

## Chemical Bondings around Intercalated Cr and Fe Atoms in TiS<sub>2</sub>

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A study of the electronic structure and chemical bonding of the transition-metal intercalated titanium disulfide, MTiS<sub>2</sub> (M = Cr and Fe), is performed by a first-principles molecular-orbital method using a model cluster composed of 75 atoms. The discrete-variational (DV)-X $\alpha$  method was employed and Mulliken's population analyses were thoroughly conducted. The intercalation in the so-called "van-der-Waals gap" is found to change the local electronic structure significantly in the following manner: The net charge of the intercalated M-layer is decreased by 0.559 and 0.307 when M = Cr and Fe, respectively. The bond overlap population (BOP), a measure of the covalent bond-strength, decreases by approximately 20% as for the Ti-S bond. Both the BOPs of the Cr-S and Fe-S bonds are found to be as large as that of the Ti-S bond.

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### 1. Introduction

Transition metal dichalcogenides have been studied extensively to determine their dimensional character and their specific properties. These materials have layered structures with "van der Waals gaps", into which various atoms and organic and inorganic molecules can be intercalated. Depending on the intercalated species, quite dramatic changes in the physical properties of the host transition metal dichalcogenides can occur.<sup>1,2)</sup> Intercalation phenomena in various transition metal dichalcogenides TX<sub>2</sub> with layered structures have attracted much attention. In particular, intercalation of 3d transition metal atoms M into the "van der Waals gaps" of TX<sub>2</sub> layers, expressed as M<sub>x</sub>TX<sub>2</sub>, has been studied over many years.<sup>3-6)</sup>

Unique properties are expected in M<sub>x</sub>TX<sub>2</sub> because of its layered arrangement of M atoms. It is therefore of great importance to obtain quantitative information of chemical bondings that can be used as a guiding principle for designing of this type of compounds. However, only a few studies from the viewpoint of chemical bonding have been reported.<sup>7)</sup>

TiS<sub>2</sub> has a layered structure. The Ti-S bonding inside the layer shows strong covalent bonding in addition to ionic attraction. On the other hand, the interaction between the layers is weak. We made a quantitative analysis of the magnitude of the covalent bonding in our previous report<sup>8)</sup> and found that the interlayer S-S interaction as measured by bond overlap population (BOP) is 10-20 times smaller than intralayer interaction. The weak interlayer interaction offers the possibility of intercalating various atoms, organic and inorganic molecules, and hence the interlayer region is often denoted as "van der Waals gaps".

The objective of the present study is to understand the chemical bondings of non-magnetic state of MTiS<sub>2</sub> using a first-principles linear combination of atomic orbitals (LCAO) method. The advantage of the LCAO method as compared with the plane-wave type method is its straightforward derivation of atomic-orbital components such as net charges and bond-overlap populations through Mulliken's population analysis method.<sup>9)</sup> In this paper, we are especially interested

in the charge state of M and the magnitude of covalency around M atoms when they are intercalating the TiS<sub>2</sub> host.

### 2. Computational Procedures

In this work, first-principles molecular orbital calculations using the DV-X $\alpha$  cluster method<sup>10,11)</sup> are employed. The molecular orbital wave function is expressed by a linear combination of atomic orbital (LCAO) as,

$$\phi_l = \sum_i c_{il} \chi_i, \quad (1)$$

where  $c_{il}$  is a coefficient. As the basis functions  $\chi_i$ , we use numerical atomic orbitals obtained by solving the Schrödinger equation for individual atoms in a cluster. The atomic orbitals used in the present study are 1s-3d for S, 1s-4p for Cr, Fe and Ti. They are minimal basis sets that have a great advantage for simple and most intuitive understanding of chemical bondings.

In the DV-X $\alpha$  method, the matrix elements  $H_{ij}$  and  $S_{ij}$  in the secular equation  $(H - \epsilon S)C = 0$ , are evaluated by numerical integration as,

$$H_{ij} = \sum_k^N \omega(\mathbf{r}_k) \chi_i(\mathbf{r}_k) h \chi_j(\mathbf{r}_k) \\ S_{ij} = \sum_k^N \omega(\mathbf{r}_k) \chi_i(\mathbf{r}_k) \chi_j(\mathbf{r}_k) \quad (2)$$

where  $\mathbf{r}_k$  is the one of the total  $N$  sampling points that is taken in the three-dimensional real space,  $\omega(\mathbf{r}_k)$  is the reciprocal of sampling point density at  $\mathbf{r}_k$ ,  $\chi_i$  is an atomic basis function, and  $h$  is one-electron hamiltonian.

