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ELECTRONIC STRUCTURES OF INCOMMENSURATE LAYERED COMPOUNDS $(MS)_xTaS_2$ (M=RARE EARTHS, Pb, Sn)

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Abstract Reflectance spectra, Hall coefficient and magnetoresistance were measured for incommensurate layered compounds $(MS)_xTaS_2$ in order to elucidate their electronic band structures. The charge transfer from MS to TaS_2 is found to be much smaller in Pb and Sn compounds than in the rare earth compounds. The Fermi energy and magnetoresistance have the same M-atom dependence among the rare earth compounds, which is related to the number of electrons transferred from the MS layers to TaS_2 layers. The electronic structures are described in terms of a two-hole carrier system in the compounds with small charge transfer. With increasing the charge transfer rate, it becomes a one-hole carrier system as one of the Fermi surfaces vanishes.

INTRODUCTION

Layered sulfides having chemical formulae $(MS)_xTaS_2$ are known to have a unique crystal structure consisting of the alternate stacking of pseudo-hexagonal TaS_2 and pseudo-tetragonal MS layers.[1] The difference in lattice symmetry between these two layers causes stacking misfit and lattice incommensuration in $(MS)_xTaS_2$. Then the sublattices of MS and TaS_2 do not have a common unit cell, and x is no longer a rational number. Structural and physical properties of $(MS)_xTaS_2$ have been intensively studied recently,[1-4] focusing on the lattice incommensurability. The lattice incommensurability brings about the quasi-periodic potential to the electronic structure, since it produces mutual lattice modulations in both the MS and TaS_2 layers. We have studied physical properties of $(MS)_xTaS_2$ and have shown that electrical conduction is dominated by hole carriers on the TaS_2 layers while the conduction carriers in the MS layers are localized due to the quasi-periodic potential.[4] Here, we report the reflectance spectra and magnetoresistance of $(MS)_xTaS_2$ and propose an electronic structure for $(MS)_xTaS_2$, which is affected by the lattice incommensurability.

REFLECTANCE SPECTRA FOR $(MS)_xTaS_2$

Polarized reflectance spectra were measured at room temperature by a microphotometoric technique between 750 and 25000cm^{-1}. Crystals suitable for the reflectivity measurement were cleaved by adhesive tapes to obtain a flat and flush surface. Spectra were taken on (00l) crystal surfaces in the polarization direction parallel to the *b*-axis (commensurate direction, *E//b*). In the measured energy region, we did not find any remarkable difference in the spectra for *E//a* and *E//b*. Figure 1 is the polarized reflectance spectra for $(LaS)_{1.13}TaS_2$ and $(PbS)_{1.13}TaS_2$. These spectra have common features; the spectra in the low frequency region show high reflectivity and a sharp drop suggesting a free-electron Drude type reflectivity. The Drude edges are estimated at 5000cm^{-1} for La compound and 6500cm^{-1} for Pb compound, respectively, which are decreased from the Drude edge of 10000cm^{-1} for pristine 2H-TaS_2.[5] The reflectivity increases up to 40% above the Drude edge, originating from interband

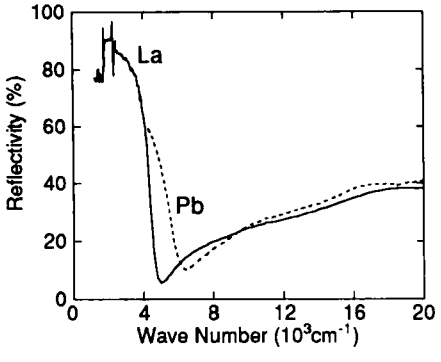

FIGURE 1. Reflectance spectra for $(MS)_xTaS_2$ with M=La (solid line), and Pb (dotted line).

