

Angle-Resolved Photoemission from TiSe_2 Using Synchrotron Radiation

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Angle-resolved photoemission has been used to study the occupied density of states in TiSe_2 . Results show that the conduction band overlaps the valence bands in k space along the Γ - M direction indicating that stoichiometric TiSe_2 is a semimetal.

TiSe_2 has been of recent interest because of a $2a_0$ by $2c_0$ low-temperature superlattice and its probable connection with a nearly two-dimensional energy band structure.¹⁻³ Band-structure calculations⁴ have indicated that both TiSe_2 and TiS_2 are semiconductors; however, this depends upon accurately evaluating a narrow gap separating occupied p -like valence bands from unoccupied d bands. The experimental situation is complicated by the difficulty of preparing stoichiometric crystals. There is now evidence⁵ that TiS_2 can be prepared stoichiometric and that it is still metallic or at least semimetallic. The best TiSe_2 still appears to be excess in titanium perhaps by as much as 2-4%. Such samples show strong metallic characteristics with a carrier concentration of approximately $1 \times 10^{21} \text{ cm}^{-3}$.¹ Photoemission results on TiSe_2 have been obtained previously using the usual angle-integrated technique both in the soft-x ray⁶ and in the ultraviolet region.⁷ Neither of these measurements was definitive on the question of overlapping conduction and valence bands.

We have investigated the occupied density of states of TiSe_2 using angle-resolved photoemission at a photon energy at 45 eV. Past prediction^{8,9} and recent measurements^{10,11} on layer crystals have shown that angle-resolved photoemission can provide a direct probe of energy versus wave vector. This arises because the tangential component of momentum is conserved on specular transmission through a surface. Our results on TiSe_2 reveal the partially filled bands due to excess Ti and they strongly indicate that stoichiometric TiSe_2 would be a semimetal.

The TiSe_2 crystals studied were grown in sealed quartz ampoules by iodine vapor transport. The carrier concentration was in the range 2-4% excess Ti as estimated by infrared reflectivity and electron-beam-microprobe analysis. Samples

were cleaved *in situ* within the photoemission chamber at a pressure of 2×10^{-10} Torr. The resulting cleave was smooth and optically specular as determined by reflectivity measurements as a function of angle.

The angle-resolved photoemission measurements were made on the 4° beam line¹² at the Stanford synchrotron radiation project¹³ using a time-of-flight technique which takes advantage of the short bunch length in SPEAR.¹⁴ In this method photoemitted-electron energy distributions are determined by measuring the transit time between the sample and the detector. Because of its mechanical simplicity, the time-of-flight spectrometer allows independent variation of electron escape angle θ and φ as well as the photon incidence angle θ_c and sample azimuth φ_c . Timing, with 0.5-nsec resolution, is performed by detecting single electrons using a statistical delayed-coincidence technique. Absolute times are obtained by referring to the reflected photon signal. An angular resolution of 1° was achieved using a 17-cm drift length. The energy resolution, ΔE , is given by $\Delta E \approx 4 \times 10^{-3} E^{3/2}$ where E is the electron kinetic energy. The excitation radiation was monochromatized with a novel grazing-incidence ultrahigh-vacuum monochromator which provides photon flux in the range 30-500 eV.¹² The measurements reported here were made at 45 eV with SPEAR running at 4-6 mA. Most of the spectra and those shown here were taken without retarding. The differential resolution is 1 eV. Several spectra were taken with 20-V retarding or 0.3-eV differential resolution, and showed that the prominent features were obtained.

Figure 1 shows a composite of valence-band spectra taken at selected electron escape angles θ relative to the sample normal which was oriented at 38° relative to the incident photon wave

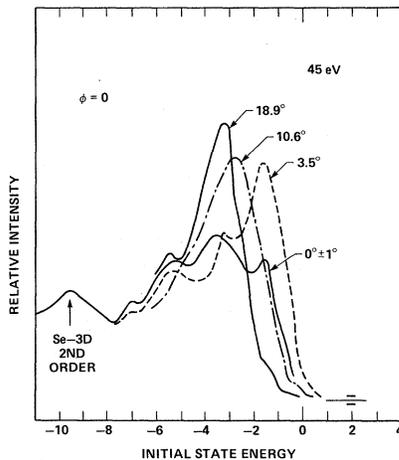


FIG. 1. Relative intensity versus initial-state energy for several polar angles spanning the first Brillouin zone in the Γ - M direction.

vector. The angle $\varphi = 0^\circ$ was held fixed. The sample had been preoriented with respect to a cleavage plane so that for different polar angles θ , the parallel component of momentum, k_{\parallel} , sampled points along Γ to M in the Brillouin zone. X-ray measurements confirmed the orientation. The point M on the first-Brillouin-zone boundary occurs at a wave vector of 1.03 \AA^{-1} , or from the relation¹¹

$$\sin\theta = 0.511k_{\parallel}\sqrt{E}$$

at an angle of approximately 20° . The spectra show large changes in shape and intensity as a function of angle. The overall intensity is a minimum for near-normal emission and correlates with the change in density of states across the zone. This variation is shown in Fig. 2, which is a plot of the maximum spectral intensity versus polar escape angle. The magnitude of the variation with angle shows the importance of having high angular resolution.

