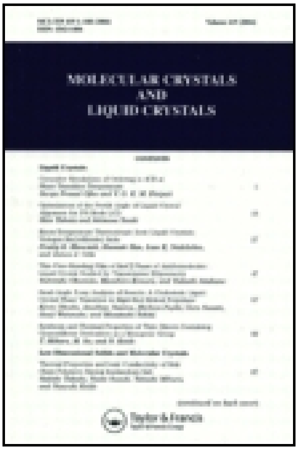

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Masasi Inoue [a] , Shingo Kakita [a] , Hiroshi Negishi [a] & Minoru Sasaki [a]

[a] Graduate School of Advanced Sciences of Matter, Hiroshima University, Higashi-Hiroshima, 739-8526, Japan

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Impurity Scattering in 3d Transition Metal Intercalation Compounds M_xTiS_2

MASASI INOUE, SHINGO KAKITA, HIROSHI NEGISHI
and MINORU SASAKI

*Graduate School of Advanced Sciences of Matter, Hiroshima University,
Higashi-Hiroshima 739–8526, Japan*

From the resistivity measurements of 3d metal intercalates M_xTiS_2 (M = Mn, Fe, Co and Ni; $x = 0.05$) at 4.2 K in pulsed magnetic fields up to 31 T, we have found that the residual resistivity depends on the kind of guest species. Taking into account these results and available information, we have proposed a possible band model to understand the scattering mechanism by ionized impurities of the intercalated guest M^{2+} and host Ti^{3+} ions, in satisfactory agreement with the experiments.

Keywords: intercalation compounds; impurity scattering; band model

INTRODUCTION

The electronic and magnetic properties of 3d transition-metal intercalation compounds M_xTiS_2 have been in general explained by a band picture, since there is a strong 'hybridization' among the guest M 3d and the host Ti 3d and S 3p orbitals[1-3]. However, the valence state of the intercalated guest atoms is not well understood and usually treated by a simple model. In the host TiS_2, exactly written as $Ti_{1+x}S_2$ ($x \leq 0.02$), the self-intercalated Ti atom is assumed to be Ti^{4+} or Ti^{3+} ion as an ionized impurity scattering center, where the impurity level of Ti^{3+} lies above the Fermi energy by about 5 meV[4]. In the present work, we have paid attention to other guest atoms, M = Mn, Fe, Co and Ni, with low concentration $x = 0.05$ in M_xTiS_2.

EXPERIMENT

Electrical resistivities of Mn_xTiS_2 were measured at 4.2 K by a conventional dc potentiometric method in magnetic fields up to 31 T using a home-made pulsed magnet[5]. The magnetic field was applied along the *c* axis and the sample current along the *a* axis.

RESULTS AND DISCUSSIONS

Experimental results show that the residual resistivity in zero and magnetic field, say 30 T, ρ_0 and $\rho_0(H \sim 30\ \mathrm{T})$, respectively, depend on the kind of guest atoms, as shown in Fig. 1. We shall discuss these results by considering the ionized impurity center of guest atom M in M_xTiS_2, similar to the excess Ti atom in $Ti_{1+x}S_2$. Upon intercalation of the guest atom M, a charge transfer from M to the host Ti 3d conduction band occurs. As a result, the intercalated atom becomes divalent ion, M^{2+}, in the van der Waals gaps in TiS_2, and hereby the following three different cases may be possible:

Case 1: $M^{2+} + 2e^- + Ti^{4+}$,
Case 2: $M^{2+} + e^- + Ti^{3+}$,
Case 3: $(1-\beta)(M^{2+} + 2e^- + Ti^{4+}) + \beta(M^{2+} + e^- + Ti^{3+})$.

