Angle-resolved photoemission studies of the band structure of TiSe₂ and TiS₂

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The electronic structure of high-quality TiSe₂ and TiS₂ crystals has been investigated using angle-resolved photoemission with He₁, He₁, and Ne₁ resonance radiation. Results compare well with recent self-consistent energy-band calculations although differences occur which may be due to the three- rather than two-dimensional nature of specific bands. Occupied d states at the zone edge are observed in both materials. A small overlap with the s/p valence band at Γ is observed in the case of TiSe₂ in approximate agreement with other workers. TiS₂ appears to be a defect semiconductor with a band gap of 0.3 ± 0.2 eV.

I. INTRODUCTION

The group IV transition metal dichalcogenides crystallize in a 1-T layer structure in which the transition metal is octahedrally coordinated by six chalcogen atoms. Among these compounds TiSe₂ and TiS₂ have received much recent attention. Titanium diselenide forms a very interesting $2a_0 \times 2c_0$ superlattice below 200 K, reminiscent of the charge-density-wave (CDW) transitions which form in the group Vb compounds. Recent angleresolved photoemission results^{1,2} indicate that TiSe₂ is a semimetal with small indirect (Γ to L) band overlap. It has been suggested that the CDW transition is driven by an electron-hole coupling mechanism,^{3,4} although other mechanisms have also been proposed.⁵⁻⁷

The electronic structure of TiS₂, on the other hand, is less clear. The resistivity of TiS₂ shows an interesting T^2 dependence over a wide temperature range (4 to 400 K).⁸ Kukkonen and Maldague⁹ have suggested that this T^2 dependence may arise from strong electron-hole scattering. In contrast to TiSe, no superlattice has been reported in TiS_2 , although a subtle feature in the resistivity at 130 K has been reported.⁸ Since sulfur is more electronegative than selenium, it is expected that the band overlap in TiS, would be smaller or even nonexistent, in which case the conductivity is due to a fairly high concentration of electrons ($\sim 10^{20}$ cm⁻³) deriving from defects. Wilson¹⁰ has taken this point of view citing the early work of Takeuchi and Katsuda¹¹ and also the possibility of homopolar optical phonon scattering.

The current view of TiS_2 is then that of a small band-gap semiconductor but with highly unusual electronic properties. Its temperature-dependent electrical resistivity, like that of a metal, approximately fits a simple power law over several decades of temperature. As cited above, numerous attempts have been made to explain the resistivity as associated with carrier-carrier or polar phonon scattering. All of these attempts have been unsuccessful in predicting *both* the temperature dependence and the magnitude of the electrical resistivity. The calculations underestimate the resistivity so that an enhancement of the carrier scattering cross section appears necessary.

Recent measurement of the pressure dependence of the Hall coefficient of TiS_2 suggests that the metallic conductivity does not arise from p/d band overlap but rather from partial band occupation, possibly due to defects such as excess Ti.¹² Thus, the pressure measurements give very strong support for the extrinsic semiconductor model of TiS₂.

Band-structure calculations of TiS_2 produce conflicting results. A recent review has been written by Calais.¹³ Values of the p/d indirect band overlap range from 0.2 to 1.5 eV. The most recent band calculation¹⁴ using a localized atomic orbital approach yields an indirect gap of about 0.8 eV. It is known that the magnitude of such p/d indirect gaps is very difficult to calculate with high accuracy. Angle-resolved photoemission spectroscopy, which has been shown to be a very powerful tool for mapping the energy *versus* wave vector relation, would therefore be very useful in resolving electronic structure such as band overlaps.

In this paper, we report angle-resolved photoemission studies of the electronic structure of TiSe₂ and TiS₂ using HeI (21.22 eV), HeII (40.81 eV) and NeI (16.85 eV) resonance radiation. Previous angle-resolved photoemission measurements^{1,2} of TiSe₂ showed the existence of electron states derived from the Ti 3d band at L(M), however, there were questions about the states at Γ

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derived from Se 3p band and the amount of overlap with the Ti *d* band. If electron-hole coupling is the driving force for CDW transitions in TiSe₂, the existence of hole-like states at Γ is essential. Our data here clearly indicate the existence of such holelike states near Γ in TiSe₂ but no such features in the case of TiS₂. On the other hand, electronlike states are observed near the zone boundary in both cases. Implications of our data in connection with the magnitude of the p/d indirect band gap will be discussed. Experimental details are given in Sec. II. Results and discussion for TiSe₂ and TiS₂ are presented in Sec. III and Sec. IV, respectively.