The feature in Fig. 1 at -10 eV is the Se- $3d$ core emission appearing from excitation by second order from the monochromator. Its prominence is exaggerated by the large photoemission cross section. The magnitude of this peak and the ratio of the second-order to third-order peaks were found to be constant for the angular range investigated in this experiment. In these spectra, the Se $3s$ is very weak compared to the x-ray-photoemission-spectroscopy result⁶ because of the cross section variation with energy. The angle-integrated spectra^{6,7} are similar to the 18.9° curve of Fig. 1. Our data on TiS_2 , which was on-

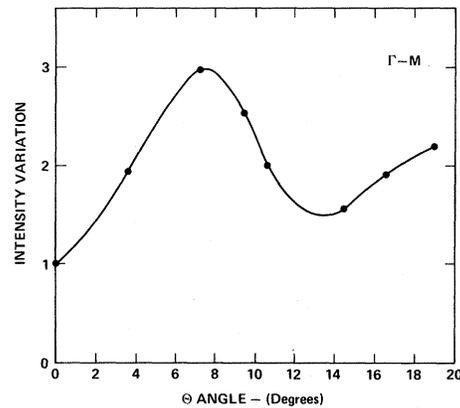


FIG. 2. Peak intensity variation as a function of angle. The photoemission intensity correlates with the variation of the density of states across the zone.

ly measured at 20° , showed a similar comparison. This results because the angle-integrated photoemission emphasizes the regions of highest density of states.

As the polar angle increases and the wave vector scans toward the zone boundary, the major spectral features in Fig. 1 move toward lower energy due to the valence-band dispersion. As the polar angle increases above 10.6° , a small shoulder appears near the Fermi level. These shoulders are absent in the spectra for smaller angles. These shoulders are associated with electrons in the lowest conduction band.

The data in Fig. 1 have been analyzed for energy wave vector information using Eq. (1). The data points, plotted in Fig. 3, are obtained from the peak or shoulder positions found in the spectra. As a comparison, the band-structure-calculation results of Myron and Freeman,⁴ shown by the continuous lines, are plotted in the same figure. The highest-lying valence-band points are from the strong shoulder occurring before the first peak. With respect to the calculated bands, the points have been shifted so that the top of the valence band is aligned at the zero energy. The extent and dispersion of the valence bands are generally reproduced. The conduction-band position, however, is not. The points plotted as solid dots show that the conduction-band minimum near M strongly overlaps the valence-band maximum at Γ . Previous angle-integrated photoemission, which tends to emphasize the maxima in the density of states, does not show this because of the large valence-band dispersion. Obviously the conduction bands of the early band calculation⁴ must be shifted down so that

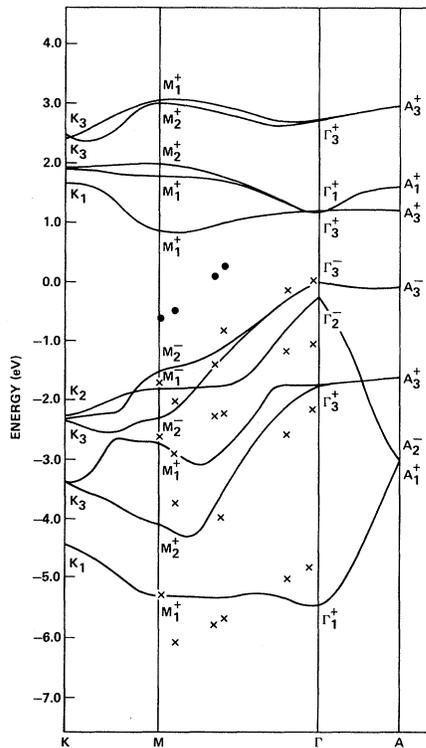


FIG. 3. Energy versus wave-vector data for the Γ - M direction plotted on the bands calculated by Myron and Freeman in Ref. 4. The conduction electrons indicated by circles are found to overlap the valence band, indicating that TiSe_2 is a semimetal. The crosses indicate points associated with the valence bands.

stoichiometric TiSe_2 would be a semimetal. There are no holes at Γ in these nonstoichiometric crystals, and the Fermi level lies above Γ_3^- , a little less than midway from M to Γ .

Using the Myron and Freeman calculation⁴ for the conduction-band density of states, one can estimate the wave vector at the Fermi surface as 60% of the zone along Γ - M . More recent calculations by Freeman¹⁵ have indicated that as the band gap decreases in these layered dichalcogenides, the band at M falls faster than at Γ . This would lead to a band shape similar to that found, and yield enough states to be consistent with the

observed carrier concentration. A determination of effective mass at the Fermi surface would confirm this point.

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