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# EXAFS and XANES Studies on 3d Transition Metal Intercalation Compounds $M_xTiS_2$

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EXAFS and XANES spectra of Ti K-edge have been measured for 3d transition metal intercalation compounds $M_xTiS_2$ (M = Mn, Fe, Co and Ni; $x \leq 0.33$). We have found that the interatomic distance between Ti and the first nearest neighbor S atoms, $R$(Ti-S), increases with the guest concentration $x$.The variation in XANES spectra with $x$ reveals the reduction of the valence state of Ti atoms upon intercalation of M. From these results as well as the M K-edge EXAFS data studied previously, we have proposed a simple model on the local structure of $M_xTiS_2$ to reproduce the observed values of $R$(Ti-S) by averaging local shift of S atoms caused by intercalation.

*Keywords:* EXAFS; XANES; $M_xTiS_2$; local structure; interatomic distance

## INTRODUCTION

Intercalation of guest 3d transition metal atoms M into the layered host $TiS_2$ leads to an appreciable change in the interlayer spacing $c$ that depends on the guest species but less change in the intralayer spacing $a$; upon Mn guest intercalation, $c$ expands remarkably while for Co and Ni ones it contracts with increasing $x$ [1, 2]. The bonding nature in $TiS_2$, its intercalation compounds $FeTiS_2$ and $M_{1/3}TiS_2$ (M=Mn, Fe, Co and Ni) has been discussed using the concept of "bond orders" obtained by APW self-consistent calculations [3, 4], which reveals the existence of two additional covalent-like bonds in the Fe intercalates, one between the Fe $d\gamma$ and S p states and the other between the Fe $d\varepsilon$ and Ti $d\varepsilon$ states.

The variation of interlayer distance $c$ can be understood qualitatively by taking account of the interatomic distance between the guest M and the

neighboring sulfur atom S, $R$(M-S), as evidenced from our earlier guest atom M K-edge EXAFS spectra [5]. However, a quantitative comparison of $R$(M-S) with the lattice constants $a$ and $c$ indicates that the host S-Ti-S layers are also varied upon intercalation. For further understanding of the local structures in these intercalates, in the present work we have measured both EXAFS and XANES spectra of Ti K-edge for $M_xTiS_2$ (M = Mn, Fe, Co and Ni; $x \leq 0.33$) at 30 K and room temperature.



## EXPERIMENTAL

Single crystals $M_xTiS_2$ were grown by a chemical vapor transport method, as reported previously [1]. For EXAFS and XANES measurements, the grown crystals were ground into fine powders, which were mixed with BN powders to disperse the sample homogeneously and randomly. $TiS_2$ was also measured as the standard sample. The EXAFS spectra near the Ti K-edge were taken at room temperature and 30 K using a Si (111) monochromator over the photon energy range $E$ = 4.85-5.45 keV at BL7C, Photon Factory, Tsukuba, Japan.

## RESULTS AND DISCUSSION

Typical Fourier transformed EXAFS spectra of $k^3\chi(k)$ of the Ti K-edge and Co K-edge at 30 K for $Co_{0.33}TiS_2$ are shown in Fig. 1. The Ti K-edge spectrum has three strong peaks around 2.0, 2.9 and 4.1 Å, which correspond to the nearest neighbor between the host Ti atom and S atom, Ti-S(1), the second nearest neighbor between the Ti atoms, Ti-Ti, and the third neighbor, Ti-S(2), respectively. On the other hand, the Co K-edge spectrum yields two remarkable peaks around 2.0 and 3.9 Å with no peak around 2.9 Å, indicating that there is no large clusters consisted of the second nearest neighbor Co-Co pairs but the Co atoms distribute rather homogeneously and relax some local distortions caused by intercalation. Here, we should notice that a weak feature appeared at ~ 2.5 Å is spurious due to the Fourier transformation over the restricted region. Nearly the same spectra have been obtained for different guest concentration $x$ and other Mn, Fe, and Ni guest atoms. We have evaluated the interatomic distance $R$(Ti-S) between Ti and neighboring S atoms in the host layers from the analysis by a least-square fit to the Fourier-filtered spectra for Ti-S(1) with respect to $TiS_2$ employed as the standard material [$R$(Ti-S) = 2.427 Å and coordination number $N$ = 6]. The obtained values of

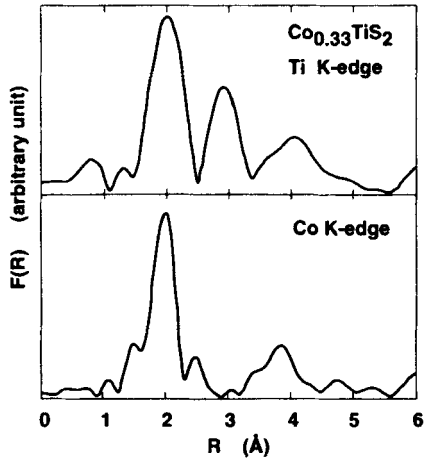


FIGURE 1 Fourier transform of $k^3\chi(k)$ of Ti K-edge EXAFS (upper part) and that of Co K-edge one (lower part) for $Co_{0.33}TiS_2$.

