Both conditions and the steady-state parts of Eqs. (1)-(3) must be satisfied for stability. For example, Rognlien and Self implicitly use σ^e = const and σ^i = const. This choice is stable only if the current is held fixed and not the electric field. This condition is also necessary for the runaway stability of the three-dimensional heat-transfer models investigated by Furth, Rutherford, Rosenbluth, and Stodiek.⁴

If the plasma is runaway unstable, then the stability of long-wavelength ion-acoustic waves must be computed from the time-dependent formalism with energy sinks and/or sources included. However, if the plasma is in a runaway-stable steady state, then the simpler time-dependent formalism yields the stability criterion

$$1 - \frac{1}{2} \sum_{n}^{i} - (\frac{4}{3} + \frac{1}{3} \sum_{i}^{i}) R \leq (1 - u/V) (Z/4C_{e_{X}}) (1 + \frac{5}{3} R/Z)$$

(14)

for the wavelength range

$$M^{-1} \ll K^2 T_{\rho} \ll M^{-1/2} R^{-5/2} \ll 1.$$

Note that stability depends critically on the nature of the ion heat sink. Rognlien and Self's results are reproduced if σ^i is independent of *n* and T_i . However, a physically more reasonable example follows from the scaling of the classical heat transfer across a plasma slab; one finds σ^i $\sim n^2 T_i^{1/2}$, $\sigma^e \sim n^2 T_e^{1/2}$; this is runaway stable only if the current is held fixed and is stable to the above range of ion-acoustic waves for all values of *R* as long as U < V. Clearly the results change dramatically with different heat sinks.

In summary, it is shown here that the stability of long-wavelength ion-acoustic waves is determined not only by the temperature ratio and relative drift, but also by time dependence of the uniform background state and by the nature of the ion heat sink as a function of density and ion temperature. I would like to thank Paulo Sakanaka, Harold Weitzner, and Harold Grad for their many useful comments.

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Photoemission Studies of the Layered Dichalcogenides NbSe₂ and MoS₂ and a Modification of the Current Band Models*

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Ultraviolet photoemission measurements have been used to determine the electronic structure of two of the layered transition-metal dichalcogenides, NbSe₂ and MoS₂, which show trigonal prismatic coordination. Although the electronic structures of the two materials have rather different character, the results are consistent with a loose interpretation of a rigid-band model. The observed energy of the Fermi level above the valence-band maximum in MoS₂ indicates that the splitting between the nonbonding d bands is in excess of 1 eV, a value considerably larger than some previous suggestions.

The layered transition-metal dichalcogenides (TX_2) form a structurally and chemically similar family of compounds having a wide range of electrical properties. These layered materials are of particular interest because of their "two-dimensional" superconducting properties which

can be changed by intercalating them with organic molecules¹ or alkali-metal atoms.² Wilson and Yoffe³ have proposed a rigid-band model for the TX_2 compounds in which the electrical properties are determined by the degree of filling of narrow nonbonding *d* bands lying in the basic



FIG. 1 (a) Wilson and Yoffe model (Ref. 3) for TX_2 compounds; (b) HJHJ model (Ref. 4) for trigonal prismatic TX_2 compounds; (c), (d) simple band models for NbSe₂ and MoS₂ as determined by our photoemission data. The conduction-band structure is as estimated from optical (Ref. 3) and soft-x-ray absorption (Ref. 12) data.

bonding-antibonding band gap. Wilson and Yoffe assign the exciton peaks in the optical absorption spectra of MoS_2 etc. to transitions from the top of the *p* valence band to the d/p band,³ both initial and final states showing spin-orbit splitting. This model is shown in Fig. 1(a).

