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# XPS Study of One-Dimensional Compounds: $TiS_3$

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X-Ray photoelectron spectra of $TiS_3$ with a one-dimensional structure were measured. $TiS_3$ may be regarded as $Ti^{4+}(S_2)^{2-}S^{2-}$ with pairs of S atoms ($S_2$) and isolated S atoms. The spectra of the sulfur core-levels are assigned by comparison with those of $TiS_2$, where all S atoms are largely separated. The binding energy of the $S_2$ pairs is found to be 1.4 eV higher than that of the isolated S atoms, which is consistent with the larger negative charge of the isolated atoms. The structures of the valence band of $TiS_3$ are discussed in terms of a molecular orbital scheme for the $S_2$ pairs.

## Introduction

In recent years there has been considerable interest in transition metal trichalcogenides with the chemical formula of $MX_3$ (where $M$ = group IV and V elements; $X$ = S, Se, and Te) exhibiting pseudo-one-dimensional anisotropic features. They are similar in crystal structures, but their transport properties are markedly different. Numerous studies have been carried out on their transport properties, in particular, on the resistance amomalies associated with charge density wave (CDW) formation in $NbSe_3$ (*1–28*). However, to date there have been few experimental reports on the valence band structures of these compounds, which are closely related to their transport properties (*29–35*).

Previously, we have made X-Ray photoelectron spectroscopic (XPS) measurements for $NbSe_3$ and $TaSe_3$ (*34*), confirming recent band calculations after Bullet (*36, 37*) and Hoffmann *et al.* (*38*). In addition, we have given evidence to show that the transition metal $d_z^2$ band is located at the top of the valence band in $NbS_3$ and $TaS_3$ and that $d_z^2$ band separation occurs in $NbS_3$, leading to semiconducting properties. Jellinek *et al.* (*33*) reported the XPS spectra of $ZrS_3$ and $ZrSe_3$ and gave a clear description of chalcogen core-levels and valence bands compared with those of $ZrS_2$ and $ZrSe_2$.

The crystal structure of $TiS_3$ is the most simple among the $MX_3$ compounds. Other compounds, such as $NbSe_3$, $TaSe_3$, and $TaS_3$, contain the structure of $TiS_3$ as a structural element. Since $TiS_3$ is regarded as an archetype of these compounds, $TiS_3$ is useful for the study of band structures. $TiS_3$ crystallizes in the $ZrSe_3$-type structure. The crystallographic symmetry of this type is described by the $P2_1/m$ space group (*39*). As shown in Fig. 1a, crystals are made up of infinite chains of distorted trigonal $MX_6$ prisms stacked parallel to the $b$ monoclinic

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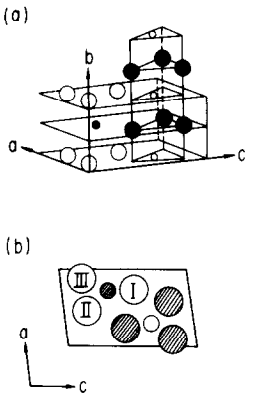


FIG. 1. (a) Schematic drawing of $TiS_3$ crystal structure. (b) Projection of $TiS_3$ structure on the *ac* plane. Open circles are at 0 and solid circles at $\frac{1}{2}b$.

axis. Neighboring chains are displaced by one-half of the unit cell along the *b* axis and linked together by Ti–S bonds. The unit cell contains two molecular units, as shown in Fig. 1b. Three types of sulfur site ($S_I$, $S_{II}$, $S_{III}$) and one metal site (Ti) are distinguished in the planes in Fig. 1b. The distance between the $S_{II}$ and $S_{III}$ sites is 2.04 Å, which is considerably shorter than other S–S distances ($S_I$–$S_{II}$, $S_I$–$S_{III}$) of 3.29 and 3.76 Å. This structure implies strong S–S bonding within $S_{II}$–$S_{III}$ pairs.

From the structural features, in particular, the presence of the $S_2$ pairs, and the observation of the semiconducting properties of $TiS_3$ (*29, 41*), the ionic charge of $TiS_3$ is expected to be formulated as $Ti^{4+}(S_2)^{2-}S^{2-}$, although this formula does not imply that the compound is fully ionic. This type of formula holds true for $ZrS_3$ and $ZrSe_3$ (*33*).

The purpose of the present study is to obtain the XPS spectra of $TiS_3$ and to examine the validity of the formula $Ti^{4+}(S_2)^{2-}S^{2-}$ and to clarify the contribution of the $S_2$ pairs to the electronic structure by comparing the spectra of $TiS_3$ with those of $TiS_2$, where S atoms are regarded as largely separated with S–S distance being over 3 Å (*40*).

## Experimental

The crystals used in this study were prepared by heating a mixture of sulfur and metal powder in an evacuated quartz tube in a furnace with a temperature gradient of 400 to 900°C, as described previously (*35*).

