Electronic Structure and Chemical Bonding of TiS₂ by Cluster Calculation

Yang-Soo Kim, Masataka Mizuno, Isao Tanaka and Hirohiko Adachi

Department of Materials Science and Engineering, Kyoto University, Sakyō, Kyoto 606-8501, Japan

First-principles molecular orbital calculations for layered compound TiS₂ have been made by the use of the discrete-variational (DV-Xα) method. Model clusters used are composed of 55 and 135 atoms. The magnitudes of individual chemical bondings are investigated by analyzing the bond overlap populations. The valence band structure measured by X-ray photoemission spectroscopy is well reproduced by the calculation, and each peak is identified from the viewpoint of chemical bonding. There is a considerably strong covalent bonding between Ti and S atoms in TiS₂. Both of the Ti-Ti and S-S bondings are found to be much weaker than the Ti-S bonding. The interlayer S-S bonding is also very weak, but virtually the interaction is not the van der Waals type.

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I. Introduction

Various materials which undergo reduction by intercalation of lithium have been studied as positive electrodes for rechargeable lithium batteries\(^{(1-5)}\). Among these, titanium disulfide, TiS₂, is known as a highly promising material from the viewpoint of their attractive electrochemical characteristics and commercialization. The beneficial features of TiS₂ include its high reduction potential against lithium metal and high electrochemical equivalents, both producing high energy density. Furthermore, TiS₂ have a layered structure with the van der Waals gaps, which is thought to be advantageous for rapid diffusion of lithium ions inside the cathode, thus permitting discharges at high rates\(^{(6)}\).

Because of its technological importance, intensive experimental and theoretical researches have been devoted to the study of the energy band structures and related properties of this compound\(^{(7-10)}\). In order to understand a guiding principle for the improvement of TiS₂, fundamental knowledge on chemical bonding should be essential. However, to our surprise, little is known from this viewpoint.

The objective of the present study is to understand the nature of chemical bondings of TiS₂ with relation to its atomic arrangement. Bonding mechanism in an isolated layer and interlayer interactions are investigated separately by using model clusters composed of monolayer and three layers. Calculations are made by a first-principles molecular orbital method, and the magnitudes of chemical bondings are evaluated quantitatively through Mulliken's population analysis\(^{(11)}\).

II. Computational Procedures

1. DV-Xα cluster method

In this work, the first-principles DV-Xα cluster method\(^{(12,13)}\) is used for the electronic state calculation. The molecular orbital wave function is expressed by a linear combination of atomic orbital (LCAO) as,

$$
\phi_i = \sum_j c_{ij}\chi_j,
$$

where the \(c_{ij}\)'s are coefficients. As the basis function \(\chi_i\), we use the numerical atomic orbitals obtained by solving the Schrödinger equation for the individual atoms in the cluster. The atomic orbitals used in the present study are 1s-3d for S and 1s-4p for Ti.

In the DV-Xα method, the matrix elements \(H_0\) and \(S_0\) in the secular equation, \((H-E}\mathcal{S})C=0\), are evaluated by numerical integration as,

$$
H_0 = \sum_{k} \omega(r_k) \chi_k(r_k) \cdot \chi_k(r_k),
$$

$$
S_0 = \sum_{k} \omega(r_k) \chi_k(r_k) \chi_k(r_k),
$$

where \(r_k\) is one of total \(N\) sampling points which is taken in the three-dimensional real space and \(\omega(r_k)\) is the reciprocal of sampling point density at \(r_k\).