Huisman, deJonge, Haas, and Jellinek (HJHJ)⁴ have proposed an alternative band model for the TX_2 compounds which have trigonal-prismatic coordination. The model of HJHJ has a similar ordering of the d states to the Wilson and Yoffe (WY) model.³ However, among other differences is a larger spacing of the nonbonding d bands. This larger spacing causes the d_{z^2} band to be completely overlapped by the p valence band, while the upper d bands overlap the conduction s band as shown in Fig. 1(b). This model does not account for any hybridization of the d bands. HJHJ⁴ assign the exciton peaks to transitions from the d_{z^2} band to the spin-orbit-split $d_{x^2-y^2}/dy^2$ d_{xy} band. Because neither model has been completely successful in explaining all the electrical properties of the trigonal-prismatic TX_2 compounds, experimental work leading to modified models of the electronic structure of these materials seemed useful. Also, since the available semiemperical band-structure calculations^{5,6} are to some extent based on one of these simple band models, an improvement in the model might lead to more accurate calculations.

In this Letter we present the results of ultraviolet photoemission studies and determine electronic structures for the metal $NbSe_2$ and the semiconductor MoS_2 which have some features of both the WY and the HJHJ models. In addition, we note significant differences between the photoemission data from the two materials which argue against strict interpretation of a rigid-band model connecting $NbSe_2$ and MoS_2 .

The NbSe₂ crystal used for these measurements was grown in 2-H form by R. E. Schwall of Stanford University using an iodine-vapor transport technique. The MoS₂ crystal (also 2-H form) was cut from a piece of natural molybdenite supplied by J. V. Acrivos of San Jose State University. The photoemission samples measured about 6×6 $\times 0.1$ mm³. The crystals were cleaved in the ultrahigh-vacuum $(2 \times 10^{-9} \text{ Torr for NbSe}_2, 4 \times 10^{-10}$ Torr for MoS₂) photoemission chamber developed by Powell and Derbenwick.⁷ For neither material were changes in the measured energy distribution curves (EDC's) observed over the period of time from 5 min after cleaving to 1 month after cleaving. The EDC's were measured at room temperature using an ac-modulated retardingfield technique similar to that of Eden.⁸ The resolution of the energy analyzer was approximately 0.2 eV. An aperture had to be used to restrict the size of the light beam from the McPherson 225 monochromator to an area smaller than the sample. The absolute quantum yield was measured with a calibrated Cs₃Sb photodiode and corrected for aperture effects and reflectivity.⁹ The location of the Fermi level is accurately determined by using a copper back shutter on the energy analyzer.¹⁰

Normalized EDC's for electrons photoemitted from NbSe₂ by photons with energies between 7.4 and 11.6 eV are shown in Fig. 2. Although only a few of the measured curves have been presented here, the important structure can be easily recognized. n(E), the number of electrons photoemitted per absorbed photon per electron volt, is given as a function of the final energy minus



FIG. 2. Energy distribution curves for electrons photoemitted from NbSe₂.

the incident photon energy. Thus, features appearing directly above each other originate from the same initial state energy. At the high-energy end (i.e., the right-hand side) of the EDC's are two peaks labeled A and B, which are each assigned to a high initial density of states in the valence bands 0.4 and 2.2 eV below the Fermi level (E_F), respectively. The constant energy of the right-hand edge of peak C indicates that it is at least partially derived from a high initial density of states, although there is probably some contribution from scattering.¹¹ The apparent shift in the position of C in Fig. 2 is caused by the peak moving from below the vacuum level.

Comparison of the EDC's with the band mod $els^{3,4}$ suggests that peak A corresponds to the nonbonding $4d_{z^2}$ -derived band, and peak B and probably peak C correspond to high densities of states in the lower p valence band. The bands for NbSe₂ based on this analysis are as shown in Fig. 1(c). The dashed structure above $E_{\rm F}$ has been estimated from the available optical³ and soft-x-ray absorption¹² data. This model differs from that in the WY paper in two ways: (1) The photoemission data suggest that there is some overlap of the d_{z^2} band with the *p* valence band (rather than a separation of almost 1 eV), and (2) the half-filled d_{z^2} band is about 1 eV wide, twice as wide as originally deduced by Wilson and Yoffe.³ Except for these differences, our results for NbSe, are in general agreement with the WY model for NbSe₂. There are also differences between our results and the HJHJ model.⁴ However, it might be possible to remove these if strong mixing causes the d_{z^2} band to broaden and