In the XPS measurements the quartz tube was put into a glove box attached to the XPS spectrometer and broken in an atmosphere of argon. The crystals were taken from the quartz tube and mounted on the sample holder. Then they were placed in the XPS analyzing chamber without exposing them to air. The XPS spectra of $TiS_3$ and $TiS_2$ were measured at room temperature with an HP 5950A ESCA spectrometer using a monochromated Al $K\alpha$ (1486.6 eV) X-ray source. The resolution energy was 0.6 eV. During the experiment the base vacuum was in the $10^{-9}$-Torr range. The core-level spectra reveal that the samples were free from oxygen.

## Results and Discussion

The S 2*p*-level spectra of $TiS_3$ and $TiS_2$ are shown in Figs. 2a, b, respectively.

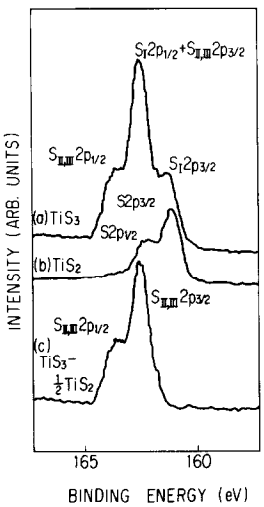


FIG. 2. XPS spectra of S 2*p* levels in (a) $TiS_3$, (b) $TiS_2$, and (c) $TiS_3$–$\frac{1}{2}$ $TiS_2$.

There is a single spin-orbit split doublet of S $2p$ level in $TiS_2$, and in $TiS_3$ two spin-orbit split doublets are overlapping with an intensity ratio of 2 : 1. It is also noted that the doublet of $TiS_3$ at the lower energy side corresponds to that of $TiS_2$ in energy.

The results imply that the two doublets of S $2p$ in $TiS_3$ result from the inequivalence of S atoms, that is, the $S_2$ pairs ($S_{II}$ and $S_{III}$ atoms) and the isolated $S_I$ atoms. The 2 : 1 intensity ratio and chemical shift of their doublets suggest that the higher energy doublet can be assigned to the levels due to the $S_2$ pairs, and the lower energy one belongs to the isolated S atoms. This suggests that the isolated $S_I$ atoms have a larger negative charge than the $S_2$ pairs. Such an assignment is consistent with the formula $Ti^{4+}(S_2)^{2-}S^{2-}$.

In $TiS_2$, only one S $2p$ doublet appears at the same binding energy as the lower binding energy doublet in $TiS_3$. This is because S atoms are largely separated from each other in $TiS_2$.

In order to examine the contribution of the $S_2$ pairs we try to subtract half of the intensity of the $TiS_2$ spectrum from that of $TiS_3$, because there is only one $S_I$ site per formula in the trisulfide. Here, to normalize the intensities of the S $2p$ level between samples, the intensity of the Ti $2p$ level was used. Such a procedure has been successfully applied to the XPS spectra of $ZrS_3$ and $ZrSe_3$, which have pairs of chalcogen atoms, $S_2$ or $Se_2$ (*33*). Figure 2c shows a subtracted spectrum. This is considered to be the spectrum of $S_{II,III}$ $2p$ levels resulting from the $S_2$ pairs. The difference of the binding energy between $S_I$ $2p$ and $S_{II,III}$ $2p$ is 1.4 eV.

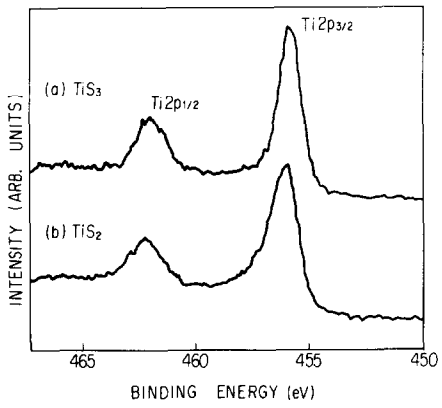


FIG. 3. XPS spectra of Ti $2p$ levels in (a) $TiS_3$ and (b) $TiS_2$.

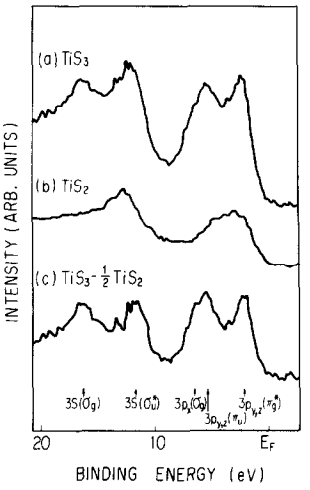


FIG. 4. XPS spectra of the valence band in (a) $TiS_3$, (b) $TiS_2$, and (c) $TiS_3$–$\frac{1}{2}$ $TiS_2$.