In order to discuss about the charge density and chemical bonding of the cluster, the Mulliken population analysis\(^{(14)}\) is employed. The orbital population, \(Q_i\), and the overlap population, \(Q_o\), for the \(l\)th molecular orbital are defined by,

$$
Q_i(l) = \sum_j f_{il} c_{ij} c_{lj} S_{ij},
$$

$$
Q_o(l) = f_{il} c_{ij} c_{lj} S_{ij},
$$

(3)

(4)
where \( f_i \) is the occupation number of the \( l \)th molecular orbital. We also define the effective charge \( Q_A \) and the net charge \( N_A \) of atom A as

\[
Q_A^{(l)} = \sum_{i \in A} Q_i^{(l)}, \quad Q_A = \sum_{i \in A} Q_i, \quad N_A = Z - Q_A,
\]

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 atoms A and B, \( Q_{AB} \), is given by,

\[
Q_{AB} = \sum_l Q_{AB}^{(l)},
\]

where

\[
Q_{AB}^{(l)} = \sum_{i \in A} \sum_{j \in B} Q_{ij}^{(l)}.
\]

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

2. Cluster model

The layered compound, TiS\(_2\), belongs to a hexagonal structure of the space group \( D_{3d} (P\bar{3}m1) \) with the lattice parameters of \( a = 0.3408 \text{ nm} \) and \( c = 0.5699 \text{ nm} \), which is essentially constructed by a close-packed S ion framework. In this structure, one Ti plane is sandwiched by two S planes, and the stacking of the layers forms the crystal structure. Thus the crystal is a layered structure by the periodic stacking of these planes, (S–Ti–S)(S–Ti–S)… In this compound, every Ti atom is located in a slightly distorted octahedron composed of six S atoms with the Ti–S distance of 0.243 nm. As is known, the S–S interlayer distance is 0.3463 nm, a slightly larger than intralayer S–S intralayer distance of 0.3408 nm. Furthermore, all the spacings between the S planes in a typical layered-structure are the same, regardless of the Ti planes, and this distance between the S planes is 0.2849 nm.

The calculation of the electronic states of TiS\(_2\) is carried out using cluster models taken from a bulk crystal. First, a single-layer model is investigated in order to understand the fundamental electronic structure of intralayer interactions, then a model cluster which includes three layers is adopted to study the interlayer interactions. The model clusters which are composed of 55 atoms (Ti\(_{10}\)S\(_{35}\))\(^{4+}\) and 135 atoms (Ti\(_{45}\)S\(_{90}\)), are employed for these purposes. Figure 1 shows the structure together with a brief explanation of both the clusters.

III. Results and Discussion

In order to discuss the valence electronic state and chemical bonding of TiS\(_2\), we first calculate using the single-layer model cluster of (Ti\(_{10}\)S\(_{35}\))\(^{4+}\). Figure 2(a) shows the density of states (DOS) of the cluster. By the molecular orbital calculation for the cluster model, the discrete MO energy levels is first obtained. They are replaced by Gaussian functions of 1.0 eV full width at

![Fig. 1](image1)

The structure of clusters model for TiS\(_2\), (a) Ti atom in the structure is octahedrally coordinated by six sulfur atoms, (b) The (001) projection of single-layer model clusters of the TiS\(_2\). Closed circles which are connected with each other by using lines are Ti atoms, and open and gray-closed circles are S atoms on the S planes, (c) The (100) projection of the three-layers model cluster of TiS\(_2\). In the middle of the cluster, there is the single-layer model cluster, which consists of one Ti plane and two S planes, (d) The stacking of the Ti and S layers in TiS\(_2\).
Electronic Structure and Chemical Bonding of TiS$_2$ by Cluster Calculation

Fig. 2 Total and partial density of states and the overlap population diagram for single-layer (Ti$_3$S$_6$)$_{16}$$. The values written in each figure are obtained by summing up the overlap populations up to the Fermi level, (a) total (thin solid line) and partial density of states, and (b) overlap population diagram for the Ti–S bond, (c) for the Ti–Ti bond, and (d) for the S–S bond.

half maximum (FWHM) to obtain the DOS for easy visualization. The energy scale is shifted so that the Fermi level ($E_F$) is equal to zero. In the figure, the partial density of states (PDOS) is also shown by analyzing the molecular orbitals in terms of the individual atomic orbital components following the eq. (1).