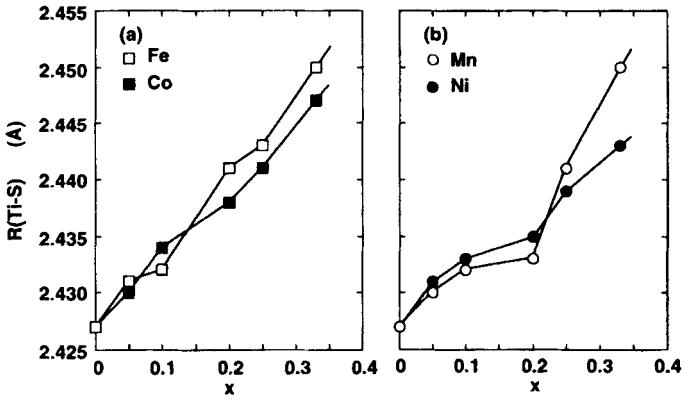


FIGURE 2 Interatomic distance $R$(Ti-S) between the host Ti and S atoms in $M_xTiS_2$ plotted against the guest concentration $x$ for (a) Fe and Co guest atoms, and (b) Mn and Ni ones.

$R$(Ti-S) at room temperature are plotted against $x$ for $M_xTiS_2$ in Fig. 2. With increasing $x$, the values of $R$(Ti-S) for Fe and Co intercalates increase almost linearly to $x$ [Fig. 2(a)]; with further careful attention, we can see a break at $x = 0.10$. On the other hand, those for Mn and Ni intercalates increase with a

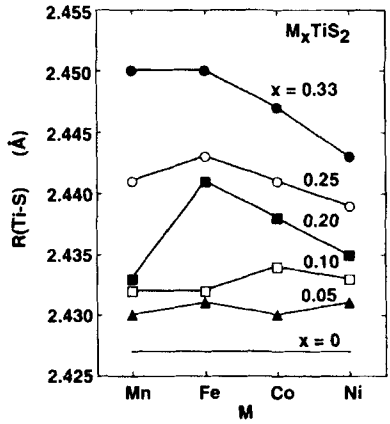


FIGURE 3 Interatomic distance $R$(Ti-S) of $M_xTiS_2$ plotted against the atomic number of the guest M for different guest concentrations $x$.

break at $x = 0.20$ [Fig. 2(b)]. The increment of $R$(Ti-S) upon intercalation is at most 0.023 Å even at $x = 0.33$, which plays a minor but important role in the variation of the interlayer lattice spacing $c$, especially for Fe intercalates. Fig. 3 depicts the variations in $R$(Ti-S) with the atomic number of the 3d atom M for various guest concentrations $x$. For low concentrations ($x \leq 0.10$) $R$(Ti-S) is almost independent of guest M, while that for high concentrations ($0.20 \leq x \leq 0.33$) dependent on M; especially the values for Fe atoms are larger compared with those for other guest atoms. These results of $R$(Ti-S) indicate that the host layers expand by the intercalation of the guest atoms M, and suggest that the variation in their atomic distribution with $x$ plays an important role.

XANES spectra of Ti K-edge for $Co_xTiS_2$ are shown in Fig. 4, as typical results, where the values of the absorption coefficient $\mu t$ are plotted against photon energy $E$ near the Ti K-edge. With increasing $x$ the intensity of the precursory peak around 4964 eV decreases and the position of the K-edge shifts to a low energy side. Such changes are due to the shift of XANES spectral weight to a high energy side with $x$, as shown in the inset, indicating the reduction of the valence of the host Ti atoms from $Ti^{4+}$ into $Ti^{3+}$ ions upon interaction of the guest atoms.

Here we propose a simple model on the local structure of $M_xTiS_2$, in which the host layers consist of $Ti^{3+}$ around the guest atoms and $Ti^{4+}$ around vacant sites in the van der Waals gaps, and thus through this distortion, the sulfur atom shifts its position depending on the number of the surrounding

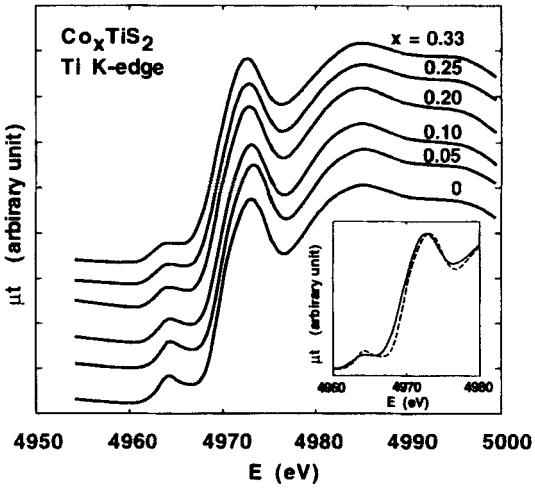


FIGURE 4 XANES spectra of Ti K-edge for $Co_xTiS_2$. The spectra are offset for clarity. The inset shows the spectra for the host $TiS_2$ (dashed line) and for $Co_{0.33}TiS_2$ (solid line) with no offset to see the details of the variation in the spectra upon intercalation.