Figure 3 shows the Ti $2p$-level spectra of $TiS_3$ and $TiS_2$. In contrast to the S $2p$ levels, only one spin-orbit split doublet of the Ti $2p$ level is seen in both $TiS_3$ and $TiS_2$. These doublets are similar to each other, though the doublet of $TiS_2$ is located 0.2 eV higher than that of $TiS_3$. The result suggests the presence of one kind of Ti atom in their structures, as expected from their crystal structures (see Fig. 1). From the chemical shift of Ti $2p$ state, charge transfers from the surrounding S atoms to the Ti atom in $TiS_3$ and $TiS_2$ are estimated at about +0.32 and +0.30 electrons, respectively. A detailed description of the method of estimation is given elsewhere (*42*). These values are larger than those of $NbSe_3$ and $TaSe_3$ (*34*), which suggests that the ionic bonds of sulfides are stronger than those of selenides.

The valence band spectra of $TiS_3$ and $TiS_2$ are shown in Figs. 4a and b, respectively. Applying the above-mentioned procedure to the S $3s$ and $3p$ valence bands, we obtained the subtracted spectra in Fig. 4c. In order to clarify the subtracted spectra, we use the molecular orbital diagram of the $S_2$ pairs, which has been useful in the interpretation of XPS spectra of the compounds with $S_2$ pairs, such as $ZrS_3$ and $ZrSe_3$. Such a molecular orbital diagram of the $S_2$ pairs is shown schematically in Fig. 5. The overlap of the $3s$ orbitals of the two S atoms, $S_{II}$ and $S_{III}$, forming the $S_2$ pairs leads to a bonding $3s$ ($\sigma_g$) and an antibonding $3s$ ($\sigma_u^*$) molecular orbital and both orbitals are occupied by two electrons. The $3p_x$ orbitals (the axis connecting the two S atoms $S_{II}$ and $S_{III}$ is taken as the $x$ axis) lead to an occupied bonding $3p_x$ ($\sigma_g$) and an empty $3p_x$ ($\sigma_u^*$) orbital. The $3p_{y,z}$ orbitals lead to the occupied bonding $3p_{y,z}$ ($\pi_u$) and antibonding $3p_{y,z}$ ($\pi_g^*$) orbitals.

The expected splitting between the bonding $3s$ ($\sigma_g$) and the antibonding $3s$ ($\sigma_u^*$) molecular orbitals is observed in the subtracted spectra of S $3s$ level in Fig. 4c. The magnitude of the splitting, $\Delta E$, correlates well with the $S_{II}$–$S_{III}$ distance $r$. For a small $r$, the overlap of the $3s$ orbitals of the two S atoms is large, leading to a large value of $\Delta E$. Indeed, for $ZrS_3$ with $r$ of 2.09 Å, $\Delta E$ is 4.0 eV, (*33*) and for $TiS_3$ with $r$ of 2.04 Å, $\Delta E$ is 4.6 eV.

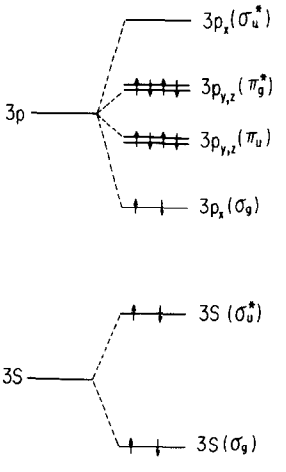


FIG. 5. Molecular orbital diagram of the $S_2$ pairs.

In Fig. 4c, a shoulder at 6.6 eV and peaks at 5.6 and 2.2 eV in the band between $E_F$ and 10 eV may be interpreted as arising mainly from a bonding $3p$ ($\sigma_g$), doubly degenerate bonding $3p_{y,z}$ ($\pi_u$), and antibonding $3p_{y,z}$ ($\pi_g^*$) of the $S_2$ pairs $3p$ states, respectively, although S $3p$ band is admixed with Ti $3d$ states. Here, the value of splitting, $\Delta E'$ between $3p_{y,z}$ ($\pi_u$) and $3p_{y,z}$ ($\pi_g^*$) for $TiS_3$, is around 3.4 eV, which is 0.4 eV larger than $\Delta E'$ of $ZrS_3$. Probably this is resulting from the difference of the distance, $r$, between $S_{II}$ and $S_{III}$ forming the $S_2$ pairs in these compounds.

## Conclusion

The XPS spectra of $TiS_3$ were measured at room temperature. Two doublets of the S $2p$ level with an intensity ratio of 2 : 1 were observed, which gives evidence for the existence of inequivalent S atoms, that is, pairs of S atoms ($S_2$) and isolated S atoms. The binding energy of the $S_2$ pairs is 1.4 eV higher than that of the isolated S atoms. This is consistent with the formula $Ti^{4+}(S_2)^{2-}S^{2-}$. In the valence band of $TiS_3$, there are large bonding–antibonding splittings in contrast with $TiS_2$. These splittings result from the interaction within the $S_2$ pairs and are interpreted in terms of a simple molecular orbital scheme.

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