In order to discuss the charge density and chemical bonding of the cluster, the Mulliken's population analysis<sup>9)</sup> is employed. The overlap population,  $Q_{ij}^l$ , for the  $l$ -th molecular orbital is defined by

$$Q_{ij}^l = c_{il} c_{jl} S_{ij}. \quad (3)$$

The  $i$ -th atomic orbital population  $Q_i$  is given by

$$Q_i = \sum_l \sum_j f_l Q_{ij}^l, \quad (4)$$

where  $f_l$  is the occupation number of the  $l$ -th molecular orbital.

The effective charge  $Q_A$  and net charge  $N_A$  of atom A are given by,

$$Q_A = \sum_{i \in A} Q_i \quad \text{and} \quad N_A = Z_A - Q_A, \quad (5)$$

where  $Z_A$  is the atomic number of atom A.  $N_A$  can be regarded as a measure of ionicity.

The bond overlap population between A and B atoms,  $Q_{AB}$ , is given by

$$Q_{AB} = \sum_l f_l Q_{AB}^l, \quad (6)$$

where

$$Q_{AB}^l = \sum_{i \in A} \sum_{j \in B} Q_{ij}^l \quad (7)$$

Table 1 Lattice constants and bond lengths used in this calculation.

	$a = b$ (nm)	$c$ (nm)	$d_{\text{Ti-S}}$	$d_{\text{M-S}}$
CrTiS <sub>2</sub> <sup>7)</sup>	0.3418	0.5925	0.2467	0.2467
FeTiS <sub>2</sub> <sup>7)</sup>	0.3428	0.5809	0.2455	0.2455
TiS <sub>2</sub> <sup>12)</sup>	0.3408	0.5699	0.2430	

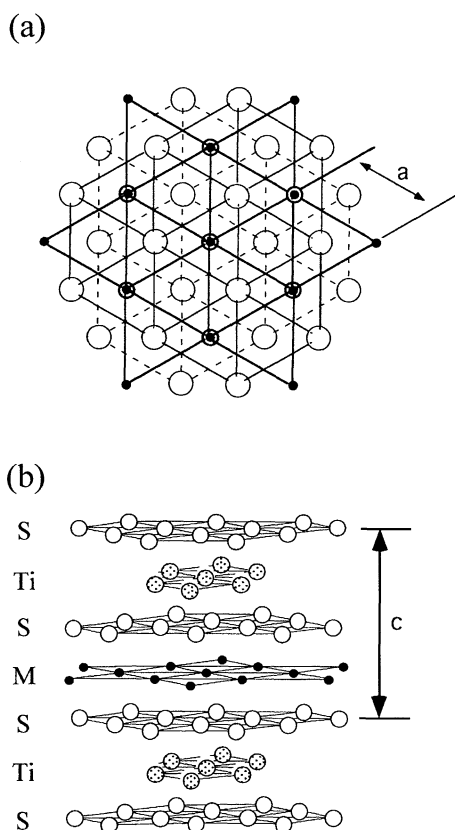


Fig. 1 Cluster model for MTiS<sub>2</sub>. Atoms: M (filled circles), S (open circles), and Ti (hatched circles). (a) The (001) projection of the structure of MTiS<sub>2</sub>, (b) The stacking of the layers in MTiS<sub>2</sub>.

$Q_{AB}$  can be used as a measure of strength of the covalent bonding between atoms A and B.

The layered compound MTiS<sub>2</sub> ( $M = \text{Cr}$  and  $\text{Fe}$ ) belongs to a hexagonal structure of the space group  $D_{3d}^3$  ( $P\bar{3}m1$ ). In these structures, one layer is composed of one Ti plane sandwiched by two S planes, and the stacking of the layers forms the crystal. Thus the crystal exhibits a layered structure due to stacking of the planes (S–Ti–S)/M/(S–Ti–S). In this compound, every Ti atom is located at the center of a slightly distorted octahedron composed of six sulfur atoms.