guest atoms M, denoted by $n$ (= 0, 1, 2, and 3). For simplicity, we assume that the Ti atoms array regularly with periodicity of the lattice spacings $a$ and $c$, and express the S position as, $[A(n), H(n)]$, from the guest atom M (or vacancy) in the plane including the direction of M(or vacancy)-S-Ti bondings. Based on this model, we obtain the relations, $A(0)= A(3)=\sqrt{3}a/3$, $H(0) = c/4$, and $A^2(n) + H^2(n) = R^2$(M-S) for $n$ = 1, 2, and 3; therefore, $H(3) = [R^2(\text{M-S}) - a^2/3]^{1/2}$. In addition, we assume a random distribution of the guest atoms for simplicity and that the S atom shift upon intercalation depends on $n$ nonlinearly as, $H(n) = H(0) + [H(3) - H(0)]\ (n/3)\ [(1+\delta)/[1+ \delta(n/3)]$ with a characteristic parameter $\delta$. Then, $R$(Ti-S) can be written as

$$R(\text{Ti-S}) = \Sigma\ p_n(x)\ R_n(\text{Ti-S}), \tag{1}$$

with the probability $p_n(x) = x^n(1-x)^{3-n}$ and the interatomic distance $R_n$(Ti-S) for $n$ with the guest concentration $x$, where $R_n$(Ti-S) is given by

$$R_n(\text{Ti-S}) = (n/3)\{A^2(n) + [(c/4) - H(n)]^2\}^{1/2} + (1- n/3)\{B^2(n) + [(c/4) - H(n)]^2\}^{1/2}, \tag{2}$$

using $B(0) = A(0)$, $B(1) = \{(a/2)^2 + [(\sqrt{3}a/2) - A(1)]^2\}^{1/2}$ and $B(2) = (\sqrt{3}a/2) -$

TABLE I The values of the best-fit parameter $\delta$ and the S atom position $[A(n), H(n)]$ surrounded by $n$ guest atoms for $Mn_{0.33}TiS_2$ and $Co_{0.33}TiS_2$.

| | $Mn_{0.33}TiS_2$ | | $Co_{0.33}TiS_2$ | |
|---|---|---|---|---|
| $\delta$ | 0.59 | | 6.34 | |
| $n$ | $A(n)$ | $H(n)$ | $A(n)$ | $H(n)$ |
| 0 | 1.975 | 1.489 | 1.967 | 1.410 |
| 1 | 2.011 | 1.526 | 1.954 | 1.343 |
| 2 | 1.990 | 1.552 | 1.963 | 1.330 |
| 3 | 1.975 | 1.572 | 1.967 | 1.325 |

$[A^2(2) - (a/2)^2]^{1/2}$. The first term in Eq.(2) is for the Ti atoms above or below the guest atoms and the second term for those around the unoccupied sites. The obtained best-fit values of $\delta$, $A(n)$ and $H(n)$ are listed in Table I for $Mn_{0.33}TiS_2$ and $Co_{0.33}TiS_2$, as typical examples. The nonlinearity is larger for Co guest than for Mn one. Furthermore, it is noted that the difference in the shift of the S atoms with $n$ is of the order of 0.09 Å along the $c$ axis, and 0.04 Å along the layer direction for both cases.

In conclusion, from the Ti K-edge EXAFS spectra we have confirmed that the interatomic distance $R$(Ti-S) between Ti and neighboring S atoms in the host layers increases upon intercalation of 3d guest atoms M. With the simple model on the local structure of $M_xTiS_2$, where the position shifts of S atoms through the distortion caused by intercalation is taken into account, we can reproduce the values of $R$(Ti-S) using the lattice spacings $a$ and $c$, the interatomic distance $R$(M-S), and evaluate the parameter characterizing the nonlinearity with the number of surrounded guest atoms.

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## *References*

[1] M. Inoue and H. Negishi, *J. Phys. Chem.*, **90,** 235 (1986).

[2] M. Inoue, H.P. Hughes and A. D. Yoffe, *Adv. Phys.*, **38**, 565 (1989).

[3] N. Suzuki, T. Yamasaki and K. Motizuki, *J. Phys. C*, **21,** 6133 (1988).

[4] T. Yamasaki, Dr. Thesis (1988, Osaka University).

[5] H. Negishi, S. Ohara, Y. Takata, T. Yokoyama, M. Taniguchi and M. Inoue, *Mater. S Forum*, **91–93,** 603 (1992).