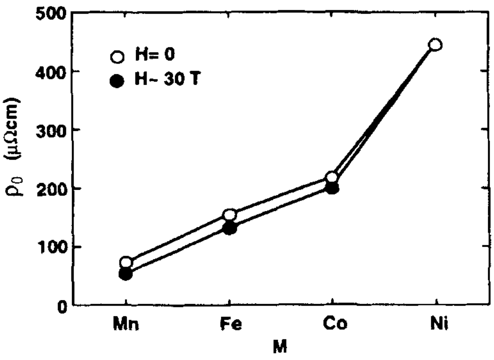


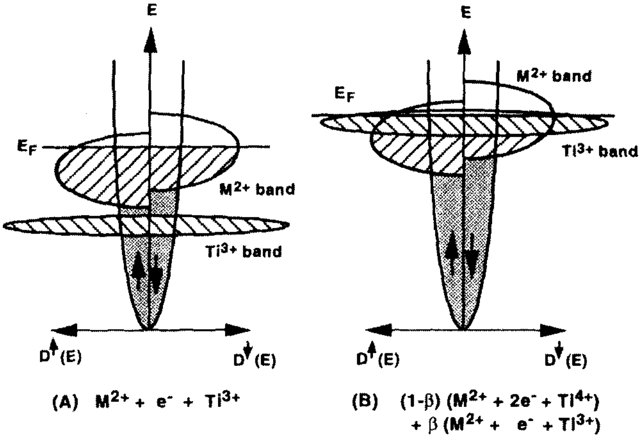
FIGURE 1 Residual resistivity ρ_0 at $H = 0$ and $H \sim 30$ T for M_xTiS_2 with $x = 0.05$ plotted against guest atom M.

In the first case, the guest atom donates two electrons per atom (denoted by $2e^-$) to the conduction band, and in the case 2 one electron to the conduction band and one to the neighboring host Ti^{4+} ion, forming a trivalent Ti^{3+} ion as a new scattering center. The last is the combined case with a fractional parameter β ($0 < \beta < 1$). For simplicity, here we neglect the self-intercalation of Ti atoms into van der Waals gaps.

According to information about the band structure of M_xTiS_2 [1-3, 6-8], we propose the tentative band assignment for M^{2+} and Ti^{3+} states, as shown schematically in Figs. 2(A) and 2(B) for the above cases 2 and 3, respectively, where the density of states with down- and up-spins, $D^{\downarrow}(E)$ and $D^{\uparrow}(E)$, are indicated in the right and left scales, respectively. The intercalated M^{2+}-derived band is located near the Fermi energy E_F and the Ti^{3+} originated band is tentatively assigned for later discussion.

Now the a axis resistivity ρ_{imp} due to impurity scatterings by M^{2+} and Ti^{3+} ions is written as[4],

$$\rho_{imp} = m_a/ne^2\tau = (m_a/m^*)(m^*/ne^2\tau), \quad (1)$$



(A) $M^{2+} + e^- + Ti^{3+}$

(B) $(1-\beta)(M^{2+} + 2e^- + Ti^{4+}) + \beta(M^{2+} + e^- + Ti^{3+})$

FIGURE 2 Tentative band model for M_xTiS_2 with low guest concentration $x = 0.05$.

where m_a is the effective mass along the a axis, m^* the total effective mass, n the carrier concentration, and τ the relaxation time for impurity scattering. Assuming the Matthiessen's rule, τ is given by the sum of those for impurity centers M^{2+} and Ti^{3+} ions, as

$$1/\tau = 1/\tau_{Ti^{3+}} + 1/\tau_{M^{2+}}, \qquad (2)$$

where τ_i (i = M^{2+}, Ti^{3+}) is given by, $1/\tau_i = (\hbar k_F n_i/m^*)\sigma_i$ (k_F Fermi wave number, n_i ionized impurity concentration, and σ_i total scattering cross-section). At low temperatures, the total cross-section is expressed as, $\sigma_i = \int\sigma_i(\theta)(1 - \cos\theta)d\Omega$, where $\sigma_i(\theta)$ is the differential cross-section at a scattering angle θ with a solid angle Ω.

As for 3d metal impurity in pure Cu metal [9], we write the differential cross-section for impurity scattering as, $\sigma_i(\theta) = k_F^{-2}|\Sigma(2L + 1)\sin\delta_L(\exp i\delta_L) P_L(\cos\theta)|^2$, where δ_L is the phase shift of conduction electrons at E_F due to electrons of 3d transition metal impurity with an azimuthal quantum number L, and $P_L(x)$ the Legendre function. Since the 3d electrons with $L = 2$ play a dominant role in impurity scattering, we can neglect other contribution from s and p electrons with $L = 0$ and 1, respectively. Therefore, τ_i is given by

$$1/\tau_i = \left(\frac{6\pi\hbar n_i}{m^* k_F}\right)\left(\sin^2\delta_i^\uparrow + \sin^2\delta_i^\downarrow\right), \qquad (3)$$

with the phase shift $\delta_i^\uparrow$ ($\delta_i^\downarrow$) due to the up-spin (down-spin) electrons of the impurity centers. Thus, ρ_{imp} is written by

$$\rho_{imp} = \left(\frac{m_a}{m^*}\right)\left(\frac{6\pi\hbar}{ne^2 k_F}\right)\sum_i n_i\left(\sin^2\delta_i^\uparrow + \sin^2\delta_i^\downarrow\right). \qquad (4)$$