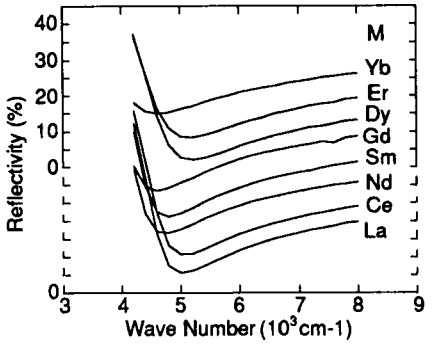

FIGURE 2. Reflectance spectra around the Drude edges for rare earth compounds. The zero reflectivity is shifted by every 5% from M=La to Yb.

transitions. These outstanding features are common in $(MS)_xTaS_2$ for M=Ce, Nd, Sm, Gd, Dy, Er, Yb and Sn. Figure 2 displays the reflectance spectra for rare earth substituted $(MS)_xTaS_2$ around the Drude edge region. All the reflectance spectra are fitted to the Drude-Lorentz model consisting of frequency dependent contributions of a Drude type from free carriers and a Lorentz type from interband transitions, and frequency independent contribution from a core term. The dielectric function is given by

$$\varepsilon = \varepsilon_c - \frac{\omega_p^2}{\omega^2 + i\omega/\tau} + \frac{B}{\omega_0^2 - \omega^2 + i\Gamma\omega} \quad ;$$

where ω is the photon frequency, ω_p is the plasma frequency, τ is the optical scattering time, B is the oscillator strength, ω_0 is the Lorentz resonant frequency, Γ is its damping factor and ε_c is the contribution of core transitions. On the basis of the two-dimensional free electron model, the Fermi energy E_F is proportional to the carrier density n, and hence, E_F is proportional to ω_p^2. Using the interlayer distance I_c between adjacent TaS_2 layers,[2] E_F is given by

$$E_F = \frac{\hbar^2 \omega_p^2 I_c}{4e^2}.$$

Fitted plasma frequency and Fermi energy are summarized in Table 1 with the parameter x in $(MS)_xTaS_2$.

TABLE 1. Plasma frequency (ω_p), Fermi energy (E_F), and chemical composition (x) in $(MS)_xTaS_2$.

M	*La*	*Ce*	*Nd*	*Sm*	*Gd*	*Dy*	*Er*	*Yb*	*Sn*	*Pb*
x	*1.13*	*1.14*	*1.16*	*1.19*	*1.20*	*1.22*	*1.23*	*1.23*	*1.16*	*1.13*
$\hbar\omega_p$(eV)	*1.70*	*1.70*	*1.64*	*1.66*	*1.61*	*1.71*	*1.70*	*1.54*	*2.38*	*2.26*
E_F(eV)	*0.57*	*0.57*	*0.53*	*0.54*	*0.50*	*0.57*	*0.56*	*0.46*	*1.11*	*1.00*

The Drude edges are slightly different among the rare earth compounds, whose energy is highest for M=La and shifts red for M going from La to Gd. Then it jumps up for M=Dy and finally decreased again for M=Er and Yb. It is also noted that the carrier density in the Pb and Sn compounds is much larger than in the rare earth compounds judging from the Plasma frequencies.

MAGNETORESISTANCE

Figures 3(a) and 3(b) show the field dependence of basal plane magnetoresistance ($H \parallel c$) for $(CeS)_{1.14}TaS_2$ and $(SnS)_{1.16}TaS_2$ at the various temperatures. The magneto-resistance shows quadratic field dependence and its magnitude at 5T and 5K reaches 3% for M=Sn and 1.2% for M=Ce, respectively. One can evidently find that the temperature dependence of magnetoresistance is more pronounced in $(SnS)_{1.16}TaS_2$ than in $(CeS)_{1.14}TaS_2$.

