X-Ray Band Spectra and Electronic Structure of TiS_2

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An electronic structure, in terms of molecular orbitals, is suggested for the layered compound TiS_2. This structure is based on the combined TiL_{III}, TiK, S$L_{II,III}$, and SK x-ray-emission and -absorption band spectra. The x-ray data appear to be compatible with the optical reflectivity spectrum but at odds with theoretical estimates of the band structure. Although the results are empirically conjectural they are used to suggest that TiS_2 is a metal or semimetal instead of a small-gap semiconductor.

INTRODUCTION

Recently, considerable attention has been directed to the layered dichalcogenides of the groups-IV*B* and -V*B* transition elements.[1-3] It has been found that in many of these compounds organic molecules can be intercalated into the van der Waals gap between the dichalcogenide layers. The resulting complexes are often highly anisotropic superconductors. Titanium disulfide, TiS_2, is one of the dichalcogenides which has been successfully intercalated.[2] There is, however, no real understanding of the bonding mechanism between the intercalate and the chalcogenide layer and hence of the resulting properties. In order to understand the bonding in the intercalation complexes, it is first necessary to have knowledge of the electronic structure of the pure dichalcogenides themselves.

Traditionally, energy-band theory has been used in the determination and discussion of the electronic structure of solids such as TiS_2. This paper, however, takes a different approach, using a molecular-orbital (MO) bonding model. The reason for going the MO route is centered primarily on the experimental x-ray band spectra. Binary transition-metal compounds yield band spectra which can be rather complicated and show large chemical effects. It is difficult to account for these strong but varied chemical effects using conventional band theory, but some recent papers by the present author have shown that a MO model can be very effective in interpreting the results.[4-6] Some physicists intuitively resist the application of MO theory to solids, but this author feels that such an approach is fundamentally sound because it recognizes the important role played by short-range order parameters (e.g., bonding distances, coordination symmetry, valence states, etc.) in influencing the x-ray bands. Detailed studies of these relationships are reported in previous papers.[4-6] It has been shown that the x-ray band spectra can be used to empirically deduce the complete molecular-orbital arrangement of binary transition-metal compounds. That same technique is used in this paper to deduce the electronic structure of TiS_2. The resultant x-ray MO energy-level diagram is rather conjectural and highly empirical and yet it is quite compatible with the reflectivity spectrum and recent Hall-mobility and Seebeck-coefficient measurements.

II. EXPERIMENTAL

The titanium L_{III}, sulfur $L_{II,III}$, and sulfur K band spectra were obtained on the same single-plane-crystal vacuum spectrometer used in previous work.[4,5] Dispersing crystals for the three spectral series were clinochlore, lead stearate, and NaCl, respectively. The spectra were produced by direct electron-beam bombardment of the specimens. The detector was a flow-proportional counter using a Formvar window (3000–4000 Å thickness) and argon-methane (P-10) flow gas at a reduced pressure of 120 Torr. The source-chamber vacuum was about 1×10^{-6} Torr. A Hitachi x-ray microprobe with curved-crystal optics and a LiF crystal was used for obtaining the TiK band.

Data points were accumulated both by continuous scanning on a strip-chart recorder and by step-scanning on a Teletype paper-punch tape. This tape was run through a computer which yielded a plot of smoothed normalized intensity versus energy position. The mean deviation of the resultant curves is no more than ± 2%. Energy positions of the intensity maxima have a probable error of ±0.2 eV. None of the spectra were corrected for the instrumental "window" or other broadening effects. This is not considered to have any significant influence on the spectral interpretations which are offered.

After obtaining the smoothed spectra, they were unfolded into their constituent components by means of the DuPont model 310 curve resolver.[4,5] Before unfolding the TiL_{III} emission band, however, everything on the high-energy side of the L_{III} edge was subtracted. This procedure removes the high-energy satellites and L_{II} band tailing, and

what remains is assumed to be the "true" L_{III} band.[5] All of the spectra unfold into Gaussian components.

Target specimens of TiS_2 used to obtain the emission-band spectra were highly pure single crystals, kindly supplied by Dr. A. H. Thompson of Esso Research and Engineering Co., Linden, N. J. Very thin platelets were cleaved from the crystals and mounted directly on the anode.