The valence state is constructed by S 3s band (peak a) at $-1.6 \times 10^{-19}$ J ($-10$ eV)–$2.4 \times 10^{-18}$ J ($-15$ eV) and S 3p band at $0$–$-8.01 \times 10^{-19}$ J ($-5$ eV). However, these states contain considerably large components of Ti atomic orbitals. Above the $E_F$, the Ti 3d band is located. This band consists of two peaks ($c_1$ and $c_2$), which can be ascribed to $t_{2g}$ and $e_g$-type bands, respectively. Moreover, $c_1$ peak divided into two peaks because the Ti atom is located at the center of distorted octahedron in this compound. The Ti 3d bands also involve a considerably large amount of S 3p components. The characteristic feature of the S 3p valence band located at $0$–$-8.01 \times 10^{-19}$ J ($-5$ eV) is the presence of three peaks labeled as $b_1$, $b_2$ and $b_3$ in it. As mentioned above, Ti atomic orbitals participate in forming this band. This is due to the very strong covalent interaction between S and Ti atoms. The details of the chemical bonding of this compound will be described below. The formal charges for S and Ti of TiS$_2$ are $-2$ and $+4$, respectively. However, according to the Mulliken population analysis the effective charges are estimated to be $-0.36$ for S and $+0.72$ for Ti, which largely deviate from the formal charges, reflecting the strong covalency between them.

The electronic structure of TiS$_2$ has previously been investigated by several workers by the band models, and the three peaks in the valence band have also been found, similar to the present result. However, any detailed discussion has not been given on the band structure. In the present work, the MO wave functions in the valence state, which cause the three DOS peaks at $0$–$-8.01 \times 10^{-19}$ J ($-5$ eV) are investigated in detail. The main component of this band is S 3p orbitals, but considerable amounts of Ti orbitals are involved in the band. The lowest energy peak ($b_1$) at about $-7.21 \times 10^{-19}$ J ($-4.5$ eV) is attributed to the bonding states due to the strong covalent interaction between S 3p and Ti 4sp, and Ti 4sp. The middle-energy peak ($b_2$) is also of the bonding states formed by the admixtures of Ti 3d with S 3p. However, the peak at highest energy ($b_3$) is of non-bonding states, essentially composed of S 3p. Strong admixture of Ti 3d, 4sp and S 3p orbitals, i.e., the strong covalent bonding between Ti and S atoms is characteristic of TiS$_2$.

The strength of the covalent bonding can be estimated from the overlap population. The bond overlap populations between Ti and S atoms for each MO level are evaluated and they are demonstrated as an energy distribution of overlap population, $Q_{ab}$ in Figs. 2(b)–(d). These diagrams are called overlap population diagrams or COOP (crystal orbital overlap population) diagrams. The bond overlap population $Q_{ab}$ between atoms is obtained by summing the $Q_{ab}^{(i)}$ for all MO levels below $E_F$. The interactions between Ti and S, Ti and Ti, and S and S have been carefully investigated separately. The values given in each figure by using shows are the bonding and the antibonding contributions to the overlap population. The sum of these two components is shown in the lower-right side of each figure.

Regarding the Ti–S bonding (Fig. 2(b)), there are two large bonding-type peaks. One peak is located at the lowest energy of about $-1.92 \times 10^{-18}$ J ($-12$ eV) in the valence band states, and this is attributable to the covalent interaction between S 3s and Ti 4sp electrons. The other one centered about $3.2 \times 10^{-19}$ J ($-2$ eV) is due to the interaction between S 3p and Ti 3d electrons. The value of the overlap population (0.418) is very large, indicating that there is a strong covalent bonding between...
Ti and S atoms. In the case of Ti–Ti and S–S bonds, the bonding and antibonding interactions coexist, even though each of the interactions are rather weak. Therefore, their contributions to the bonding states are very small. Thus, it is evident that the dominant chemical bonding in TiS₂ is the Ti–S bonding.