Figure 4 shows the rare earth variation of the magnetoresistance at 5K. The magnetoresistance is extremely small for rare earth compounds, for example, that for $(YbS)_{1.23}TaS_2$ is only 0.2% at 5T. In the electronic system with closed Fermi surfaces,

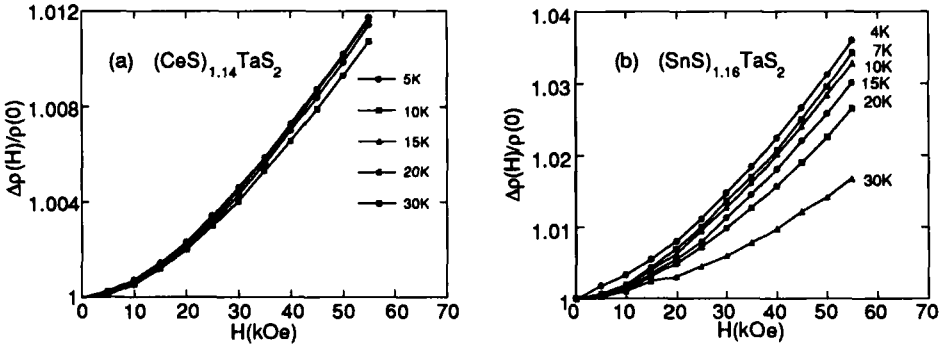

FIGURE 3. Magnetoresistance for $(CeS)_{1.14}TaS_2$ (a) and $(SnS)_{1.16}TaS_2$ (b) at various temperatures.

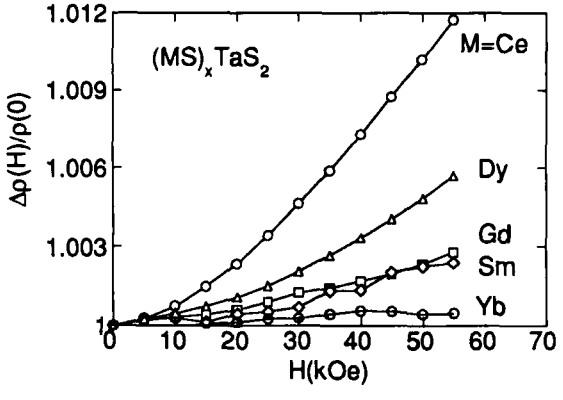

FIGURE 4. Magnetoresistance at 5K for some rare earth compounds.

magnetoresistance originates from the carriers with different band masses. Thus, one of the following two electronic structures is presumed from the small magnetoresistance in $(MS)_xTaS_2$. One is that the electronic structure consists of one kind of hole Fermi surface with the band mass depending on the Fermi wave vector. The other one consists of at least two hole Fermi surfaces with slightly different band masses.

ELECTRONIC STRUCTURE OF $(MS)_xTaS_2$

The band structure of $(MS)_xTaS_2$ is inferred from the carrier density n estimated from the reflectance spectra and Hall effect measurements. Figure 5 shows the rare earth dependence of the magnetoresistance, Fermi energy E_F and carrier density n. These three physical quantities display the same trend of rare earth variation. Note that the carrier density estimated from the Hall coefficient varies by a factor of 2-3 depending

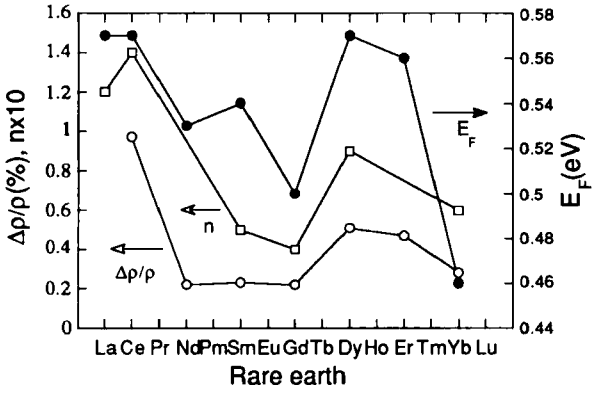

FIGURE 5. Fermi energy E_F (closed circle), magnetoresistance $\Delta\rho/\rho$ (open circle) at 5K and 5T and carrier density n (open square) as a function of rare earth compound. Data of n for M=La and Ce are taken from ref. 1. Note that the minimum in the right hand scale is not zero.

on the rare earth species (0.12 for M = Ce and 0.05 for M = Gd), whereas E_F varies only 20% within the rare earth compounds. Since E_F estimated from the plasma frequency is proportional to the carrier density on the basis of the two-dimensional single carrier free electron model, this disagreement suggests that the single carrier model is not suitable for $(MS)_xTaS_2$.