II. EXPERIMENTAL DETAILS

Figure 1 shows in outline a top view of the ultrahigh-vacuum chamber used in the photoemission experiments. A differentially pumped windowless discharge lamp¹⁵ was used in this study for the various rare gas lines. The main chamber can be evacuated to 1×10^{-10} torr when the gas supply to the lamp is turned off and to a pressure of $\sim 4 \times 10^{-10}$ torr when the lamp is running. The pressure in the differentially pumped region of the lamp is in the range of 10^{-5} torr. Such a highpressure gradient is achieved by a 12-in. long glass capillary of 0.5-mm diameter. The spot size of the light at the specimen is estimated to be ≤ 1 mm. The lamp is run by a high-voltage dc power supply capable of delivering 400 mA at 4 kV.

A hemispherical electrostatic electron energy analyzer¹⁶ with mean radius 25 mm is used to measure the energy distribution curves (EDC) of the photoelectrons. Variation of polar angle θ is achieved by mounting the electron energy analyzer on a turntable controlled by a rotary motion feedthrough. Polar angles between 18° and 85° can be



FIG. 1. Physical layout of the angle-resolved photoemission system.

obtained. The energy and polar angle resolution is about 0.2 eV and 2° , respectively. The main body of the energy analyzer is constructed of aluminum, and the hemispherical surface of the analyzer is coated with graphite before assembly to reduce secondary electron emission.

Two Varian VUV-8900 microchannel plates in "chevron" configuration are used as a detector to give a current gain greater than 10⁷. The detector is enclosed in a holder of Macor ceramic to keep out stray ultraviolet light, electrons, and ions. We also find that it is necessary to shield the entrance to the ion pump. A Canberra multichannel analyzer operating in the multichannel scaling mode is used to obtain EDC's with the sweep generator of the multichannel analyzer used to ramp the hemisphere analyzer. The signal-to-noise ratio of the distribution curves is improved by repeated scans. Typical data integration times range from 10 to 33 min.

The ambient magnetic field in the vicinity of the specimen and energy analyzer is cancelled to within 20 mG of zero by means of magnetic shielding and Helmholtz coils. The workfunction of the spectrometer could be determined by reference to a standard sample. It was also possible to locate the Fermi level from details in the energy distribution curves in some cases.

The TiSe, crystals were grown by iodine vapor transport¹⁷ at as low a temperature as possible in order to favor high stoichiometry. The transition temperature for the crystals used was close to 200 K. In the case of TiS, the crystals were sublimation grown in a gradient between temperatures of 750 and 630 $^{\circ}\text{C}$ with an excess of sulfur present as a transport agent. The samples were mounted on a precision manipulator and cleaved by pulling the layers apart in a 10^{-10} torr vacuum. By these means fresh clean surfaces could be readily obtained. The angle of incidence of the light on the sample was varied by tilting the sample through a flip mechanism provided by the manipulator. Most data was taken with the light at normal incidence (s polarization), but due to the geometrical arangement EDC's below $\theta = 18^{\circ}$ could only be obtained at non-normal incidence (mixed s and ppolarization). The azimuthal dependence (angular resolution $\Delta \phi \sim 3^{\circ}$) of an EDC was obtained by rotating the sample about an axis normal to its surface.

III. RESULTS AND DISCUSSION

A. Titanium diselenide TiSe₂

The direction in the Brillouin zone for $TiSe_2$ of main interest lies in the plane ΓALM , where a small indirect overlap occurs between a Se based

s/p band (near Γ) and a Ti d-band (near L). Figure 2 shows the dependence of the energy distribution curves on polar angle θ with 21.22 eV (HeI) light incident normal to the sample surface. The azimuthal angle was chosen such that the plane of emission coincided with the plane ΓALM . The variation of the EDC's and the evolution of additional new peaks as θ changes are quite dramatic. The two large peaks at $\theta = 20^{\circ}$ and $\theta = 25^{\circ}$ are due to emission from s/p valence bands approximately 3 and 5 eV below the Fermi level. The small shoulder or peak occurring near the Fermi energy (zero eV) arises from the Ti d-band emission and is observed most strongly near the zone boundary (L or M) for angles θ in the range $25^{\circ}-30^{\circ}$. The intensity of this peak is very sensitive to azimuthal angle θ . As θ increases to larger values, the d-band emission disappears completely and the EDC's are dominated by emission apparently derived from Se s/p bands.

