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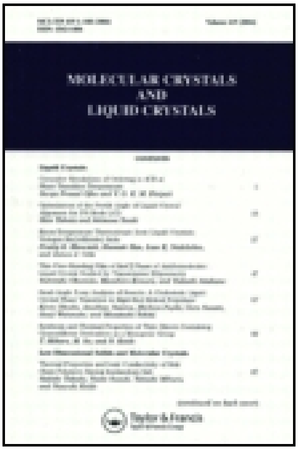

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Masasi Inoue [a] , Mikio Koyano [a] , Hiroshi Negishi [a] & Minoru Sasaki [a]

[a] Department of Materials Science, Hiroshima University, Higashi-Hiroshima, Japan

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COINTERCALATION OF Fe AND Co ATOMS INTO TiS_2 LAYERS

MASASI INOUE, MIKIO KOYANO, HIROSHI NEGISHI AND MINORU SASAKI
Department of Materials Science, Hiroshima University,
Higashi-Hiroshima, Japan

Abstract We have studied magnetic, electrical, and thermal properties of $Fe_xCo_{1/4}TiS_2$ to show that there are strong "guest-guest" interactions between the Fe and Co guest atoms cointercalated into the same van der Waals gaps of 1T-CdI_2 type TiS_2 crystal.

INTRODUCTION

Electronic and magnetic properties of guest 3d metals M intercalated into van der Waals gaps of Group V dichalcogenides, such as NbS_2 and TaS_2, are generally understood in terms of a localized electron or rigid band model,[1] whereas those in the Group IV dichalcogenides like 1T-CdI_2 type TiS_2, or M_xTiS_2, are well elucidated by an itinerant electron or band picture.[2] Characteristic of this system is the presence of strong hybridization between the guest atom M 3d orbital and the host Ti 3d and S 3p orbitals, as evidenced from the electron spin resonance (ESR), thermal, magnetic, transport, and photoemission spectroscopic measurements.[3] In particular, Fe_xTiS_2 exhibits various magnetic ordered phases depending on the guest Fe concentration x, such as paramagnetic ($x<0.01$), spin-glass ($0.01<x<0.20$), cluster-glass ($0.20<x<0.40$), and ferromagnetic phases ($x>0.40$), whereas Co_xTiS_2 shows weak ferromagnetism in the restricted range of Co concentration ($0.075<x<0.33$), the Curie temperature T_C being of the order of 120-140 K;[4, 5] in the single-guest intercalates M_xTiS_2, the Fe^{2+} ion is in the high spin state, while Co^{2+} ion is in the low spin state $(d\varepsilon)^6(d\gamma)^1$, if the guest M 3d electrons are assumed to be localized. These works are mostly concerned with the studies of "host-guest" interactions or intercalation phenomenon of a "single-guest 3d metals" in the host TiS_2 layers, in which fortunately only one stage comes into play. In this sense, the TiS_2 crystal is a suitable material to study further what is called "cointercalation or guest-guest interactions" or $M_xM'_yTiS_2$, where two different types of guest 3d metals M and M' are simultaneously intercalated into the same van der Waals gaps of the host. In the present work we have studied the magnetic, transport, and thermal properties of cointercalation compound of $M_xM'_yTiS_2$ (M=Fe and M'=Co; $x<1/3$ and $y = 1/4$) grown by a chemical vapor transport technique using iodine as a carrier gas, as done for single-guest intercalates M_xTiS_2.[6]

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RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the ac magnetic susceptibility χ for $Fe_xCo_{1/4}TiS_2$, where we see that with decreasing temperature the Co-rich samples ($x<0.01$) show a drastic increase in the susceptibilities χ at T_c

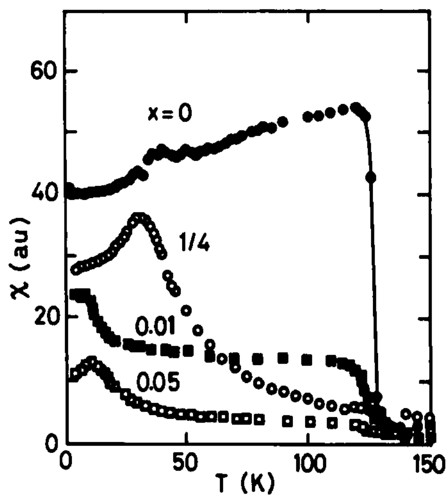

FIGURE 1 Temperature dependence of the ac magnetic susceptibility for $Fe_xCo_{1/4}TiS_2$.