The titanium L_{III} and sulfur $L_{II,III}$ absorption spectra are self-absorption replicas.[7] The sulfur K absorption is the usual photon absorption spectrum using the continuum from a platinum target passed through a very thinly cleaved platelet of TiS_2.

III. RESULTS AND DISCUSSION

In interpreting the x-ray band spectra from TiS_2, a MO bonding model is invoked in exactly the same manner as was done previously for other transition-metal compounds.[4-6] TiS_2 crystallizes in the CdI_2 layered structure[8] so that the titanium ions are in a regular octahedral coordination to the sulfur ions. Assuming that the Ti $3d$, $4s$, and $4p$ atomic orbitals and the sulfur $3s$ and $3p$ atomic orbitals are all involved in the bonding, one can construct a schematic energy-level diagram showing the resultant bonding, antibonding, and nonbonding molecular orbitals such as shown in Fig. 1. A theoretical treatment of the construction of such an atom-MO-atom diagram can be found in books such as those by Cotton[9] or Ballhausen and Gray.[10] The ordering of the molecular orbitals in Fig. 1 are shown only for schematic purposes and are not necessarily correct. This ordering will depend to some extent on the values of the parameters chosen for the initial calculation. One purpose of this paper is to suggest a method of using the x-ray band spectra to deduce the correct ordering and relative energy positions of each of the occupied and vacant orbitals within about 25 eV of the Fermi energy E_F. It is of particular interest to determine the symmetry character of the electronic states in the immediate vicinity of E_F and also their energy range because these states are primarily responsible for the electronic properties of TiS_2 as will be discussed shortly.

One of the points emphasized in previous papers[4-6] is that for transition-metal compounds there is no one single band spectrum which contains sufficient information to deduce the complete electronic structure. This is due to the dipole selection rules governing x-ray transitions. Since the various molecular orbitals are derived from the atomic orbitals, they consist of admixed s-, p-, and d-wave symmetries. According to the selection rules, the TiL_{III} band from TiS_2 will reflect the distribution of primarily the Ti $3d$ states and somewhat of the Ti $4s$ states but will tell us little about the Ti $4p$, S $3s$, or S $3p$ states. Obviously, if we expect to obtain sufficient information to deduce the complete MO arrangement for TiS_2, we will need more than just the L_{III} band. In fact, four spectral series are required: TiL_{III} ($3d$ $4s$ $\rightarrow 2p^{3/2}$), TiK ($4p \rightarrow 1s$), S$L_{II,III}$ ($3s \rightarrow 2p$), and SK ($3p \rightarrow 1s$) bands. Furthermore, since both occupied and vacant states are of interest, we will need both the emission and absorption bands. The method of relating these various x-ray spectra to each other and to the MO arrangement is illustrated in Fig. 2.

The spectra of Fig. 2 are all combined on a common energy scale with the zero of energy placed at E_F, which is coincident with the L_{III} absorption edge. Actually, E_F is chosen to be midway between the emission and absorption edges in transition-metal L_{III} spectra,[5] but in TiS_2 the two edges appear to coincide so that this point of coincidence is also the position of E_F. This is a handy reference point because the absorption edge, being at half-maximum intensity between the onset of absorption and the first absorption peak, can be determined quite accurately.

Alignment of the spectra in Fig. 2 was accomplished by assuming that the first two absorption maxima in each series arise from the same two lowest vacant orbitals. Peaks b and c were therefore positioned directly in line in all the spectra. The TiK emission band was obtained under conditions of high self-absorption, so that the first two absorption maxima are mirrored in the high-energy band tail. Lining up the spectra on these absorption peaks is not necessarily the most accurate method to use, but experience gained from the study of many other transition-metal compounds indicates that it is probably a reliable technique.[4-6] Preferably, one should use a combination of x-ray lines and core-level photoelectron spectra from which the position of E_F on each of the emission bands can be determined.[6] The bands would then be lined up at the E_F point. Most of the necessary photoelectron data is not available for TiS_2, however.