FIG. 3. Comparison of energy distribution curves for MoS_2 and $NbSe_2$. The EDC's are plotted versus the initial-state energy with the zero taken at the MoS_2 Fermi level. The $NbSe_2$ curves were shifted lower in energy by 2 eV to make the comparison of the curves as easy as possible.

increase in energy relative to the p valence band. Since for NbSe₂ the maximum density of states

n(E) in the d_{z^2} band is found to be 0.4 eV below E_F , the slope of n(E) is negative at E_F . This result has been used by Meyer and Acrivos¹³ in their explanation of the change in the superconducting transition temperature (T_s) of NbSe₂ when it is intercalated with organic molecules which are thought to donate a fraction of an electron to the band scheme. The added electron fraction moves the Fermi level up slightly, thereby decreasing n(E) at E_F which, it is proposed, causes T_s to decrease.

On the basis of a rigid-band model one would expect the EDC's from MoS_2 to look essentially like the EDC's from $NbSe_2$ with the highest-energy peak (peak A) about twice as wide. In the WY model³ as originally presented, the Fermi level has to lie less than 0.25 eV above the d_{z^2} band maximum. On the other hand, E_F could be more than 1 eV above the d_{z^2} band and remain consistent with the d-band splitting of the HJHJ model.⁴

In Fig. 3, we present the EDC's for MoS_2 and compare them with those for $NbSe_2$. The EDC's are again plotted versus the initial-state energy with the zero taken at the MoS_2 Fermi level and with the peaks *B* aligned in the EDC's of the two materials. As can be seen from Fig. 3, there is major disagreement between the location of E_F in the original WY model and in our data. Although Williams and McEvoy¹⁴ observed generally similar EDC's over a smaller energy range, they differed in the placement of the Fermi level. VOLUME 29, NUMBER 22

A very important experimental result for MoS, is that the Fermi level lies almost an electron volt above the highest filled state. To emphasize this, the zero of energy in Fig. 3 was taken as the MoS₂ Fermi level. The NbSe₂ Fermi level was shifted downward by 2 eV to make the comparison of the MoS_2 and NbS_2 structures as easy as possible. Thus, the HJHJ model seems to give more closely the actual spacing of the nonbonding d bands, while the WY model³ correctly places the d_{z^2} band as the top valence band. Using EPR techniques, Title and Shafer¹⁵ have found the top of the valence band to have d_{g^2} character. It is immediately apparent from Fig. 3 that the characters of the EDC's of the two materials are different. The marked change in the relative strength of the structure in the MoS₂ EDC's as $h\nu$ is varied is indicative of direct transitions. Since no evidence for direct transitions in NbSe₂ was observed, it is suggested that the details of the band structure and perhaps the bonding in the two materials are significantly different; the existence of direct transitions indicating a more covalent nature for MoS₂.

Figure 1(d) shows a modification of the WY model³ for MoS₂ as based on our photoemission data. The bands (shown dashed) above $E_{\rm F}$ have been estimated from the available optical data.^{3, 16} Unfortunately, this model cannot unambiguously determine the origin of the A and B exciton peaks observed in MoS₂, etc. The large forbidden gap suggests that the HJHJ assignment of a d_{z^2} to $d_{x^2-y^2}/d_{xy}$ transition is correct. However, it is possible that the p valence band overlaps the d_{z^2} band enough that the excitons could correspond to transitions from the p band to the $d_{x^2-y^2}/d_{xy}$ conduction band as suggested by Wilson.¹⁷ More detailed optical data in the 0.1- to 2-eV range are required to resolve this point.

In summary, we have shown by our photoemission measurements that for NbSe₂ and particularly MoS_2 quite large adjustments are required to either of the existing band models. Since these modifications deviate quite markedly from the results of recent band-structure calculations,^{5,6} using empirical fits to early models, it would appear that additional band calculations would be of interest.

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