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At this point, we would like to draw special attention to the uppermost s/p band which moves toward the Fermi level (E_F) as θ increases. Note that for $\theta > 30^\circ$, the wave vector associated with the *p* state lies in the second zone. Therefore, we are looking at changes of energy bands from



FIG. 2. Angular dependence of EDC's along Γ AML of TiSe₂ for using He^I line at normal incidence.

 $\Gamma(A)$ to M(L) in the first zone, and from M(L) to $\Gamma(A)$ in the second zone. The EDC taken at $\theta = 43^{\circ}$ shows a discontinuity in slope of the uppermost band near the Fermi level. As θ increases, the peak of the band moves closer and closer to E_F . At $\theta = 55^{\circ}$, this peak is ready to cross E_F , and a sudden drop of intensity occurs. At $\theta = 60^{\circ}$ and above, little or no emission from the uppermost p states is observed. We believe that this is strong experimental evidence for the existence of holelike states near the zone center. These features of the uppermost p band were not observed in previous angle-resolved photoemission experiments.^{1,2}

For $\theta \gtrsim 40^{\circ}$, a rather broad band centered around 7 eV below E_F starts to grow and dominates the spectra at larger angles. Recent band-structure calculations show a large gap in the range -6--12 eV indicating that no initial states exist in this energy region. We feel that this broad peak is most likely due to the emission of secondary electrons. We also notice that the low energy tails of the EDC's at smaller angles in Fig. 2 show very little background due to secondary electrons. This small background at low energies may be in part due to the characteristics of our analyzer: however, it is not simply due to a magnetic cutoff. Residual magnetic fields were only ~20 mG. Furthermore, under some circumstances, we have been able to detect photoelectrons with kinetic energy about 1 or 2 eV. We feel that the quality of a surface following cleavage, e.g., flatness and smoothness, is a very important factor in determining the background intensity of energy distribution curves.

As we mentioned earlier, in order to obtain EDC's for $\theta < 18^{\circ}$ we have to resort to oblique incidence of light. At non-normal incidence, one has a different transition matrix element compared to normal incidence. At normal incidence the incident light beam is s-polarized. At oblique incidence the light has both s and p components of polarization, consequently different symmetry selection rules apply. Figure 3 shows a sequence of EDC's for $\theta \leq 25^{\circ}$ taken with HeI radiation using light incident at an angle 20° to the specimen surface normal. Comparing Fig. 3 with the EDC for $\theta = 25^{\circ}$, in Fig. 2 one finds that there is not much change in line-shape and peak positions for light at oblique incidence. The Ti-derived d-band emission is again observed near the zone boundary in the $\theta = 25^{\circ}$ curve. A small band is observed for angles less than 15°. In some respects the appearance of these peaks near Γ resemble the emission from electronlike d states at larger angle: however, they do not change sensitively with angle ϕ . Similar behavior was found in TiS₂. They are



FIG. 3. Angular dependence of EDC's along Γ AML of TiSe₂ by using HeI line at an angle of incidence $\alpha = 20^{\circ}$.

due to excitation of lower-lying initial states by a 23.1 eV satellite of the HeIline. Such effects can be sorted out by employing other resonance lines or by using a monochromator.