Another point to consider is that in aligning the spectra as in Fig. 2 it must be assumed that the various ionized states giving rise to the x-ray bands do not differ very much in energy relative to the ground state. In other words, the valence-electron energies are not significantly affected, regardless of the core level in which the vacancy is produced (Koopmans's theorem). This is an argumentative point, but it appeared to be a good approximation in other transition-metal compounds,[4-6] and so it will be assumed to be an equally good approximation in TiS_2.

Once the x-ray bands are properly aligned, the

next step is to assign each component as being due to an electron transition between a specific MO and core level, as indicated schematically in Fig. 1 for the L_{III} components. The method is empirical and conjectural and depends heavily on the dipole selection rules.[4,5] It is assumed that the TiL_{III} band arises only from orbitals having partial 3*d* or 4*s* symmetry; the TiK band, from orbitals having partial 4*p* symmetry; the S*L* band, from orbitals having 3*s* symmetry; and the S*K* band, from orbitals having partial 3*p* symmetry. Each of the assignments is discussed in more detail in previous reports[4,5] for other compounds, and they apply in the same manner to the TiS_2 spectra. All of the assignments are summarized in Table I. Also included in this table are the absolute and relative energy positions of each of the spectral components. As can be seen in Fig. 2, every one of the expected molecular orbitals can be accounted for in a rather appealing manner. In the TiL_{III} emission-band peak *C* is seen to arise from an orbital derived from the sulfur 3*s* states. Peaks *G*, *A*, and *F* arise from orbitals localized primarily on the sulfur ions and result from the interaction of S 3*p* states with Ti 3*d* and 4*s* states. Absorption peaks *b* and *c* arise from orbitals localized primarily on the titanium ions and consist of mostly 3*d* states with some admix-