As mentioned above, TiS₂ has the layered structure. The next problem of interest is to understand the interaction between two layers. For this purpose, a model cluster which includes three layers, namely the (Ti₅S₃₀) cluster shown in Fig. 1 is used. The electronic state of the cluster is calculated and its valence band is shown in Fig. 3. It is worthwhile noting that both the DOS and the PDOS of the three-layers model are quite similar to those of the single-layer model shown in Figs. 2(a)–(d). The overlap population diagrams, also show the similarities. These results imply that the interlayer interaction is weak. The overlap population diagram of the interlayer S’–S’ interaction is compared with that of the intralayer S–S interaction in Figs. 3(d) and (e).

The bonding contribution of S–S is greater by 0.015 than that of the S’–S’ bonding, reflecting shorter S–S distance (0.3408 nm) than that of S’–S’ (0.3463 nm). However, the antibonding contribution of S–S is also greater by 0.027 for S–S compared with S’–S’. As a result, the net bond overlap population is smaller in S–S than in S’–S’. Although the magnitude of the interlayer interaction is rather small, the small covalency indicates that its interaction is not purely the van der Waals type. Such an interaction may play a role when impurities such as lithium ions are intercalated into TiS₂.

Several investigations for the electronic structure of TiS₂ have previously been reported. The valence band structure for the bulk crystal has been calculated by Umrigar et al.⁵⁰ using the LAPW (linearized Augmented Plane Wave) method. The experimental measurement of

![Fig. 4 Comparison between calculated DOS and experimental XPS spectrum. The Fermi level (broken line) is chosen to be the zero energy, (a) DOS for three-layers cluster of TiS₂, (b) DOS of TiS₂ calculated by the LAPW method⁵⁰, (c) XPS spectrum obtained by Wertheim et al.¹⁵⁰.](image)

![Fig. 3 Total and partial density of states and the overlap population diagram for three-layers cluster (Ti₅S₃₀). (a) Total (thin solid line) and partial density of states, (b) overlap population diagram for the Ti–S bond, (c) for the Ti–Ti bond, (d) for the S–S bond (S–S distance is 0.3408 nm), and (e) for the S’–S’ bond in interlayer (S–S distance is 0.3463 nm).](image)
XPS (X-ray photoemission spectrum) has also been carried out for studying the valence band structure. Figure 4(a) again shows the DOS’s of three-layers model (Ti\textsubscript{3}S\textsubscript{60}) of TiS\textsubscript{2}. The DOS calculated by Umrigar et al.\textsuperscript{(8)} and the valence state XPS of TiS\textsubscript{2} measured by Wertheim et al.\textsuperscript{(10)} are illustrated in Figs. 4(b) and (c), respectively. The DOS by the cluster calculation agrees well with that by the band structure calculation. These theoretical results well reproduce the experimental XPS spectrum. The three peaks, \( b_1 \cdot b_3 \), seen in the valence band spectrum is clearly interpreted by the present cluster calculation as described earlier.

**IV. Conclusion**

The electronic structure and chemical bonding of layered compound TiS\textsubscript{2} have been studied by the DV-X\alpha molecular orbital method using the single-layer model (Ti\textsubscript{10}S\textsubscript{30})\textsuperscript{4+}, and the three-layers model (Ti\textsubscript{3}S\textsubscript{60}). The calculated for the former model is almost the same as that for the latter model. It also agrees well with the result by an LAPW band-structure calculation. An experimental XPS is also well reproduced. Three peaks \( b_1 \), \( b_2 \), and \( b_3 \) appear in the S-3\( p \) band and they are interpreted as due to the following interaction; \( b_1 \): Ti 4sp-S 3\( p \) interaction, \( b_2 \): Ti 3d-S3\( p \) interaction, and \( b_3 \): S3\( p \) nonbonding. The Ti-S interaction is found, to be more than an order of magnitude greater than that the Ti-Ti and the S-S intralayer interaction. The intergranular S'-S' interaction is also found to be not purely the van der Waals type. The small covalent interaction may play a role when impurities are intercalated into TiS\textsubscript{2}.

**REFERENCES**

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