The energetics of angle resolved photoemission are such that EDC's of the type shown in Figs. 2 and 3 can be analyzed to give energy versus wave vector for initial electron states within the crystal. Two conservation relations govern the direct photoemission process: (1) $E_f(k_{\parallel}) - E_i(k_{\parallel}) = \hbar \omega$ where E_f and E_i are the final and the initial electron energies and $\hbar \omega$ is the incident photon energy; (2) conservation of the parallel component of electron momentum upon transmission through the surface $k'_{\parallel} = k_{\parallel}$. The kinetic energy of the photoemitted electron is given by a free-electron dependence upon k', i.e., $E = \hbar^2 k'^2 / 2m$. From peaks in the EDC's measured at a given angle θ it is possible to evaluate the projected component of momentum using

$$k_{\parallel} = (2mE/\hbar^2)^{1/2} \sin\theta \,. \tag{1}$$

Values of initial energy E_i can be determined as a function of k_{\parallel} for the various occupied bands by simply following the peaks in the EDC's as a function of θ . The validity of this procedure has been well demonstrated, especially for the layered compounds by Smith and Traum.¹⁸ Of course, a projected two-dimensional representation of band structure is obtained, but this is perhaps appropriate for layered crystals. A different analysis and knowledge of the final states is required in the case of three dimensions.

Experimental energy bands along $\Gamma(A)$ to M(L)are shown for $TiSe_2$ in Fig. 4(a). Here each point corresponds to a peak in an EDC taken at a given angle θ for HeI resonance radiation $\hbar \omega = 21.22$ eV. The solid and dashed lines are the theoretical energy bands calculated by Zunger and Freeman¹⁹ along A to L and Γ to M, respectively. The experimental results are presented in the reduced zone scheme; data points occurring in the second zone have been reduced to the first zone. The data points represented by closed circles are second zone data which have been folded back into the first zone. The triangles represent data points obtained for light as oblique incidence. Note that points are obtained around -2 eV toward the zone center. These probably originate from a band at this energy along Δ to Q calculated in Ref. 19 but not shown in Fig. 4.

In addition to observations along the ΓALM plane, we have also carried out measurements in the $\Gamma AL'M'$ plane (rotated 60° from the ΓALM plane). Although points within the zone on these two planes are not equivalent for the 1T-layer compounds, the points M and M', L and L' are equivalent. Furthermore, contours on the zone surface are mirrored in the ΓAHK plane, therefore differences in the electronic structure between the primed and unprimed directions are believed to be small. They are certainly zero in a two-dimensional approximation. Our data on peak positions indicates that the energy bands along ΓALM and $\Gamma AL'M'$ are very similar. On the other hand, photoemission intensities can be very different between these two directions.

The evolution of a new peak and gradual disappearance of an old peak is a very interesting phenomena in angle-resolved photoemission spectroscopy. Although significant theoretical progress has been made, the phenomenon is still under investigation. In the photon energy range used here, the final-state effects are expected to be important. To explore such final-state effects and to sort out possible satellite peaks, we have extended our measurements by using the He II resonance line at 40.81 eV and Net line at 16.84 eV.

Figure 5 shows a set of EDC's obtained using HeII resonance radiation 40.81 eV. Light is incident normal to the specimen surface in this case, and the azimuthal angle is chosen such that only photoelectrons coming from the ΓAML plane are detected by the energy analyzer. The photon flux of the HeII line is roughly one-fifth the photon flux of the HeI line. This makes the data acquisition process very time-consuming. Only data with



FIG. 4. Experimentally determined energy bands of $TiSe_2$ (a) using HeI resonance line, (b) the HeII line, and (c) NeI radiation. The triangles represent data collected at oblique incidence. Open circles represent data which have wave vector in the 1st zone. Filled circles represent data which have been folded back from the second zone in the reduced zone scheme. Solid and dashed lines represent theoretical bands along AL and TM, respectively (Ref. 19).

relatively poor statistics are obtained. As can be seen from Fig. 5, the features of p-band emission are generally reproduced as compared to He I data (see Fig. 2). Note that, due to the large momentum associated with the photoelectrons in this



FIG. 5. Angular dependence of EDC's along ΓALM of TiSe_ using He π line.

case, most peaks observed in Fig. 5 correspond to points in the second zone. We have also obtained data at oblique incidence so that peaks occurring in the first zone can be examined. We did not unambiguously pick up the Ti *d*-band states near the zone boundary in the He II data. This could be due to final-state effects, or to the poor statistics of the EDC, which might obscure the small *d*-band peak near E_F . The energy bands generated from the He II data are shown in Fig. 4(b). These energy bands agree qualitatively with the He I data shown in Fig. 4(a). Moreover, they show peaks which agree with the deep calculated bands at -12.5 eV.

