$TiSe_2$: Semiconductor, semimetal, or excitonic insulator

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The electronic structure of high-quality $1T$-$TiSe_2$ has been investigated using angle-resolved synchrotron ultraviolet photoemission. Occupied Ti d states are clearly observed in small pockets around the zone-edge centers and are found to be roughly degenerate with the highest-lying Se p states at Γ. The results are relevant to various explanations of the $2a_0 \times 2c_0$ lattice instability in this material, including a possible excitonic electron-hole interaction.

Considerable attention has focussed on the layer compound $1T$-$TiSe_2$,[1-4] particularly since the discovery of an anomalous $2a_0$ superlattice in this material below 200 K. Suspecting a $2c_0$ distortion as well, Wilson and Mahajan[1] proposed that the structural instability arises through an excitonic insulator-type mechanism[5] in which Ti d electrons around the L point in the Brillouin zone can nest with holes in the Se p bands near Γ. Underlying their proposal was the supposition that $TiSe_2$ is a semimetal with band edges that overlap by not much more than the binding energy of the indirect exciton (i.e., ~0.1 eV). In recent angle-resolved photoemission measurements, however, Bachrach *et al.*[3] indicate that the p-d overlap in nonstoichiometric material is at least 0.5 eV. By contrast, early band-structure calculations for $TiSe_2$ went in the opposite direction and produced semiconducting gaps of $\gtrsim 0.8$ eV.[6] In view of this and other interesting suggested mechanisms for the lattice instability, it is important to have the issue of the band-edge separation resolved.

We have performed our own angle-resolved photoemission measurements on specially prepared[4] high-stoichiometry crystals (<0.3-at.% excess Ti, ~0.3-at.% iodine impurity). In agreement with Bachrach *et al.*,[3] we find structure near the top of the p bands which is attributable to d-band emission. In disagreement with their results, though, we conclude that the p and d band edges are quite close in energy, so that an excitonic instability in $TiSe_2$ must be considered a real possibility after all. Furthermore, our experiments reveal the Ti d states for the first time as well-defined peaks in the electron energy spectra. This enables us to obtain dimensions for the d-like parts of the Fermi surface directly and to deduce carrier concentrations. These are in accord with those recently estimated by Di Salvo *et al.*[4] from transport measurements on the same material. Our results also turn out to be in excellent agreement with a new independent band structure calculation by Zunger and Freeman.[7]

The photoemission data were collected at room temperature using p-polarized synchrotron radiation from the Tantalus I storage ring. The experimental apparatus and method of measurement are described elsewhere.[8] Figure 1 contains a sequence of electron energy distribution curves taken at a photon energy of $\hbar\omega = 23$ eV with the light incident at an angle of about 45° from the surface normal (c axis). The spectra are presented for various polar angles of emission, θ, with the azimuthal angle held constant so that the plane of emission coincides with a $\Gamma M \Gamma$ azimuth.

The inset of Fig. 1 shows the normal emission spectrum for the highest few volts of initial-state energy. The leading edge of the valence-band structure extends all the way up to the Fermi level (E_F). The edge moves downwards in energy as θ is increased, and at $\theta = 15°$ it has shifted to more than 0.6 eV below E_F. Now for still larger θ, a peak emerges near E_F with its maximum growing to around one-eighth the height of the typical valence-band structure and then diminishing toward zero again by $\theta \sim 40°$. The relative size and position of the peak are reminiscent of the d-band structure found previously in $1T$-$TaSe_2$ and $1T$-TaS_2,[9] suggesting it to be the Ti-3d-like conduction-band emission.

Let us briefly compare this prominent peak with the small shoulder at the foot of the valence-band edge reported by Bachrach *et al.*[3] In that work the weak shoulder is ill defined in energy for want of a clear-cut maximum. Emission from the shoulder might not be limited to larger θ as suggested, since near the normal it could be masked under the valence edge. In any case, almost 1 eV of dispersion is depicted for the shoulder where it does appear, and more than half of this dispersion occurs below the designated top of the valence bands. On the other hand, the present work on nearly stoichiometric material shows a very nondispersive band which unambiguously gives rise to emission over only a narrow range of θ.

Portions of the energy bands $E(\vec{k}_\parallel)$ are shown in

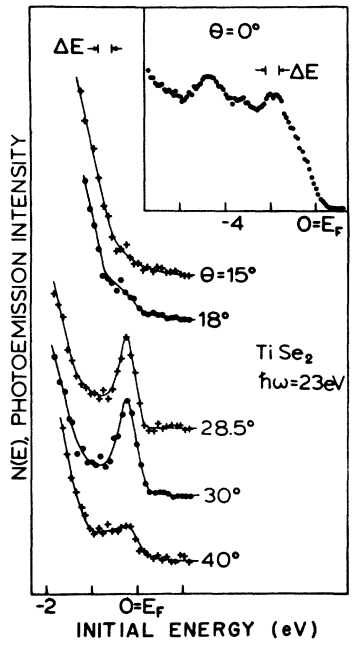

FIG. 1. Energy distribution of photoemitted electrons along the $\Gamma M\Gamma$ (mirror plane) azimuth for various polar angles θ from the surface normal (c axis). Smooth curves have been drawn through the data points.