In the case of the rare earth compounds, it has been discussed that the carriers in the TaS_2 layer govern the electrical conduction of $(MS)_xTaS_2$ and the carriers on the MS layer are localized due to the non-periodic potential.[4] According to the band structure calculated by Mattheiss,[6] the conduction band of pristine 2H-TaS_2 consisting of the Ta $5d_{z^2}$ orbital is half-filled. In $(MS)_xTaS_2$, the electrons transferred from MS fill the band more than half, and the presence of the MS layer between TaS_2 layers makes the conduction band more two-dimensional. The dispersion curve of the two-dimensional TaS_2 conduction band is shown in Figure 6. If the charge transfer is considerably large and nearly fills the conduction band, the band has a hole Fermi surface around K-points

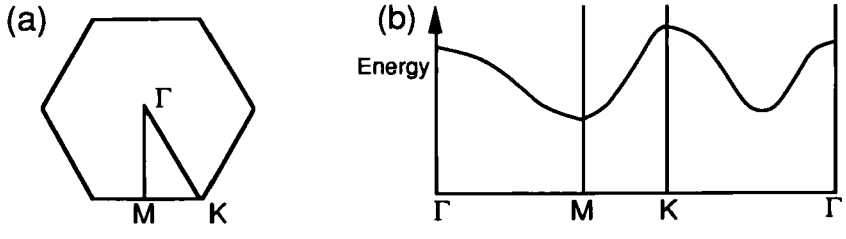

FIGURE 6. (a) Brillouin zone for the hexagonal lattice with the symmetry points according to the standard notation. (b) schematic illustration of the dispersion curve of the TaS_2 conduction band.

as seen in Figure 6. With decreasing the charge transfer and lowering the Fermi level, the band tends to have another hole Fermi surface around the Γ point, and the density of states increases suddenly at the energy where the second hole Fermi surface appears at the Γ point. Using this notion, the disagreement of the rare earth variation between n and E_F is resolved. A small change in E_F gives rise to a large change in n due to the enhancement of the density of states. Taking into account the experimental fact that $\Delta\rho/\rho$ varies in a similar manner to n as seen in Figure 5, it is considered that the enhancement of $\Delta\rho/\rho$ is due to the pronounced two-hole carrier conduction. Thus, $(GdS)_{1.20}TaS_2$ having the lowest carrier density and highest charge transfer is considered to have one-hole carrier conduction resulting in the smallest magneto-resistance and lowest Fermi energy, while $(LaS)_{1.14}TaS_2$ has two-carrier conduction resulting in the larger magnetoresistance and Fermi energy.

It is noted that n and E_F show a discontinuous change between M = Gd and Dy, suggesting a significant difference in the charge transfer. The discontinuity appears at the chemical composition around x =1.2 so that the electronic structure of $(MS)_xTaS_2$ is supposed to be different for x > 1.2 and x < 1.2. The parameter x is correlated to the ratio of the lattice constants in the incommensurate direction, namely, x =1.2 corresponds to the 5:3 ratio of the lattice constants in the incommensurate direction between MS and TaS_2 layers. This means that the lattice constants in the MS and TaS_2 layers become commensurate with a common lattice constant, corresponding to a 3-fold superlattice for the MS layer and a 5-fold one for the TaS_2 layer, respectively. It is considered that the electronic structure of $(MS)_xTaS_2$ is stabilized by the forming a locally commensurate structure, namely, the discommensurate structure. Thus, the electronic structure of $(MS)_xTaS_2$ is fundamentally related to the lattice incommensurability.

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