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Since the 1-T layer compounds have threefold rotational symmetry, the energy bands should also exhibit threefold symmetry. This threefold symmetry is clearly demonstrated by measuring the *d*-band emission as a function of azimuthal angle ϕ .¹⁸ Figure 6 is a threefold symmetrized radial plot of the aximuthal dependence of the *d*-band peak intensity at $\theta = 20^{\circ}$. The large lobe which is confined to a narrow azimuthal angle ~15° exists along the $\Gamma M(L)$ and equivalent directions. The azimuthal angular width is determined in part by the transverse dimension of the occupied electron pocket, and the data in Fig. 6 yields a lateral dimension ~0.2 LH, in good agreement with previous measurements.² The dimensions of the occupied



FIG. 6. Azimuthal dependence of *d*-band intensity of TiSe₂. The large lobes are along $\Gamma(A)-M(L)$ directions. The filled circles represent the actual data, while the open circles are simply symmetrical projections.

electron pocket along Γ to *M* and *L* to *A* can be determined from the dependence of the EDC's on polar angle θ . The resulting span reduced to the first zone is ~0.4*LA*, slightly larger than previous results.²

Let us now turn to experimental results obtained with Ne I resonance radiation at 16.85 eV. Energy distribution curves were obtained as in the previous cases, and the experimental points are compared with theoretical energy bands in Fig. 4(c). Again we find reasonable agreement with the calculated bands of Z unger and Freeman except that emission from the uppermost d-states is weak and difficult to follow at this photon energy.

The photoemission experiment as carried out maps the bands in k-space projected into the layered plane, namely it maps the bands in two dimensions. Furthermore, the emission intensities appear to involve final-state effects so that the azimuthal patterns take on a threefold rather than sixfold rotational symmetry. This is as expected, considering the D_{3d} space group of the crystal, but no the symmetry of a projected two-dimensional band structure. Considering both experiment and theory,¹⁹ our view of the electron and hole pockets near the Fermi surface within the Brillouin zone is shown in Fig. 7. Zone boundary wave vectors that may be important in the formation of the superlattice are shown connecting occupied



FIG. 7. Schematic view of the first Brillouin zone for TiSe_2 showing the occupied electron surfaces near L and the hole surface at Γ . Two $\Gamma \rightarrow L$ spanning vectors are shown.

(electron) states near L with unoccupied (hole) states along ΓA .

B. Titanium disulfide TiS₂

As we mentioned earlier, the size of the p/d indirect band gap in TiS_2 is still uncertain, although self-consistent band calculations are now available.²⁰ Experimental efforts to understand the electronic structure of TiS, have been plagued by the tendency toward nonstoichiometry due to excess Ti and by the possible presence of defects involving the movement of a titanium atom from a filled layer to an otherwise empty layer.¹¹ Previous angle integrated photoemission experiments by Williams and Shepherd²¹ showed the existence of free carriers close to the Fermi surface-as in a semimetal or metal. However, their results may be affected by nonstoichiometry and excess Ti. Here we report the first angle-resolved photoemission experiments on sublimitation grown TiS_2 . The samples were grown at 630 °C and are believed to be stoichiometric within the resolution of chemical analysis ($\sim 0.5\%$).

As in the case of TiSe₂, the reciprocal lattice plane of most interest is the ΓALM plane. Figure 8 shows the angular variation of energy distribution curves along the ΓALM direction using HeI radiation incident normal to the sample. At $\theta = 19^{\circ}$ three peaks due to s/p-band emission are just resolved. The uppermost peak becomes well separated at larger angles. The evolution of EDC's as a function of θ is very similar to TiSe, (see Fig. 2). The broad shoulder occurring around -8 eV, we believe, is again due to secondary electron emissions. The dominant secondary electron component apparent at large angles for $TiSe_2$ does not appear in TiS_2 . This is probably due to differences of surface quality of the two samples. As can be seen in Fig. 8, the uppermost sulfur-derived p band comes close, but still stays below E_F as θ increases to 65° (close to the zone center in the second zone) as opposed to the case in TiSe₂. The small peak near E_F for θ around 30° is identified as Ti-derived *d*-band emission.