In the intercalation compound MTiS<sub>2</sub>, as would be expected, the greatest change is the expansion of the  $c$  lattice-parameter. M atoms can occupy all the available octahedral sites between the neighboring sulfur planes. The lattice constants used in the present calculation are  $a = b = 0.3418$  nm,  $c = 0.5925$  nm for CrTiS<sub>2</sub>,  $a = b = 0.3428$  nm,  $c = 0.5809$  nm for FeTiS<sub>2</sub>, and  $a = b = 0.3408$  nm,  $c = 0.5699$  nm for TiS<sub>2</sub>, respectively, as shown in Table 1. The electronic properties and chemical bonding of MTiS<sub>2</sub> are examined using a cluster model composed of 75 atoms, *i.e.*,  $(M_{13}Ti_{14}S_{48})^{42-}$  as shown in Fig. 1. The cluster is embedded in Madelung potential generated by point charges outside the cluster. Total charge of the cluster  $-42$  is obtained by counting the formal charges of  $M^{2+}$ ,  $Ti^{2+}$  and  $S^{2-}$ . The magnitude of point charges is chosen in the same way. Spin polarization is not taken into account.

### 3. Results and Discussion

Figure 2 shows the density of states (DOS) of MTiS<sub>2</sub> and TiS<sub>2</sub> obtained in the present study. In order to minimize the surface effect of the cluster, local DOSes for atoms located near the center of the cluster are summed up to make the total DOS keeping the atomic ratio of the compounds. The molecular orbital calculation yields discrete molecular orbital (MO) levels. The discrete MO levels are convoluted by Gaussian functions with a full width at half maximum (FWHM) of 1.0 eV for easy visualization of DOS. The energy scale is shifted to make the Fermi level ( $E_F$ ) zero. In Fig. 2, the partial density of states (PDOS) for each atomic orbital is also plotted. A band calculation by the APW (augmented plane wave) method has been reported by Yamasaki *et al.*<sup>7)</sup> Their DOS ranged from  $-8$  to 4 eV when converted to the energy scale as in Fig. 2. The shape of DOS including their partial components is in good agreement with the present result, which confirms that the cluster size is large enough to reproduce the electronic structure of the bulk compounds.

The structure of non-intercalated TiS<sub>2</sub> was analyzed in our previous reports.<sup>8)</sup> The valence state is constructed by S 3s band (peak a) and S 3p band. However, these bands also contain components of Ti-3d and 4sp orbitals due to the notable contribution from strong Ti–S covalent bonding. The origin of the three peaks in the S 3p band are,  $v_1$ : Ti 4sp–S 3p bonding,  $v_2$ : Ti 3d–S 3p bonding, and  $v_3$ : S 3p nonbonding. The Ti 3d band is located just above  $E_F$ , *i.e.*, at the bottom of the conduction band. This band consists of two peaks ( $c_1$  and  $c_2$ ), that can be ascribed to  $t_{2g}$ - and  $e_g$ -type bands, respectively. Moreover the  $c_1$  peak is divided into two peaks, because the Ti atom is located at the center of the distorted octahedron in

this compound. A band mainly composed of Ti-4*sp* orbitals starts to appear from approximately 5 eV above the Fermi energy. The Ti 3*d* and 4*sp* bands also involve a considerably

large number of S 3*p* components making antibonding interaction for Ti-S.

