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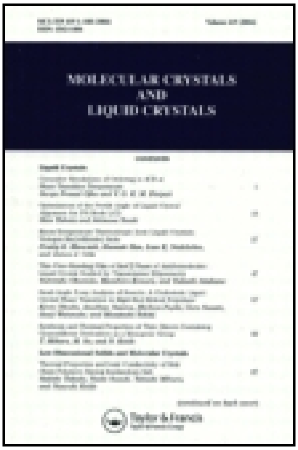

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Magnetism in Incommensurate Layer Compounds (RES) $_x$ VS$_2$ (Re=Rare Earths)

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MAGNETISM IN INCOMMENSURATE LAYER COMPOUNDS $(RES)_xVS_2$ (RE=RARE EARTHS)

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Abstract Magnetic properties are presented for incommensurate layer compounds $(RES)_xVS_2$. Antiferromagnetic transitions were observed in the compounds of RE=Ce and Gd at T_N=5.6K and 4.8K, respectively. The magnetic ordering of the compound of $(CeS)_{1.19}VS_2$ is discussed in relation to the two dimensionality coming from layer structure of this material.

INTRODUCTION

The structure and physical properties of incommensurate layer compounds $(MS)_xTS_2$ (M=rare earth, Pb,Sn,Bi, T=Ti,V,Cr,Nb,Ta) have attracted much attention in recent years.[1–4] The distorted cubic MS layers and distorted hexagonal TS_2 layers are alternately stacked in these compounds. The differences in symmetry of each layer lead to the incommensurate nature in the in-plane periodicity of these compounds. In the compounds of M=RE, the rare earth elements have localized 4f magnetic moments. The NaCl type structure of pristine RES is deformed to two atom thick (001) slices of the distorted tetragonal RES layers that are separated by conducting TS_2 slabs. Such structure forms good conditions for realizing two dimensional magnetism. In our previous investigation, electric conduction of $(RES)_xVS_2$ was found to be semiconducting.[5] This is an advantage in studying magnetic interactions by comparing with metallic T=Nb, or Ta analogues, because the effect of the conduction carriers is excluded. With these conditions, we carried out detailed research for $(RES)_xVS_2$ by means of susceptibility and specific heat. Emphasis is laid on $(CeS)_{1.19}VS_2$ that shows an antiferromagnetic long range ordering accompanied by a metamagnetic transition. Some comparison with T=Nb or Ta analogues will be discussed.

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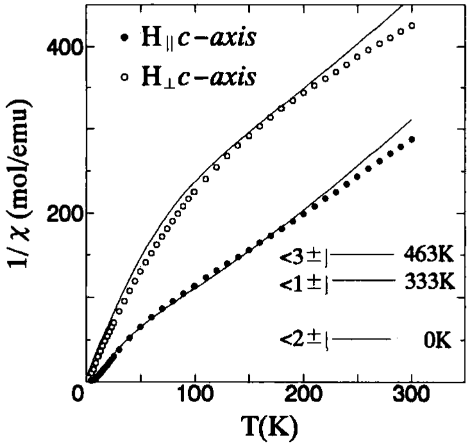

FIGURE 1 Inverse susceptibility vs temperature plot of $(CeS)_{1.19}VS_2$ at 10kOe. The solid lines are calculated susceptibility.

B_2^0(K)	-18.5
B_4^0(K)	0.16
B_4^4(K)	7.9
α	0.549
β	0.836
$g_{\|\|c}$	2.23
$g_{\perp c}$	2.01

TABLE 1 Crystal field parameters of $(CeS)_{1.19}VS_2$.

EXPERIMENTAL

$(RES)_xVS_2$ were synthesized from the constituent elements or RE_2S_3 by heat treating under a temperature gradient of 850 to 950°C. Structural characterization of the resulting materials is performed by in-plane electron diffraction and powder X-ray (001) diffraction. Magnetic susceptibility and magnetization were measured by SQUID magnetometer and Faraday balance method. Specific heat measurements were performed by the standard adiabatic heat pulse method.

RESULTS AND DISCUSSION

i)Magnetic properties of $(CeS)_{1.19}VS_2$

The magnetic susceptibility is presented as a function of temperature in Figure 1. The susceptibility shows convex curvarture and deviates from the Curie-Weiss law at low temperature below c.a. 100K. This deviation comes from crystal field effect. In order to clarify the microscopic character of the localized magnetic moments, we analyzed the crystal field effect in $(CeS)_{1.19}VS_2$ by means of Stevens's equivalent operator method.[6,7] In cubic crystal field symmetry, the Ce^{3+} 4f-states ($J=5/2$) split into a Γ_7 doublet and a Γ_8 quartet. In a crystal field lower than cubic symmetry,