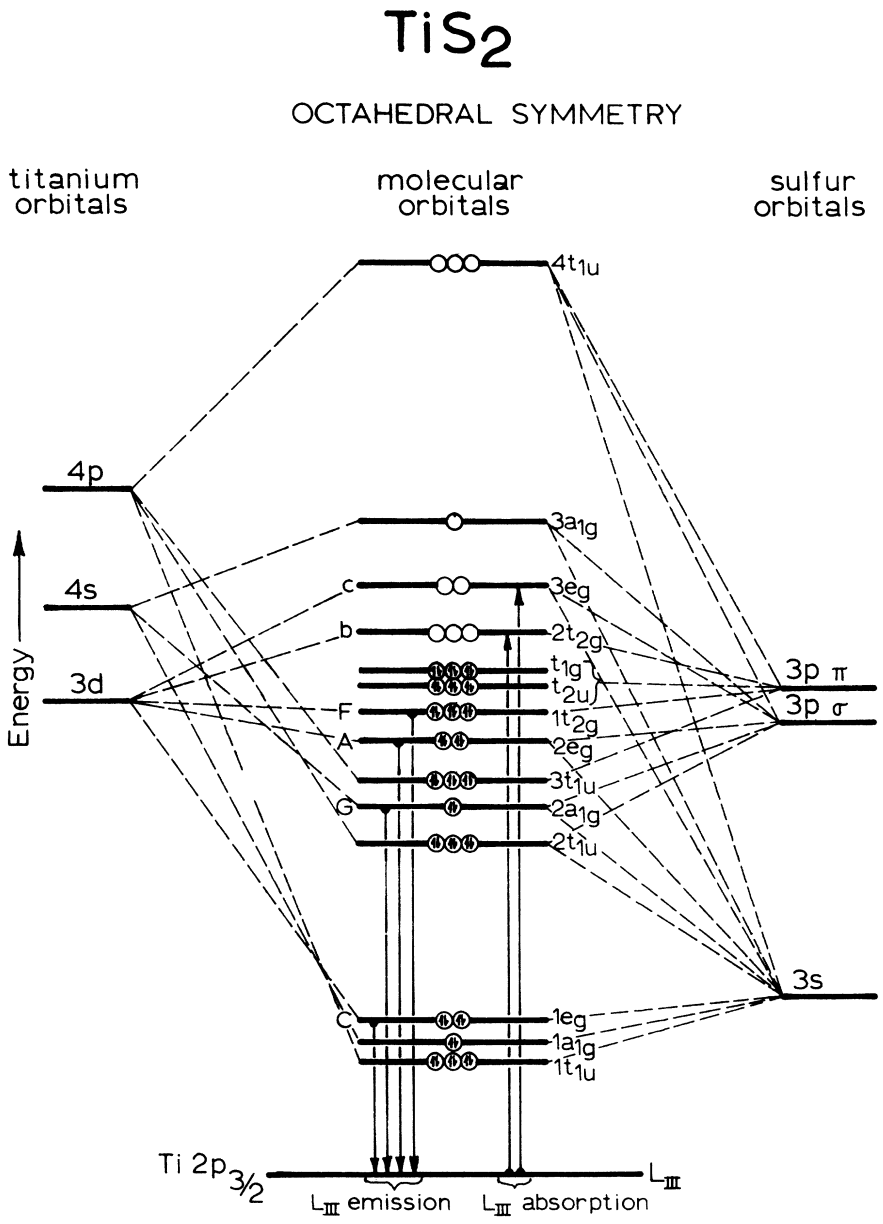

FIG. 1. Schematic atom-MO-atom energy-level diagram for titanium octahedrally coordinated to sulfur. Not drawn to scale.