The total charge Z relative to the host Ti^{4+} ions (sum of the charges with the up-spin and down-spin electrons, $Z = Z^\uparrow + Z^\downarrow$), is unity for the host Ti^{3+} ions and 5, 6, 7, 8 for the guest Mn, Fe, Co, Ni divalent ions, respectively. Thus the phase shift is given by, $\delta_i^\uparrow = Z_i^\uparrow/(2L + 1) = Z_i^\uparrow/5$ and $\delta_i^\downarrow = Z_i^\downarrow/5$ for M^{2+} with $L = 2$. Using Eq.(4), the values of the effective masses obtained for the host

$Ti_{1+x}S_2$, $m^* = m_0$ and $m_a/m_c = 0.008$ [6], the carrier concentration n evaluated by a single-carrier model from the Hall coefficient R_H, $n = 1/eR_H$, $n = 3.13 \times 10^{21}$ cm^{-3} for Mn, Fe, Co guests, and 0.72×10^{21} cm^{-3} for Ni one, and the Fermi wavenumber $k_F = (3\pi^2 n)^{1/3}$, we have calculated ρ_{imp} for M_xTiS_2 with the charge Z as a function of the occupancy of the up-spin electrons of the M^{2+} band, $n^{\uparrow}$ ($= \delta_{M2+}{}^{\uparrow}/\pi$). For simplicity, we here assume that the charge of the up-spin electrons of Ti^{3+} is equal to that of the down-spin electrons of Ti^{3+}, $Z^{\uparrow} = Z^{\downarrow} = 1/2$ at zero magnetic field. The occupancy for the down-spin electrons, $n^{\downarrow}$, is evaluated by $n^{\downarrow} = Z/(2L + 1) - n^{\uparrow}$.

By comparing the calculated curves and experimental data for different ions, we have obtained the best-fit values of β, $n^{\uparrow}$, and $n^{\downarrow}$, as listed in Table I. For Ni intercalate, we cannot determine their values, because the magnetoresistance does not show any saturation behavior up to 30 T; only the possible ranges of β and $n^{\uparrow}$ can be determined from the value of $\rho_0(H=0)$, as β = 0.76-0.96 and correspondingly $n^{\uparrow}$ = 1.00-0.80. From Table I, we see that the occupancy for up-spin electrons is nearly equal to unity for all guest species ($n^{\uparrow}$ = 0.80 ~ 1.00), while that for down-spin electrons increases with the total charge Z, from $n^{\downarrow}$ = 0.056 for Mn guest to 0.60~0.80 for Ni guest.

These results indicate that the observed variation of the residual resistivity with the guest atom M are mainly due to the impurity scattering by down-spin electrons of the M^{2+} impurity centers rather than by up-spin electrons. In addition, the fractional parameter β decreases with Z from 0.91 for Mn to 0.34 for Co guest, while it is appreciably large for Ni guest (β = 0.76-0.96), which suggests that the bandwidth of the M^{2+} band increases with Z from Mn to Co guest and its overlap with the host Ti^{3+} band becomes smaller. For Ni guest, the M^{2+} bandwidth is very narrow and well overlaps with the

TABLE I Best-fit parameters of β, $n^{\uparrow}$, and $n^{\downarrow}$ obtained from comparison of calculated impurity scattering with the experimental data for different guest atoms in M_xTiS_2 (M = Mn, Fe, Co and Ni).

M	Mn	Fe	Co	Ni
β	0.910	0.746	0.340	0.76 ~ 0.96
$n^{\uparrow}$	0.944	0.976	0.960	1.00 ~ 0.80
$n^{\downarrow}$	0.056	0.224	0.440	0.60 ~ 0.80

Ti^{3+} band near E_F. In order to confirm the above band model, photoemission spectroscopic studies with very high resolution of the order of several or a few meV will be needed.

In conclusion, the variation of the residual resistivity with the guest M (=Mn, Fe, Co, and Ni) in M_xTiS_2 (x = 0.05) can be explained by impurity scattering by intercalated guest M^{2+} (in particular, with down-spin electrons) and the host Ti^{3+} ions formed by a charge transfer from M to the host Ti 3d conduction band.

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