FIG. 8. Angular dependence of EDC's along ΓAML of TiS_2 using He I line at normal incidence.

The appearance of d-band emission in TiS_2 is similar to that in $TiSe_2$. Both show azimuthal variations with sharp lobes as in Fig. 6.

Energy distribution curves obtained with light incident at an angle $\alpha \sim 45^{\circ}$ to the surface normal are displayed in Fig. 9. EDC's with $\theta \ge 20^{\circ}$ agree very well with those obtained at normal incidence as shown in Fig. 8. The *d*-band peak appears to increase for light off normal incidence, indicating a polarization effect. It is noted that, below $\theta \sim 10^{\circ}$, a relatively weak fourth valence band peak appears and moves to within about 0.2 eV of E_F near the center of the zone. A second small peak occurs still closer to E_F due to the He I satellite line.

We have also made observations on TiS_2 using the NeI resonance line (16.85 eV). Results compare very closely with the HeI data. In fact, taking the difference of photon energy into account, peaks in the neon EDC's evolve θ almost exactly as shown in Fig. 8 for helium (except for satellite derived lines).

Let us turn to a comparison of the experimental and theoretical energy bands for TiS_2 . Rather flat s/p valence bands predicted by the band calculations are located around -4 and -3 eV as can be seen clearly in Fig. 10. Again occupied d states are seen near E_F at the zone boundary. In Fig. 10, the open circles and triangles represent data ob-



FIG. 9. Angular dependence of EDC's along FALM of TiS₂ using He^I line at an incidence angle $\alpha = 20^{\circ}$.

tained at angles corresponding to points within the first zone. The closed circles are data points folded back from the second zone. As before, the solid and broken lines are the band results of Zunger and Freeman²⁰ in the direction A to L and Γ to M, respectively. In general, remarkable agreement between theory and experiment is observed. In particular, as one proceeds from -2eV at the zone boundary toward the zone center, a band appears to split- off and rise toward E_F . Weak but reproducible peaks due to initial states in this band were observed near Γ , and Γ_2^- rather than Γ_3^- is probably uppermost, an inverted order compared to the selenide.^{19,20} With the occupied d-band states close or slightly below E_F , we conclude that the indirect p/d band gap in TiS₂ is 0.3 ± 0.2 eV. Again the experimental points extending across the zone to -2 eV at Γ are believed to arise from initial states on an intermediate line along Δ to Q.

IV. CONCLUSIONS

The present angle-resolved photoemission results on titanium diselenide $TiSe_2$ are in good



FIG. 10. Energy bands of TiS_2 (a) mapped from He I data; (b) mapped using Ne I radiation. The notation of experimental data points is similar to that in Fig. 4. A comparison with the theoretical bands of Zunger and Freeman (Ref. 20) are also shown as in Fig. 4.

agreement with previously published results.^{1,2} They are more detailed, however, and indicate how the band peaks evolve more or less continuously with polar angle θ for different photon energies. The overlap of valence and conduction bands for the selenide is found to be less than reported in Ref. 1, and this is probably due to experimental uncertainties. The early work utilized the new technique of angular-resolved photoemission with energy resolution by time of flight.²² This method suffers from the fact that energy resolution is poor for the most energetic groups of emitted electrons. Because the highest kinetic energies occur for initial states close to E_F (near the top of the valence band and the bottom of the d conduction band), the overlap in the uppermost experimental points are most uncertain. The present experimental results on TiSe₂ are a refinement and also confirm the existence of small peaks corresponding to localized pockets of occupied states near the zone boundary associated with the d band. The narrow azimuthal patterns for these states reported by Traum and co-workers² are confirmed.

The experimental band structure reported here for both titanium diselenide and titanium disulphide are in very good agreement with the theoretical band structure as calculated by Zunger and Freeman.^{19,20} The agreement shown in Figs. 4 and 10 is remarkable in that no arbitrary adjustment of relative band positions was made. The experiments give only a two-dimensional projection of the energy bands in k space, and certain bands, with the most two-dimensional character, are in best agreement.

