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XPS Study on Valence Band Structures of Transition-Metal Trisulfides, TiS_3, NbS_3, and TaS_3

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Transition-metal trisulfides, TiS_3, NbS_3, and TaS_3, with a quasi-one-dimensional structure are investigated by X-ray photoelectron spectroscopic (XPS) measurements to obtain information on the valence band structures. The band structures at the Fermi level of these compounds correspond well to their transport properties. A shoulder is observed at the top of the valence band in NbS_3 and TaS_3, suggesting that this band is made up of the metal d_{z^2} electrons. The d_{z^2} band is occupied in NbS_3 and TaS_2 and empty in TiS_3. The characteristic features at the top of the valence band in NbS_3 imply the occurrence of d_{z^2} band separation, which leads to a semiconducting nature.

Introduction

In recent years, transition-metal trichalcogenides have attracted special attention, partly because of their quasi-one-dimensional character which leads to formation of a charge density wave (CDW) and partly because of the possibility of a one-dimensional superconductor with high transition temperature. All these compounds form needle-shaped crystals with the common structural feature that each metal atom lies at the center of a trigonal prism of chalcogen atoms; successive prisms are arranged in infinite chains along the *b* axis (*1*).

TiS_3 is a typical compound of the group IV transition-metal trisulfides; and NbS_3 and TaS_3 is typical of the group V transition-metal trisulfides. In spite of the similarity of their crystal structures, there is a marked difference in the transport properties of TiS_3, NbS_3, and TaS_3. TiS_3 (*2, 3*) and NbS_3 (*4–6*) are semiconductors and TaS_3 (*7*) is a metal. The transport properties are closely related to the valence band structure. To date, however, there is little knowledge of the band structure of these compounds. The purpose of the present study is to obtain a picture of the valence band structure for TiS_3, NbS_3, and TaS_3 by X-ray photoelectron spectroscopic (XPS) measurements and to find a correlation between the band structures and the characteristic transport properties of these compounds.

Experimental

The crystals used were grown by heating a mixture of sulfur and metal powder in an evacuated quartz ampoule in a furnace with

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a temperature gradient of 400 to 900°C. The shape of TiS_3 and NbS_3 crystals was thin and ribbon-like 0.5 × 0.05 × 10 mm in size and that of TaS_3 was fiber-like and 0.04 × 0.01 × 10 mm. In the case of the Ti–S system, in particular, the plate-like crystals of *lT*–TiS_2 with golden luster were obtained at the higher temperature side together with TiS_3 at the lower temperature side. These crystals were identified by an X-ray diffraction method. The quantity of impurities in these crystals was found to be under 1 ppm from X-ray fluorescence analysis, chemical analysis, and back-scattering methods. In our XPS spectra, no impurities have been detected. The semiconducting properties of TiS_3 and NbS_3 and the metallic properties of TaS_3 at room temperature are confirmed by measurements of the temperature dependence of resistivity over a wide temperature range from 4.2 to 650 K.

In the XPS measurements the crystals were taken out from the quartz ampoule and mounted on the sample holder in an atmosphere of argon and then introduced into the XPS analyzing chamber without being exposed to air. The XPS spectra were taken with an HP 5950A ESCA spectrometer at room temperature under a pressure of 10^{-9} Torr. The excitation source is a monochromatized Al*Kα* line with the resolution energy 0.6 eV. The core-level spectra reveal that the samples are free from oxygen. The XPS measurements were carried out for several samples from different batches which were prepared under the same conditions.

Results and Discussion

Figure 1 shows the XPS valence band spectra of TiS_3, NbS_3, and TaS_3. The Fermi level was determined from that of gold evaporated on the surface of the samples. The spectra of the three compounds differ markedly from each other in the following two respects.

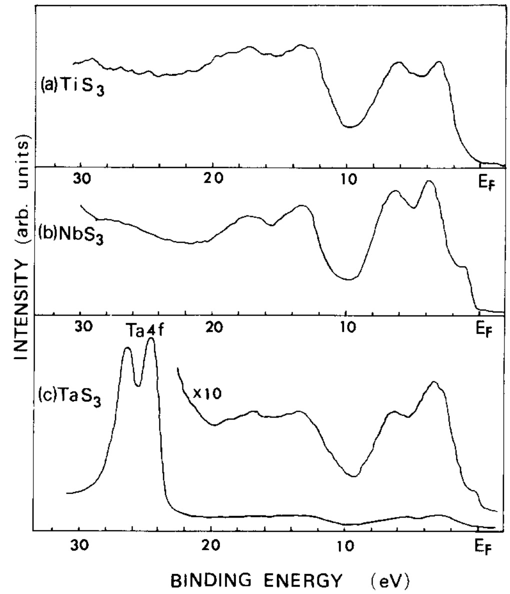

FIG. 1. Valence band spectra of TiS_3, NbS_3, and TaS_3 by XPS measurements.