(=125 K) characteristic of Co_xTiS_2, whereas with increasing cointercalating Fe atom the magnitude of the jump becomes drastically small. On the other hand, the χ-T curves for the Fe-rich samples ($x>0.05$) do not exhibit any anomaly at T_c but a pronounced cusp at T_s (=10-50 K) characteristic of a spin-

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glass or cluster-glass behavior of Fe_xTiS_2 (x <0.40). Moreover, measurements of the anisotropy in the ac susceptibilities for single crystalline samples show that when the ac field is applied parallel or perpendicular to the c-axis, the χ-T curves at T_c do not change, whereas those at T_s exhibit a strong anisotropy, in much the same way as found for Fe_xTiS_2;[5] in the parallel direction a characteristic cusp is observed in the χ-T curves, while in the perpendicular direction the χ-T curves are almost temperature independent. These results indicate that the Fe spins align preferentially along the c-axis and this tendency is not affected by the presence of counterpart of Co guest-metal. In other words, the spin-orbit coupling of Fe metal is stronger than that of Co metal in the TiS_2 layers.

Figure 2 (a) shows the electrical resistivity ρ vs. temperature curves for $Fe_xCo_{1/4}TiS_2$ in the temperature range 1.5-40 K; the overall temperature dependence of the electrical resistivities over the entire temperature range 1.5-300 K can be explained by taking account of impurity scattering, intra-, and intervalley scatterings via longitudinal acoustic phonons.[7] We note that $Fe_xCo_{1/4}TiS_2$ shows a resistivity minimum at T_{min} in the ρ-T curves, as indicated by arrows, where the resistivity can be expressed in the form, $\rho = \rho_0 + A\log T +$ (phonon term) [ρ_0: a residual resistivity; A: a constant]. Such resistivity minima have been also observed in the single-guest intercalates of paramagnetic Fe_xTiS_2 (x <0.1) and of weak-ferromagnetic Co_xTiS_2 (0.075<x <0.33),[8] as for various Kondo alloys. These anomalies are due to magnetic scatterings of conduction carriers through the guest 3d metals, in addition to the phonon scatterings. In Fig. 2 (b) are shown the variations of T_{min} with x, together with the Curie temperatures T_c and spin-glass temperature T_s determined from the ac magnetic susceptibility measurements. We should note that the resistivity minimum appears in the Co-rich region (x<0.05), where T_{min} decreases with increasing the Fe concentration x, and it disappears in the Fe-rich region (x>0.05; spin-glass phase) (Fig. 1). The appearance of the resistivity minimum in the ferromagnetically ordered state of the Co-rich region of $Fe_xCo_{1/4}TiS_2$ is unusual, which is not commonly found for various magnetic materials such as dilute alloys or dense Kondo systems.[9,10] In this sense our material system is a unique one. At any rate, we see that

