalated compound $(LaS)_{1.14}[Mn_{0.33}(NbS_2)_2]$ is quite different from that of the Fe intercalated compound. The ionic state of Mn is considered as Mn^{2+} from our susceptibility measurements and the similarity of the chemical environment around Mn atoms to that in $Mn_{0.33}NbS_2$[8]. Then the Mn^{2+} has the high spin d^5 state, in which the sum of the orbital angular momentum vanishes. In such case the single ion magnetic anisotropy is not present, therefore, the magnetic system becomes quasi two-dimensional triangle Heisenberg one. It is well known that the two-dimensional Heisenberg system does not have magnetic ordering at finite temperature. The susceptibility of $(LaS)_{1.14}[Mn_{0.33}(NbS_2)_2]$ shows a peak at 3 K when the magnetic field is applied with in the layer. This result indicates a three dimensional antiferromagnetic transition where the magnetic moments lie in the layer. The magnetic transition temperature is significantly lowered from the transition temperature of 40 K in $Mn_{0.33}NbS_2$.

In the series of compounds $(RS)_x[M_{0.33}(NbS_2)_2]$, we revealed various features as low-dimensional triangle magnets including spin frustration, partially ordered state, dependence of single ion anisotropy and intra-layer magnetic interaction.

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