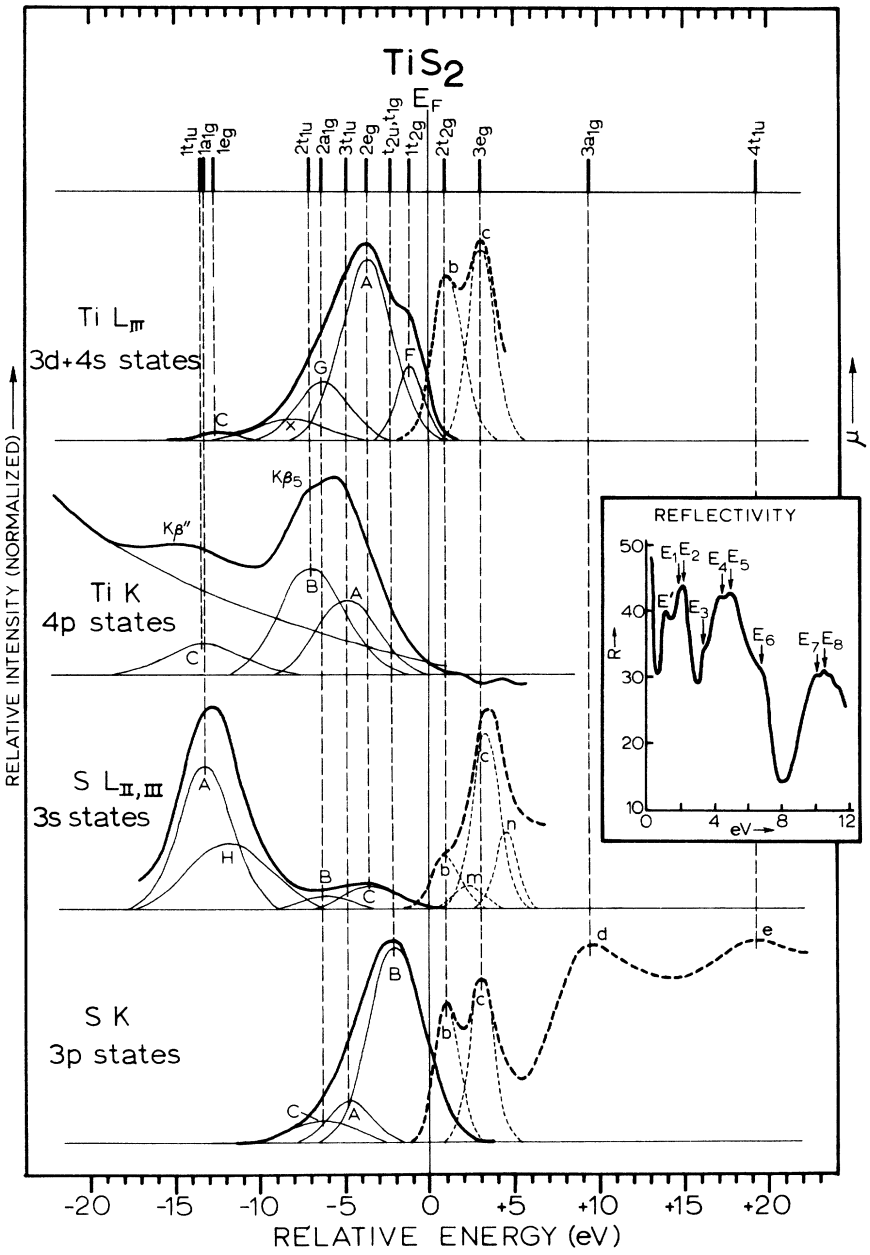

FIG. 2. Empirical deduction of MO structure of TiS_2 from combined x-ray band spectra. Solid line curves are emission bands; dashed curves are absorption bands. Inset at right shows reflectivity spectrum of Greenaway and Nitsche (Ref. 8).

ture of 3*p*, 4*p*, and even 3*s* states. The sulfur *K* band is due mainly to the 3*p* nonbonding states, but there is also some contribution from bonding orbitals derived from the 3*p* states. As seen in the sulfur $L_{II,III}$ band, the main concentration of 3*s* states is at −13.3 eV which is about 11 eV below the 3*p* nonbonding states. Bonding orbitals which consist of admixed cation-anion states are seen to contribute to the spectra of both, as would be expected.

This empirically deduced MO energy-level diagram for TiS_2 is rather conjectural, but let us assume for the sake of argument that it is reasonably correct. How then would it relate to other types of experimental data, specifically the optical reflectivity? The reflectivity spectrum measured by Greenaway and Nitsche is shown in the inset on the right-hand side of Fig. 2. Reflectivity peaks are commonly believed to represent interband transitions and possibly some structure due to exciton effects. An attempt was therefore made to empirically match each of the reflectivity peaks to the x-ray MO diagram. The results are summarized in Table II. Considering the fact that the probable error in determining the position of the x-ray components is ±0.1 eV, all of the re-

TABLE I. Energy positions and transition assignments for x-ray band components in TiS_2.

Spectrum	Component	Energy (eV)	λ (Å)	Relative position (eV)[a]	Assignment
TiL_{III}	*C*	442.0	28.05	−12.6	$1e_g \rightarrow 2p_{3/2}$
	X	446.4	27.77	···	Extended tailing effect
	G	448.3	27.66	−6.3	$2a_{1g} \rightarrow 2p_{3/2}$
	A	451.0	27.49	−3.6	$2e_g \rightarrow 2p_{3/2}$
	F	453.5	27.34	−1.1	$1t_{2g} \rightarrow 2p_{3/2}$
	b	455.6	27.21	+1.0	$2p_{3/2} \rightarrow 2t_{2g}$
	c	457.7	27.09	+3.1	$2p_{3/2} \rightarrow 3e_g$
Ti*K*	*C*	4955.6	2.502	−13.4	$1t_{1u} \rightarrow 1s$
	B	4962.0	2.499	−7.0	$2t_{1u} \rightarrow 1s$
	A	4964.2	2.497	−4.8	$3t_{1u} \rightarrow 1s$
S$L_{II,III}$	*A*	146.3	84.74	−13.3	$1a_{1g} \rightarrow 2p_{3/2}$
	H	147.5	84.05	−12.1	$1a_{1g} \rightarrow 2p_{1/2}$
	B	153.4	80.82	−6.2	$2a_{1g} \rightarrow 2p_{3/2}$
	C	156.0	79.47	−3.6	$2e_g \rightarrow 2p_{3/2}$
	b	160.5	77.25	+1.0	$2p_{3/2} \rightarrow 2t_{2g}$
	m	161.8	76.63	+2.3	$2p_{1/2} \rightarrow 2t_{2g}$
	c	162.7	76.20	+3.2	$2p_{3/2} \rightarrow 3e_g$
	n	164.0	75.60	+4.5	$2p_{1/2} \rightarrow 3e_g$
S*K*	*C*	2461.7	5.036	−6.3	$2a_{1g} \rightarrow 1s$
	A	2463.2	5.033	−4.8	$3t_{1u} \rightarrow 1s$
	B	2465.8	5.028	−2.2	$t_{2u}, t_{1g} \rightarrow 1s$
	b	2469.0	5.021	+1.0	$1s \rightarrow 2t_{2g}$
	c	2471.1	5.017	+3.1	$1s \rightarrow 3e_g$
	d	2477.5	5.004	+9.5	$1s \rightarrow 3a_{1g}$
	e	2487.4	4.984	+19.4	$1s \rightarrow 4t_{1u}$