Perhaps the best comparison and most rigorous test of theory is made by comparing energy gaps. Certainly the indirect gap between the s/p valence bands and the *d* conduction bands is of utmost importance with respect to the physical properties. It appears that titanium diselenide is almost certainly a semimetal with a definite, although small, band overlap. We cannot tell the exact overlap, but believe it to be of the order of 0.2 ± 0.1 eV.

Titanium disulphide appears to be a semiconductor in agreement with the pressure dependent resistivity and Hall coefficient measurements of Friend et al.¹² Our photoemission results show that the energy gap in TiS_2 is of the order of 0.3 ± 0.2 eV. The semiconducting behavior of TiS₂ must then be ascribed to defects of either excess titanium, titanium displacement, or of both. A 0.3 eV gap is close to the result obtained in the self consistent calculations of Zunger and Freeman.²⁰ It is in less agreement with the 1.4 eV non-self-consistent result found earlier by Myron and Freeman.²³ Likewise the band calculations of Krusius²⁴ predict an approximately 1.5-eV gap which is too wide. The LCAO calculation of Bullett¹⁴ produces a gap of 0.8 eV. Finally, considering the band details overall, as well as the indirect gap, we conclude that agreement with the Zunger-Freeman self-consistent result is more than fortuitous.

There are remarkable similarities in the EDC's for titanium diselenide and titanium disulphide. The way in which the energy distribution curves evolve, including the appearance and disappearance of peaks under certain circumstances, are nearly the same for the two compounds. Although the interpretation of peak positions in the photoemission experiment is simple and straightforward, an understanding of the photoemission intensities as a function of angle, excitation wavelength, and polarization is not yet entirely clear. Dramatic changes in peak intensity occur as a function of $\boldsymbol{\theta}$ and many of these effects are still to be sorted out. An adequate theory requires the use of appropriate final state wave functions (not just plane waves) and probably also multiple scattering theory. For example, Liebsch²⁵ has interpreted experiments of Smith and co-workers on the group V layer compounds. The theory is involved, although quite successful, and has not yet been extended to other materials.

In the course of experiments in the group IV compounds we found that, although the peak positions in the EDC are quite reproducible from sample to sample, intensity profiles sometimes vary noticeably. Even with the same samples the shape of EDC's can be observed to change by moving the sample so as to illuminate a different area on the surface. We believe that this is caused by the presence of microdefects related either to distortion or irregularities, such as steps during cleaving. It also appears that surface defects change the relative contribution of secondary electrons to the EDC's. Such effects are most noticeable at larger angles of emission. Thus, besides an adequate theory for the intensity of angle-resolved photoemission (applicable to specific materials), there is the need for experimental and theoretical work on defects, both within the bulk and at the surface.

Electron diffraction patterns of both titanium disulphide and titanium diselenide show diffuse lines corresponding to the $2a_0 \times 2c_0$ superlattice. This diffuse streaking is weak at room temperature, but observable, and is also found in other group IV compounds, compounds such as hafnium diselenide and hafnium disulfide, which have relatively wide band gaps.²⁶ Such effects may be characteristic of the 1-T crystal structure. For example, they may correspond to softening of the L_2 zone boundary phonon frequency as observed directly from inelastic neutron scattering data on TiSe₂.²⁷ Short-range order and a *tendency* toward $2a_0$ superlattice formation may thus be of lattice origin. On the other hand, only titanium diselenide shows a locked-in superlattice below $T_c = 200$ K.

Thus it may be that *long-range-order* of this special $2a_0 \times 2c_0$ type requires the gain in energy associated with changes in the band structure. The hole wave function in the semimetal TiSe, is mainly associated with the selenium atom, whereas the d-electron wave functions are related to the titanium atoms. It has been directly shown that the displacements during superlattice formation involve the formation of TiSe₂ molecular units.⁴ Titanium and selenium atoms tend to move together below T_c . In this sense electrons and holes are associated in pairs during superlattice formation as suggested by Wilson.¹⁰ In another sense a change in the average Ti-Se bond length produces a change in the electronic structure so that a semimetal-to-semiconductor transition takes place.²⁸ Clearly, zone boundary phonons, strong electron-lattice interaction, and the appropriate electronic structure are all important.

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