When M is intercalated, M 3*d* band appears near the bottom of the Ti-3*d* band. It should be emphasized that the position of  $E_F$  is located in the M 3*d* band when M is present. Relative position of  $E_F$  with respect to the Ti-3*d* and S-3*p* bands is therefore shifted by 2.5 eV. This implies that the M-layer donates electrons to the host TiS<sub>2</sub>. The magnitude of the charge transfer can be quantitatively analyzed by the Mulliken's population analysis. The results of net charges are summarized in Table 2. The M atom at the center of the cluster lost 0.559 electrons when M = Cr, and 0.307 when M = Fe. Besides the shift in  $E_F$ , significant contribution of M-3*d* and M-4*sp* can be noted in the S-3*p* band. The magnitude of the contribution looks almost the same as that of Ti-3*d* in TiS<sub>2</sub>, which is suggestive of strong covalent bonding between M and S. The manner of the covalent bonding can be analyzed using overlap population diagrams or crystal orbital overlap population (COOP) diagrams in which  $Q_{AB}^i$ , given by eq. (7), are plotted as a function of molecular orbital energy after broadening the values at discrete levels by Gaussian functions of 1.0 eV FWHM similar to DOS in Fig. 2. Figures 3 and 4 display the diagrams for the Ti-S bonds and M-S bonds. The sum of bonding and antibonding contributions up to  $E_F$  is called bond overlap populations (BOP). It is shown in the lower-right side of each panel. Little antibonding contribution can be seen below  $E_F$  for both Ti-S and M-S. Regarding the Ti-S bonding, shapes of DOS as well as overlap population diagrams of Ti-S are not significantly changed by the M-intercalation. It implies that the

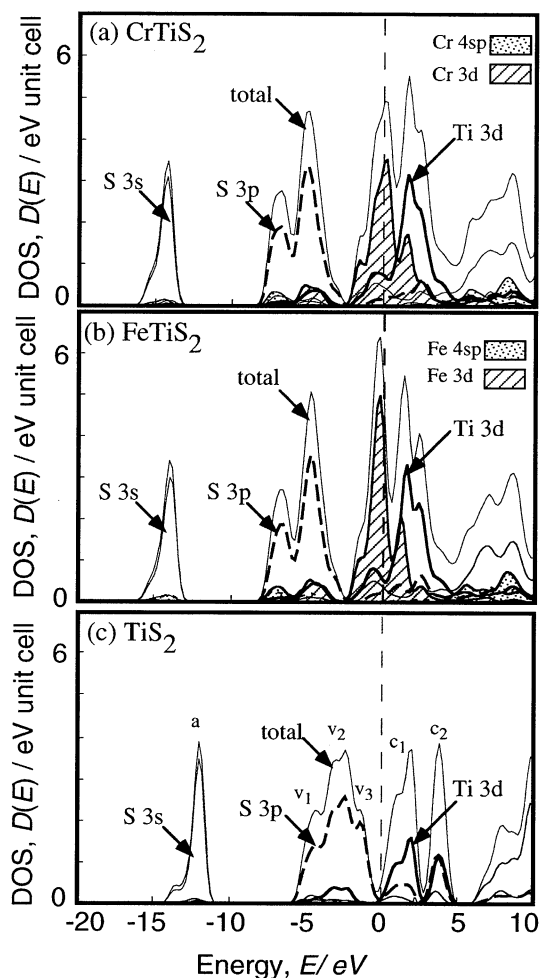


Fig. 2 Comparisons of the total and partial density of states of (a) CrTiS<sub>2</sub>, (b) FeTiS<sub>2</sub>, and (c) TiS<sub>2</sub>.

Table 2 Net charges for atoms located close to the center of the cluster.

	Ti	S	M
CrTiS <sub>2</sub>	0.996	-0.656	0.559
FeTiS <sub>2</sub>	1.019	-0.519	0.307
TiS <sub>2</sub>	0.689	-0.285	—