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the Ce 4f-states split into three Kramers doublet states. In $(\mathrm{CeS})_{1.19}\mathrm{VS}_2$, the CeS slabs are expected to have symmetry lower than orthorhombic. Since the in-plane anisotropy of the susceptibility has not been measured, we treat the crystal field to have tetragonal symmetry as a preliminary approach. The crystal field Hamiltonian with tetragolal symmetry is expressed as

$$H_{cr} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4 \,, \tag{1}$$

where O_m^n are the Stevens operators and B_m^n are the crystal field parameters that are evaluated empirically. The eigen functions of Kramers doublets under this crystal field symmetry are $|1\pm>= \alpha|\pm\frac{5}{2}> +\beta|\mp\frac{3}{2}>$, $|2\pm>= \beta|\pm\frac{5}{2}> -\alpha|\mp\frac{3}{2}>$, $|3\pm>= |\pm\frac{1}{2}>$, where α and β are the normalization factors of the eigen functions. Table 1 summarizes the crystal field parameters for this fitting. The calculated susceptibility is also shown in Figure 1 with the experimental data. The lowest lying doublet is $|2\pm>$. The g-factors of the lowest lying doublet are expressed as $g_{\|c} = 2g_J < 2+|J_z|2+>$, $g_{\perp c} = 2g_J < 2+|J_x|2->$, where g_J is the Lande's factor (g_J=6/7). The deduced g-values of $g_{\|c}$=2.23 and $g_{\perp c}$= 2.01 have an anisotropy of about 10%.

Figure 2 presents the magnetic susceptibility of $(\mathrm{CeS})_{1.19}\mathrm{VS}_2$ in a field of 150Oe. The susceptibility has a sharp peak at 6.0K when the field is applied parallel to the c-axis, indicating that an antiferromagnetic transition occurs around this temperature. Figure 3 is the magnetization curve of $(\mathrm{CeS})_{1.19}\mathrm{VS}_2$ at 2.0K, in a field up to 5kOe. The magnetization parallel to the c-axis increases abruptly at 1.5kOe and saturates above 2kOe. The magnetization shows a clear field dependent hysteresis without remnant magnetization at zero-field, indicating a field dependent first-order phase transition. Thus, the magnetic state of $(\mathrm{CeS})_{1.19}\mathrm{VS}_2$ is assigned to the metamagnetic transition. The saturation moment along the c-axis 1.1μ_B is in good agreement with the value calculated from the crystal field parameter $M_{sat} = 1/2 g_{\|c}\mu_B$. The metamagnetic transition where the easy axis is the c-axis suggests that ferromagnetic CeS layers are antiferromagnetically stacked. The interlayer exchange constant J' correlates with the critical field of the magnetization process H_c with the relation expressed as $g_{\|c}\mu_B H_c = z'|J'|$ where z' is the number of interlayer nearest neighbors, i.e. z'=4 and J' becomes −0.04K.

The anisotropy of the susceptibility exceeds 40 at 6.0K. Such large anisotropy of the susceptibility does not arise from the anisotropy of the g-values (about 10%).

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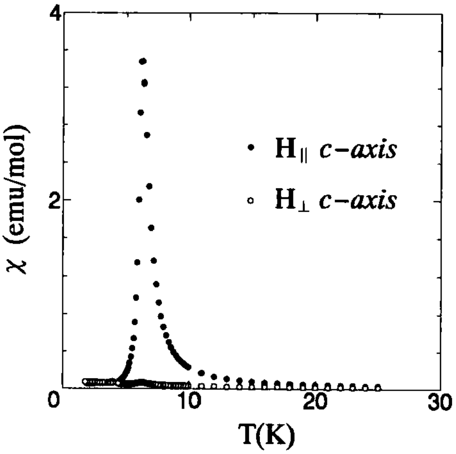

FIGURE 2 Temperature dependence of the susceptibility of $(CeS)_{1.19}VS_2$ at 150Oe.

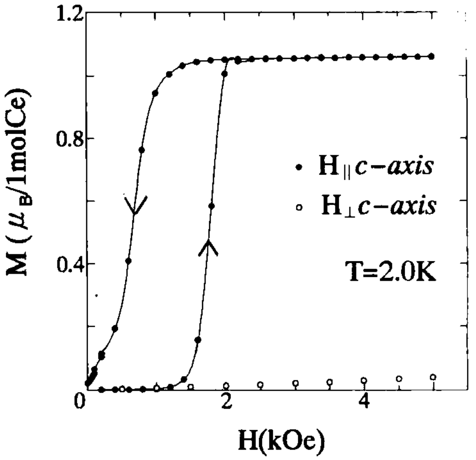

FIGURE 3 Magnetization curve of $(CeS)_{1.19}VS_2$ at 2K. The solid line is a guide for the eye.