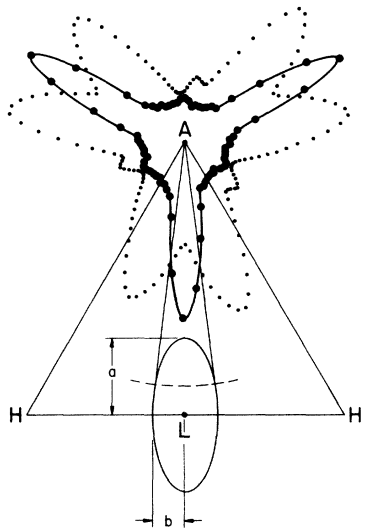

FIG. 3. Radial plots of the azimuthal dependence of the d-peak emission intensity at $\theta = 25°$ for $1T$-$TiSe_2$ (solid curve with data points) and $1T$-TaS_2 (dotted curve). A sector of the upper zone face (HAH) is shown with an ellipse of semimajor axis $a \sim 0.3LA$, centered about L. The semiminor axis b is chosen so that the ellipse passes through the intersections of the dashed arc (radius $k_{\parallel} \sim 0.9AL$) with the radial lines at the Ti-d lobe half-maxima (discounting background). Note that the points A and L have the same $\vec{k}_{\parallel}$ as Γ and M, respectively.

Fig. 2. The mapping from structure in a set of spectra taken at $\hbar\omega = 23$ eV has been performed in the usual way,[9] where the surface-parallel component of the electron wave vector $\vec{k}_{\parallel}$ is obtained from $k_{\parallel} = (2mT/\hbar^2)^{1/2} \sin\theta$, and T is the kinetic energy of the electron *in vacuo*. As θ varies from 0° to 70°, $k_{\parallel}$ changes from 0 to about twice the distance from Γ to M—corresponding to emission from the first and second Brillouin zones, as illustrated by the dashed arrow in the upper half of the figure. (The surface-normal component of the internal electron wave vector $\vec{k}_{\perp}$ is not well defined in this kind of experiment, and the labels Γ and M are intended to identify points anywhere on the normal lines ΓA and ML, respectively.) The flat d band near E_F appears only in the region $0.7\Gamma M < k_{\parallel} < 1.3\Gamma M$, and is associated with the lowest conduction band just dropping below the Fermi level close to the edge of the zone. This provides us then with a direct measure of the radial extent of the d-like portion of the Fermi surface.

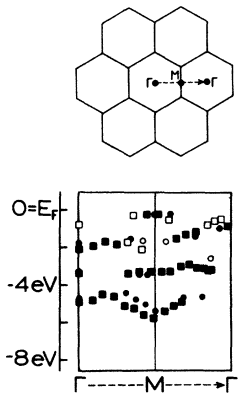

FIG. 2. Initial-state electron energy vs $k_{\parallel}$ along the $\Gamma M\Gamma$ azimuth. Strong (weak) features in the $\hbar\omega = 23$ eV energy distribution curves are represented by filled (unfilled) symbols. Circles (squares) denote the plane of incidence of the radiation being parallel (perpendicular) to the plane of emission.

With regard to the overlap, we note that the uppermost peak in the Se p band does not rise higher in energy than the Ti d-band minimum—although it does come rather close for certain experimental conditions. See, for example, the data near the second-zone Γ point in Fig. 2.[10] Considering the resolution of our experiments, the top of the valence bands and the bottom of the conduction bands are degenerate to within ~0.2 eV, allowing $TiSe_2$ to be either just semiconducting or, indeed, semimetallic. In any case, the band edges are evidently close enough to permit the possibility of an excitonic electron-hole instability. The present data are also consistent with some other likely explanations for the superlattice, including electron-hole coupling via phonons[4,11] and electron-hole–parallel-band effects on the generalized susceptibility.[7]