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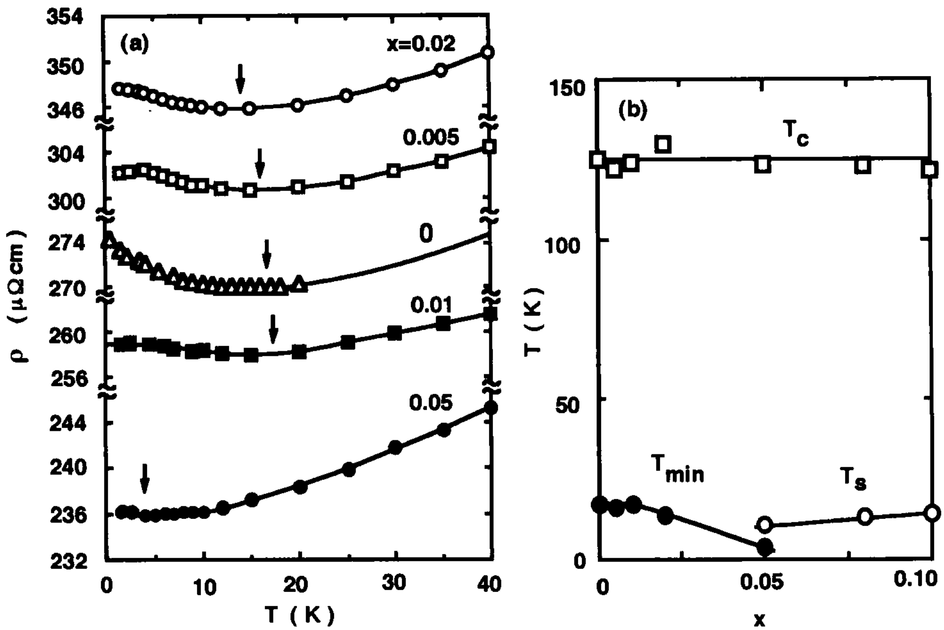

FIGURE 2 (a) Temperature dependence of the electrical resistivity for $Fe_xCo_{1/4}TiS_2$. Arrows mark the resistivity minima at T=T_{min}. (b) Resistivity minimum temperature T_{min}, Curie temperature T_C, and spin-glass temperature T_S for $Fe_xCo_{1/4}TiS_2$ plotted against Fe concentration x.

even a small amount of cointercalation of Fe atoms into the van der Waals layers gives an appreciable effect on the magnetic as well as transport properties of $Co_{1/4}TiS_2$; this means that the interactions of conduction electrons with the Co atoms are sensitively affected by cointercalation of the Fe atoms.

We have also found that the effect of cointercalation on the Hall coefficient R_H is noticeable, as shown in Fig. 3 for the cointercalate $Fe_xCo_{1/4}TiS_2$ with different Fe concentration. Though not shown here, R_H of the single-intercalate $Co_{1/4}TiS_2$ is negative and almost temperature independent (carrier concentration: 10^{22} cm^{-3}); conduction electrons are regarded as the main contribution to carrier transport. Upon cointercalation of Fe atoms, R_H becomes positive and is increased appreciably with Fe concentration. The apparent positive Hall coefficients are not due to hole contribution but due to an anomalous Hall effect, as found for Fe_xTiS_2.[11] Such an anomalous Hall effect is often observed in many magnetic materials, for which the expression $R_H = R_0 + 4\pi R_s M/B$ holds, where M is a magnetization, R_0 and R_s are a normal and an anomalous Hall coefficient, respectively, and B an applied magnetic field. Thus the increase in R_H with x is regarded as the enhancement of the magnetization M with increasing Fe concentration.

As observed for single-guest intercalates M_xTiS_2,[12] the temperature dependence of the specific heat for $Fe_xCo_{1/4}TiS_2$ at low temperatures $T < 10$ K can be written in the form $C(T) = \gamma T + \beta T^3 + C_m(T)$, where $C_m(T)$ is an anomalous contribution of magnetic origin. The electronic specific heat coefficients γ for $Fe_xCo_{1/4}TiS_2$ (solid circles) are shown in Fig. 4 as a function of Fe concentration x, together with those for the single-guest intercalates

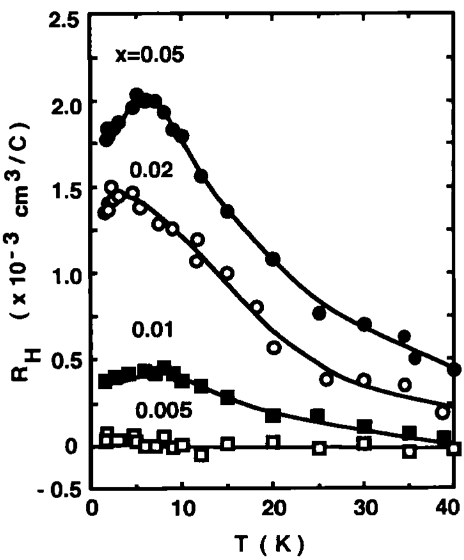

FIGURE 3 Temperature dependence of the Hall coefficient R_H for $Fe_xCo_{1/4}$-TiS_2.