[a]Measured relative to E_F, the arbitrary zero-energy point.

flectivity peaks can be matched up nicely with transitions between the uppermost occupied MO's and lowermost vacant MO's. Intuitively, one might tend to suspect that such a matchup is more fortuitous than significant because the x-ray state (core-level hole) is widely believed to distort the atom or molecule in such a way the the x-ray energy-level diagram would not be compatible with the reflectivity spectra. Previous results for some binary transition-metal compounds,[4-6] however, seem to indicate that the x-ray MO diagram is indeed compatible with the reflectivity spectra, optical-absorption spectra, ultraviolet-photoemission spectra and theoretical band-structure calculations. It is tempting to ascribe these spectral matchups to something more

TABLE II. Transition assignments for reflectivity spectrum[a] of TiS_2 on basis of x-ray energy-level diagram in Fig. 2.

Peak	eV	Assignment	
E'	1.2	$1t_{2g} \rightarrow E_F$	(1.1 eV)
E_1	2.0	$1t_{2g} \rightarrow 2t_{2g}$	(2.1 eV)
E_2	2.2	$t_{1g}, t_{2u} \rightarrow E_F$	(2.2 eV)
E_3	3.4	$t_{1g}, t_{2u} \rightarrow 2t_{2g}$	(3.2 eV)
E_4	4.5	$2e_g \rightarrow 2t_{2g}$	(4.6 eV)
E_5	5.0	$t_{1g}, t_{2u} \rightarrow 3e_g$	(5.3 eV)
E_6	6.8	$2e_g \rightarrow 3e_g$	(6.7 eV)
E_7	10.1	$2t_{1u} \rightarrow 3e_g$	(10.1 eV)
E_8	10.5	$1t_{2g} \rightarrow 3a_{1g}$	(10.7 eV)

[a]Greenaway and Nitsche (Ref. 8).

than coincidence. In the case of TiS_2, for example, the reflectivity assignments listed in Table II show that an appealing interpretation can now be given to the lowest-energy reflectivity peak labeled E'. Greenaway and Nitsche[8] do not even label this peak in their paper nor do they include it in their correlations. They mention only that it is possible that this peak corresponds to the optical gap. From the x-ray data, however, this peak can be interpreted as being due to an electron jump from the highest energy maximum in the occupied density of states ($1t_{2g}$) to the lower-most vacant state represented by the L_{III} absorption edge and coincident with E_F. It must be borne in mind that the individual MO's are not sharp, isolated energy states as indicated schematically in Fig. 2. Almost certainly there is strong interaction between neighboring octahedra for both sulfur and titanium ions in the plane of the dichalcogenide layers. Various solid-state effects will cause the MO's to broaden and overlap to some extent, forming energy bands. An orbital such as $2t_{2g}$ would therefore have its maximum density at the position indicated in Fig. 2 but may actually extend down to E_F, having a half-width on the order of 1.5 to 2 eV. So a transition assignment of $1t_{2g} - E_F$ as given in Table II for E' does not seem unreasonable. This assignment and the appearance of the x-ray spectra in the vicinity of E_F tend to suggest that the top of the occupied states and the bottom of the vacant states are coincident, or nearly so. If this is true, then TiS_2 would appear to be a metal or semimetal, which is in disagreement with the long-standing notion that TiS_2 is a degenerate semiconductor with a band gap of about 0.9 eV.[8,11] Let us now consider this point in a little more detail.