In the temperature range between T_N and ca. 10K, a deviation from the Curie-Weiss law appears, indicating the presence of ferromagnetic short range order. The Weiss temperatures estimated in the temperature range between 10 and 25K for-both crystallographic axes are $\Theta_{\|c}$=+7.9K and $\Theta_{\perp c}$=−1.7K. The interlayer exchange J'= −0.04K is two orders of magnitude smaller than T_N, suggesting the intralayer exchange is dominant in this magnetic ordering. Thus, we use the transition temperature as an appropriate parameter in discussing the intralayer exchange interaction. Under the molecular field approximation, the intralayer exchange constant J is expressed by the transition temperature $k_BT_c = zJ$. In $(CeS)_{1.19}VS_2$, the Ce ions have four nearest neighbors in the same plane as the CeS double layers and four nearest neighbors in the adjacent plane. We treat these eight neighbors as the same intralayer nearest neighbor because these neighbors have similar nearly 90° superexchange paths. Under this treatment, z=8 and J becomes 0.7K.

Figure 4 is the temperature dependence of the specific heat of $(CeS)_{1.19}VS_2$. The transition temperature is estimated to be 5.6K from the specific heat peak. The entropy is calculated from the specific heat data, where the specific heat below the lowest temperature point of the measurements(1.93K) is extrapolated as a straight line. We employ the specific heat data of non-magnetic isostructural compound $(LaS)_{1.14}NbS_2$ for the lattice contribution in the entropy.[8] The magnitude of entropy below T_N is estimated to be 3.22J/Kmol where the lattice contribution to

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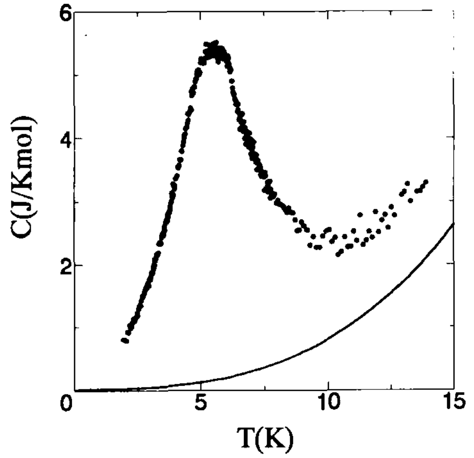

FIGURE 4 Specific heat C of $(CeS)_{1.19}VS_2$. The solid line is the C of nonmagnetic $(LaS)_{1.14}NbS_2$ (Ref.8).

RE	Property
$(CeS)_{1.19}VS_2$	AF T_N=5.6K
$(NdS)_{1.23}VS_2$	paramagnetic
$(SmS)_{1.25}VS_2$	valence fluctuation
$(GdS)_{1.25}VS_2$	AF T_N=4.8K

TABLE 2 Magnetic properties of $(RES)_xVS_2$. AF represents the antiferromagnetic transition.

the entropy is negligible (<5%). It is 56% of Rln2=5.76J/Kmol expected from the doublet 4f ground state of Ce. The specific heat has a tail trailing character above T_N. Around 10K, a ferromagnetic short range order effect appears in the susceptibility, and a magnetic contribution of ca. 1J/Kmol still remains in the specific heat. The behavior of the specific heat indicates that short range magnetic ordering grows over a wide temperature range above T_N. Short range magnetic ordering is a typical characteristic of a low-dimensional magnet. The gain of the magnetic entropy above the transition temperature ($S(\infty) - S(T_N)$) is estimated to be 57% for the two-dimensional Ising quadratic lattice and 14% for the three dimensional fcc Ising lattice.[9] The 50% gain of the magnetic entropy above the transition temperature suggests the fact that $(CeS)_{1.19}VS_2$ is a quasi two dimensional magnet.

As mentioned above, the magnetic transition in $(CeS)_{1.19}VS_2$ is dominated by the intralayer interaction of CeS slabs. Similar orderings have been observed in $(CeS)_{1.14}TaS_2$ and $(CeS)_{1.15}NbS_2$ at T_N=2.0K and 3.0K, respectively.[3,4] The higher transition temperature in semiconducting $(CeS)_{1.19}VS_2$ means that the conduction carriers have no effect in the intralayer interaction. Moreover, the transition temperature is not changed in the 2nd-stage compounds where one more TS_2 layer is inserted between the CeS slabs and the interlayer distance between Ce ions is expanded from about 8Å to 14Å.[3,4] This suggests that the intralayer interaction predominates the development of this magnetic ordering.

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ii)Magnetic properties of other compounds.

Table 2 summarizes the magnetic properties of $(\mathrm{RES})_x\mathrm{VS}_2$ for RE=Ce, Nd, Sm. An antiferromagnetic ordering was also found in $(\mathrm{GdS})_{1.25}\mathrm{VS}_2$ at 4.8K. In this compound, the magnetic moments of Gd^{3+} ions are oriented in the basal plane, different from the Ce compound where the magnetic moments point to the c-axis. The 4f magnetic moment of Gd^{3+} is an isotropic $^8S_{7/2}$ state that lacks the orbital contribution. $(\mathrm{GdS})_{1.25}\mathrm{VS}_2$ is assigned to the two dimensional Heisenberg antiferromagnet. In $(\mathrm{SmS})_{1.25}\mathrm{VS}_2$, a valence fluctuating state of 4f state was observed in our susceptibility and XPS measurements.

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