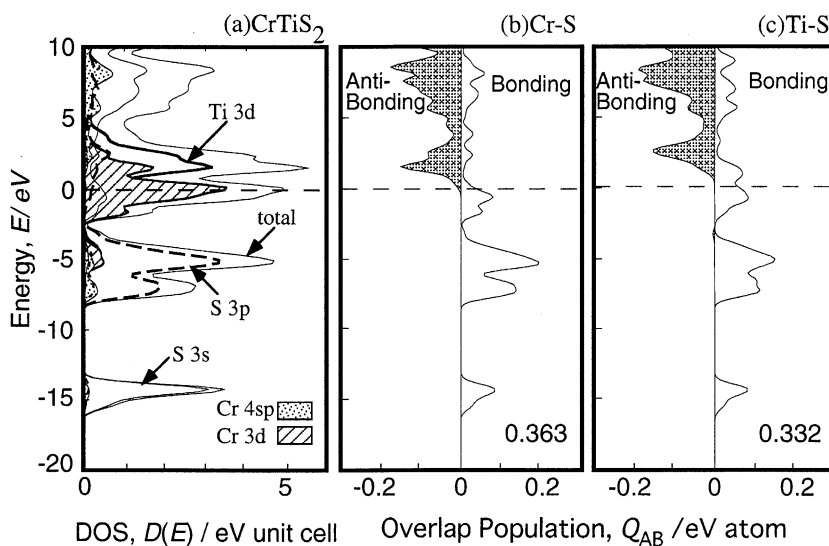


Fig. 3 (a) The total and partial density of states; and the overlap population diagram of (b) Cr-S bond, and (c) Ti-S bond for CrTiS<sub>2</sub>.

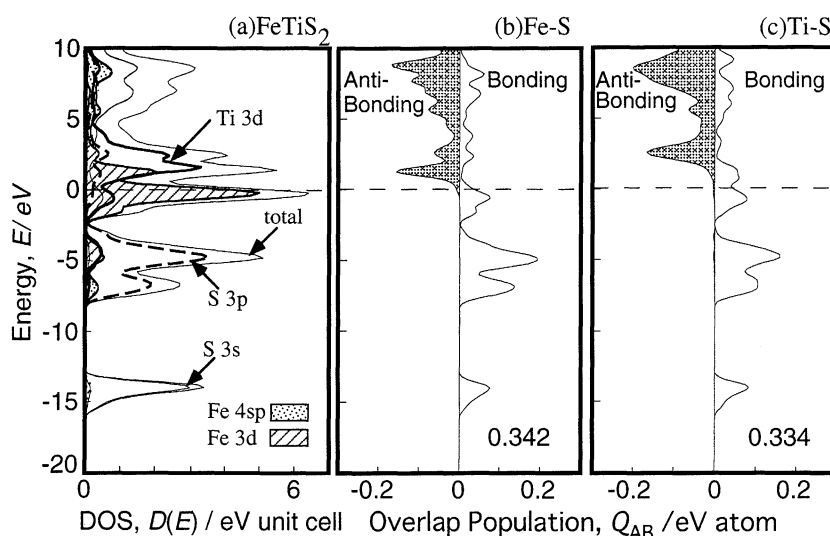


Fig. 4 (a) The total and partial density of states; and the overlap population diagram of (b) Fe-S bond, and (c) Ti-S bond for  $\text{FeTiS}_2$ .

manner of Ti-S interaction is qualitatively unaffected by the presence of M, except for additional occupation of a bonding orbital composed of Ti-3d and S-3sp. The BOP of Ti-S in  $\text{TiS}_2$  is 0.417.<sup>8)</sup> It decreases by about 20% due to the presence of M. The loss of the BOP of Ti-S associated with the M intercalation can be ascribed to the lowering of the energies of the M-3s, 3p bands relative to  $E_F$  as well as slight elongation of the bond length of Ti-S by 1.0–1.5%.

It is interesting that BOP for Cr-S and Fe-S are almost as large as that of the Ti-S in the intercalated compounds. The shape of the overlap population diagrams for the M-S bonds looks similar as well. Since the number of Ti-S bonds are unchanged by the intercalation, the strong M-S covalent bonding should have extra contribution on the stability of  $\text{MTiS}_2$ , which may balance with the decrease in the BOP of Ti-S and the charging-up effect of host  $\text{TiS}_2$  due to the intercalation. The intercalation in the so-called “van-der-Waals gap” is found to change the local electronic structure significantly in the manner as described above.

#### 4. Conclusion

The electronic structure and chemical bonding of the M (M = Cr and Fe) intercalated  $\text{TiS}_2$  have been studied by the DV- $X\alpha$  molecular orbital method using a cluster model

( $\text{M}_{13}\text{Ti}_{14}\text{S}_{48}$ )<sup>42-</sup>. Mulliken's population analysis has been thoroughly conducted to examine the net charge as well as the magnitude of covalent bondings. We found that the Mulliken's charge of M in  $\text{MTiS}_2$  is 0.559 for Cr and 0.307 for Fe. BOP of Ti-S decreases by approximately 20% due to the presence of M. Both the BOP of the Cr-S and Fe-S bonds are found to be as large as that of the Ti-S bond.

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