First, in TiS_3 and NbS_3 the Fermi level lies above the top of the valence band, which means that these compounds are semiconductors. In contrast, the Fermi level of TaS_3 is located at the top of the valence band. This means that TaS_3 is a metal. These results are consistent with those of the temperature dependence of the resistivity of TiS_3 (*2, 3*), NbS_3 (*4–6*), and TaS_3 (*7*).

Second, a shoulder is clearly observed at the top of the valence band in NbS_3 and TaS_3, whereas no shoulder appears in TiS_3. Nb and Ta belong to the group V elements and Ti is a group IV element. The ionic charges of transition-metal trichalcogenides MX_3 (M: transition-metal atom, X: chalcogen atom) are regarded as $M^{4+}X^{2-}(X_2)^{2-}$, although this formulation does not imply that the compounds are fully ionic (*8, 9*). The origin of the shoulder is likely to be the energy band caused by metal *d* electrons. According to the band calculation for NbS_3 by Bullet (*10*), an isolated band resulting from Nb–Nb bonds exists below the Fermi

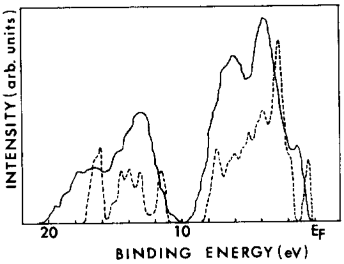

FIG. 2. XPS valence band spectra (solid lines) of NbS_3 compared with the theoretical density of states (dashed lines). The XPS spectra were obtained by subtracting the background due to inelastically scattered electrons.

level, as shown in Fig. 2. The band observed as the shoulder is thought to be the band caused by metal d_{z^2} electrons. The energy dispersion curves for $NbSe_3$ calculated by Hoffmann (9) support the present inference. The absence of the shoulder in TiS_3, as shown in Fig. 1, suggests that the metal d_{z^2} band is empty. Thus, the metallic nature of TaS_3 seems to result from the partly occupied d_{z^2} band and also the semiconducting nature of TiS_3 from the empty d_{z^2} band. The situation mentioned above is schematically represented in Fig. 3a and c.

Here, a question arises. Whereas NbS_3 is a group V compound like TaS_3, why is NbS_3 a semiconductor and not a metal? From the present results that the Fermi level of NbS_3 lies above the shoulder derived from d electrons, we can guess that there occurs a separation of the metal d_{z^2} band (see Fig. 1b and Fig. 3b). The origin of the band separation in NbS_3 is the doubling of the lattice in the axis direction, which is caused by formation of Nb–Nb pairs, as is revealed from the X-ray diffraction study (*11*) (see Fig. 4). Specifically, the d_{z^2} band opens at $b^*/2$ along the b^* axis of the reciprocal lattice. Such a situation does not occur in TaS_3, where the metal atoms are arranged with equal separation b_2 along the b axis.

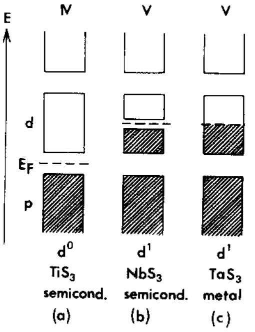

FIG. 3. Energy band scheme of TiS_3, NbS_3, and TaS_3. The hatched parts are occupied by electrons.

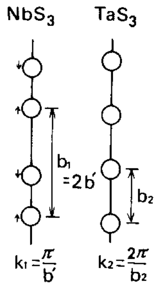

FIG. 4. Arrangement of metal atoms (open circles) along the b axis of NbS_3 and TaS_3. b_1 and b_2 are the lattice constants of NbS_3 and TaS_3, respectively. b' is the hypothetical distance between metal atoms in case of the arrangement in the equidistance, which is nearly equal to b_2. k_1 and k_2 are wave vectors of NbS_3 and TaS_3, respectively.

The existence of Nb–Nb pairs in NbS_3 suggests the formation of the CDW at room temperature, although no CDW-normal phase transitions have been observed.

In conclusion, the XPS valence band spectra of TiS_3, NbS_3, and TaS_3 have been obtained. The band structures at the Fermi level correspond well to the facts that TiS_3 and NbS_3 are semiconducting and TaS_3 is metallic. Through the appearance of a shoulder at the top of the valence band of NbS_3 and TaS_3, we have shown that the metal d_{z^2} bands of NbS_3 and TaS_3 are fully and partly occupied, respectively, and that of TiS_3 is empty. Such a band model explains well the metallic nature of TaS_3 and the semiconducting nature of TiS_3. In particular, the semiconducting nature of NbS_3 was interpreted in terms of the metal d_{z^2}

band separation resulting from doubling of the *b* axis.

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