Greenaway and Nitsche[8] have, on the basis of optical reflectivity spectra, suggested a band gap of 0.9 eV for TiS_2. Some energy bands sketched out by Wilson and Yoffe are based on optical data and also show a band gap of about 1 eV.[11] Quite recently, Murray, Bromley, and Yoffe,[12] using a semiempirical tight-binding method, have calculated the band structure of TiS_2 again showing a band gap of about 1 eV. Phillips,[13] in his discussion of bridge and layered compounds, uses a similar band model. The x-ray results do not appear to agree with this picture of the band structure. From Fig. 2 it is seen that the highest occupied orbital is $1t_{2g}$ and the lowest vacant orbital is $2t_{2g}$. These are the bonding-antibonding pair associated with the $3d$-$3p$ π bond. Ideally, since TiS_2 is octahedral and has a d^0 configuration, one would expect all the bonding orbitals to be exactly filled and all the antibonding orbitals to be completely empty. If there is a true gap in the density of states between the bonding and antibonding states, it should be visible as an energy separation between the TiL_{III} emission and absorption edges. The absorption edge can be accurately determined, but the emission edge can only be approximated indirectly from the self-absorption effect because the true edge is masked by the L_{III} satellites.[5,7] From the unfolded spectra, however, even after correction for the instrumental window and core-level widths, a band gap of 0.9 eV seems much too large. We could speculate that if a gap exists it is probably no more than about 0.1 eV or so, which is about the limit of error in the x-ray measurements. The x-ray band spectra seem to suggest, therefore, that TiS_2 is a metal or semimetal. Some very recent measurements of the Hall mobility and Seebeck coefficient by Thompson *et al.*,[14] on highly stoichiometric single crystals (the same as used in this x-ray study) of TiS_2 are also best explained on the basis of it being a metal or semimetal. Furthermore, Greenaway and Nitsche's reflectivity spectrum[8] shows, in the very low-energy range, considerable free-carrier absorption which is characteristic of a metal. Finally, the lowest-energy reflectivity peak, E', can be interpreted in a straightforward manner by assuming that the band gap is quite small ($\sim$0.1 eV) or nonexistent (see Table II).

Murray *et al.*[12] and Phillips[13] explain any conducting behavior in TiS_2 as being due to the nonstoichiometric nature of the materials, that is, an excess of Ti atoms (called supernumerary or bridge atoms by Phillips[13]). The crystals used by Thompson *et al.*[14] (and by the present author), however, appear to be quite pure and stoichiometric and so it is doubtful whether their apparent conductivity can be explained on this basis.[14] Also, any excess Ti atoms in the structure would be expected to show up as a peak in the density of states at the Fermi energy,[13] and the x-ray data show no evidence of a peak at this position.

IV. SUMMARY AND CONCLUSIONS

An electronic structure of TiS_2 has been suggested in terms of molecular orbitals which can be empirically and conjecturally constructed from the combined TiL_{III}, TiK, $SL_{II,III}$, and SK x-ray band spectra. All of the occupied and vacant orbitals within about 25 eV of E_F are placed on a relative energy scale. This same energy-level diagram is seen to be compatible with the reflectivity spectrum.

Although somewhat conjectural, the results indicate that all of the orbitals between E_F and -7 eV are fully occupied and are derived from the sulfur $3p$ states. These include the S $3p$ nonbonding "lone pairs" at -2.2 eV and the bonding orbitals associated with the $3p$-$3d$ π bond ($1t_{2g}$), the $3p$-$3d$ σ bond ($2e_g$), the $3p$-$4p$ bond ($2t_{1u}$), and the

$3p$-$4s$ bond ($2a_{1_g}$). The two lowest vacant states are antibonding orbitals localized primarily on the titanium ion and derived from Ti $3d$ states. This is at odds with the results of Murray *et al.*[12] and Phillips.[13] The S 3s states are also involved in bonding with the Ti $3d$, $4s$, and $4p$ states giving rise to the MO's at about – 13 eV.

It was speculated that if there is a band gap in TiS_2 it is probably much smaller than the 0.9 eV suggested elsewhere.[8,11,12,13] By using the x-ray data in conjunction with the reflectivity spectra[8] and the Hall-effect and Seebeck-coefficient measurements[14] it can be conjectured that TiS_2 is a metal or semimetal.

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