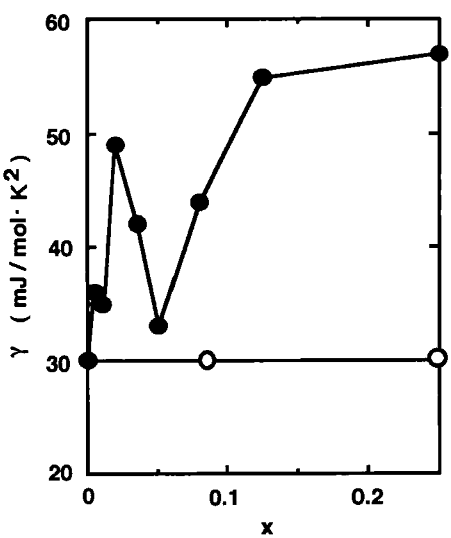

FIGURE 4 Electronic specific heat coefficients γ for $Fe_xCo_{1/4}TiS_2$ (solid circles) and for $Co_{x+1/4}TiS_2$ (open circles).

$Co_{x+1/4}TiS_2$ (open circles). We see that the γ values for the cointercalates are strongly dependent on the amount of Fe concentration x and they are higher than those of single-guest intercalates, suggesting that upon cointercalation of Fe, the Fermi energy E_F and the density of states at E_F of $Co_{1/4}$-TiS_2 are remarkably changed.

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In summary, the foregoing experimental results have clarified that there is a strong magnetic interactions between cointercalated guest atoms of Fe and Co in the same van der Waals gaps of the host. Moreover, it is expected that the cointercalation of Fe and Co atoms in the TiS_2 layers gives rise to a modification of the degree of hybridization between the guest M 3d orbital, the host Ti 3d and S 3p orbitals, leading to the changes of the Fermi energy E_F, the density of states at E_F, magnetic spin state, and magnetic scattering mechanism of conduction carriers. More quantitative discussion will be made by further experimental and theoretical studies.

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REFERENCES

1. R. H. Friend and A. D. Yoffe, Adv. Phys., 36, 1 (1987).
2. T. Yamasaki , N. Suzuki and K. Motizuki, J. Phys. C, 20, 395 (1987).
3. M. Inoue, H. P. Hughes and A. D. Yoffe, Adv. Phys., 38, 565 (1989).
4. H. Negishi, A. Shoube, H. Takahashi, Y. Ueda, M. Sasaki and M. Inoue, J. Magn. Magn. Mat., 67, 179 (1987).
5. H. Negishi,A. Shoube, M. Koyano, Y. Muneta and M. Inoue, J. Magn. Magn. Mat., 60, 259 (1986).
6. M. Inoue and H. Negishi, J. Phys. Chem., 90, 235 (1986).
7. M. Koyano, H. Negishi,Y. Ueda, M. Sasaki and M. Inoue, phys. state. sol. (b), 138, 357 (1986).
8. M. Koyano, S. Horisaka, H. Negishi, M. Sasaki, M. Inoue, N. Suzuki and K. Motizuki, J. Low Temp. Phys., 78, 141 (1990).
9. J. Kondo, in Solid State Physics, edited by F. Seitz, D. Turnbull and H. Ehrenreich, (Academic Press, New York, 1969), Vol. 23, p. 183.
10. T. Kasuya, in Theory of Heavy Fermions and Valence Fluctuations, edited by T. Kasuya and T. Sato (Springier-Verlag, Berlin, 1985), p. 2.
11. M. Inoue, M. Koyano, H. Negishi and Y. Ueda, J. Phys. Soc. Jpn., 55, 1400 (1986).
12. M. Inoue, Y. Muneta, H. Negishi and M. Sasaki, J. Low Temp. Phys., 63, 235 (1986).