Because the d peak is well resolved from the valence-band edge, a study of the d emission as a

function of azimuthal angle ϕ, was straightforward. The solid curve with data points in Fig. 3 is a threefold averaged radial plot of the ϕ dependence of the peak intensity at $\theta = 25^\circ$ ($k_\parallel = 0.9\Gamma M$). The dotted curve shows data measured under similar experimental conditions[12] on the d emission from $1T$-TaS_2, which is known to have one complete electron in the Ta d band. Both curves have a lobe structure suggestive of emission from orbitals with nonbonding t_{2g}-type d character.[9] The lobes in $TiSe_2$, however, are confined to a much narrower range of ϕ than in TaS_2, indicative of a much lower d-band occupancy. The extent of the lobe in ϕ permits us to estimate the transverse dimension of the occupied part of the Fermi surface, as illustrated in Fig. 3. Assuming ellipitically-shaped pockets, we obtain a dimension for the semiminor axis, $b \sim 0.2LH$. The semimajor axis has already been determined from the θ dependence: $a \lesssim 0.3LA$. These agree remarkably well with the pocket dimensions found theoretically.[7] If we center the pocket at L rather than at M, as shown in Fig. 3, and let the half-axis dimension along $k_\perp$ be $c \sim 0.5LM$,[7] then the volume occupied by d electrons would be ~3% of the zone. This compares quite nicely with the 1%–2% value for the zone filling estimated from earlier transport data.[4] On a more general level, these results appear to represent the first time that photoemission has been given a direct quantitative connection to transport measurements or to theory by an actual mapping of the Fermi surface from the angular dependence of the emission intensity.

Finally, returning to the subject of energy dispersion, it has been seen that the d electrons reside in band segments which are rather flat—at least along LA. These electrons, therefore, would not be expected to strongly screen their own Coulomb interaction with degenerate holes at Γ and severely reduce the indirect exciton binding energy. In conclusion, then, our findings indicate that the energy, character, $\vec{k}$-space location, and dispersion of the electronic states are all in a range favorable for the formation of some sort of excitonic state in $TiSe_2$. The results, however, do not distinguish between this and other electron-hole-related driving mechanisms for the superlattice.

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[1] J. A. Wilson and S. Mahajan, Commun. Phys. 2, 23 (1977); J. A. Wilson, Solid State Commun. 22, 551 (1977); and (unpublished).

[2] W. Y. Liang, G. Lucovsky, R. M. White, W. Stutius, and K. R. Pisharody, Philos. Mag. 33, 493 (1976); F. J. Di Salvo, D. E. Moncton, J. A. Wilson, and J. V. Waszczak, Bull. Am. Phys. Soc. 21, 261 (1976); K. C. Woo, F. C. Brown, W. L. McMillan, R. J. Miller, M. J. Schaffman, and M. P. Sears, Phys. Rev. B 14, 3242 (1976); W. G. Stirling, B. Dorner, J. D. N. Cheeke, and J. Revelli, Solid State Commun. 18, 931 (1976); M. B. Barmatz (unpublished); G. K. Wertheim (unpublished).

[3] R. Z. Bachrach, M. Skibowski, and F. C. Brown, Phys. Rev. Lett. 37, 40 (1976).

[4] F. J. Di Salvo, D. E. Moncton, and J. V. Waszczak, Phys. Rev. B 14, 4321 (1976); F. J. Di Salvo and J. V. Waszczak (unpublished).

[5] See, for example, B. I. Halperin and T. M. Rice, Rev. Mod. Phys. 40, 775 (1968); and, in *Solid State Physics*, ed. by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1968), Vol. 21, p. 115.

[6] H. W. Myron and A. J. Freeman, Phys. Rev. B 9, 481 (1974); R. B. Murray and A. D. Yoffe, J. Phys. C 5, 3038 (1972).

[7] A. Zunger and A. J. Freeman, Phys. Rev. B (to be published).

[8] N. V. Smith, P. K. Larsen, and M. M. Traum, Rev. Sci. Instrum. 48, 454 (1977).

[9] N. V. Smith and M. M. Traum, Phys. Rev. B 11, 2087 (1975); M. M. Traum and N. V. Smith, Surf. Sci. 53, 121 (1975).

[10] Although the final states excited from near the top of the valence bands at $\hbar\omega = 23$ eV do not seem to couple strongly into vacuum in the first zone, a high-lying shoulder does appear in a few of the normal emission spectra taken at other photon energies over the range $12 < \hbar\omega < 34$ eV. Limited measurements taken off normal are also consistent with the $\hbar\omega = 23$ eV results, but insufficient data have been obtained to unequivocally separate initial from final state effects. [See, e.g., A. Liebsch, Solid State Commun. 19, 1193 (1976).] The interpretation offered here, though supported by the overall evidence, should still be accepted with the usual caution.

[11] Phonon-dependent driving mechanisms have been discussed by Liang *et al.* (Ref. 2); Woo *et al.* (Ref. 2); R. M. White and G. Lucovsky, Il Nuovo Cimento B 38, 280 (1977).

[12] P. K. Larsen and N. V. Smith (unpublished).