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Energy Bands for 2H-NbSe₂ and 2H-MoS₂

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First-principles calculations of the electronic band structure for the layer-type compounds 2H-NbSe₂ and 2H-MoS₂ predict a 1-eV hybridization gap within the d_{z^2} and d_{xy}, $d_{x^2-y^2}$ manifolds of the metal-atom 4d bands. This produces a narrow (~1 eV) filled valence band in 2H-MoS₂ and a half-filled conduction band in 2H-NbSe₂, in agreement with electrical, optical, and recent photoemission date.

There has been considerable interest recently in the electronic structure of the transition-metal dichalcogenide (MCh₂) layer compounds. These rather remarkable materials consist of two-dimensional ChMCh sandwiches that are weakly bonded to one another along the third dimension. This produces highly anisotropic crystals that are readily cleaved and easily intercalated with organic molecules or alkali-metal atoms.[1]

Recent photoemission (PE) studies[2-6] on metallic 2H-NbSe₂ and semiconducting 2H-MoS₂ samples suggest a band-structure model that disagrees with that obtained from a semiempirical tight-binding calculation for 2H-MoS₂ by Bromley, Murray, and Yoffe[7] as well as the more schematic band models of Goodenough,[8] Wilson and Yoffe,[1] and Huisman et al.[9] In this Letter, we report the results of first-principles augmented–plane-wave (APW) calculations of the electronic band structures for 2H-NbSe₂ and 2H-MoS₂ which are consistent with the PE, optical, and electrical data. A significant feature of these results is the occurrence of a 1-eV hybridization gap within the M-atom 4d manifold. These results suggest that 2H-MoS₂ and related group-VIB compounds form a

new class of materials in which a hybridization gap is responsible for the observed semiconducting behavior.

The present calculations utilize no empirical data other than the space-group symmetry and the appropriate lattice parameters.[1] They involve approximate crystal potentials that are derived from neutral-atom charge densities, using techniques that have been described previously.[10a]

The results of the present APW calculations are shown in Fig. 1, where $E(\vec{k})$ curves for both compounds are plotted along symmetry lines in the ΓMK plane as well as the ΓA direction of the hexagonal Brillouin zone. The band shapes are only approximate since the APW calculations have been carried out only at the symmetry points and at the midpoints of the Σ and T lines. These compounds have similar but not identical crystal structures. Since these 2H-MCh₂ polytypes contain two molecules per cell, there are a total of ten M-atom d bands and twelve Ch-atom p bands.

Although covalency effects produce substantial p-d mixing, the ten bands in the upper portions of Fig. 1 are derived primarily from the metal 4d orbitals, whereas the twelve lower bands originate from the Ch-atom p orbitals. Covalency ef-
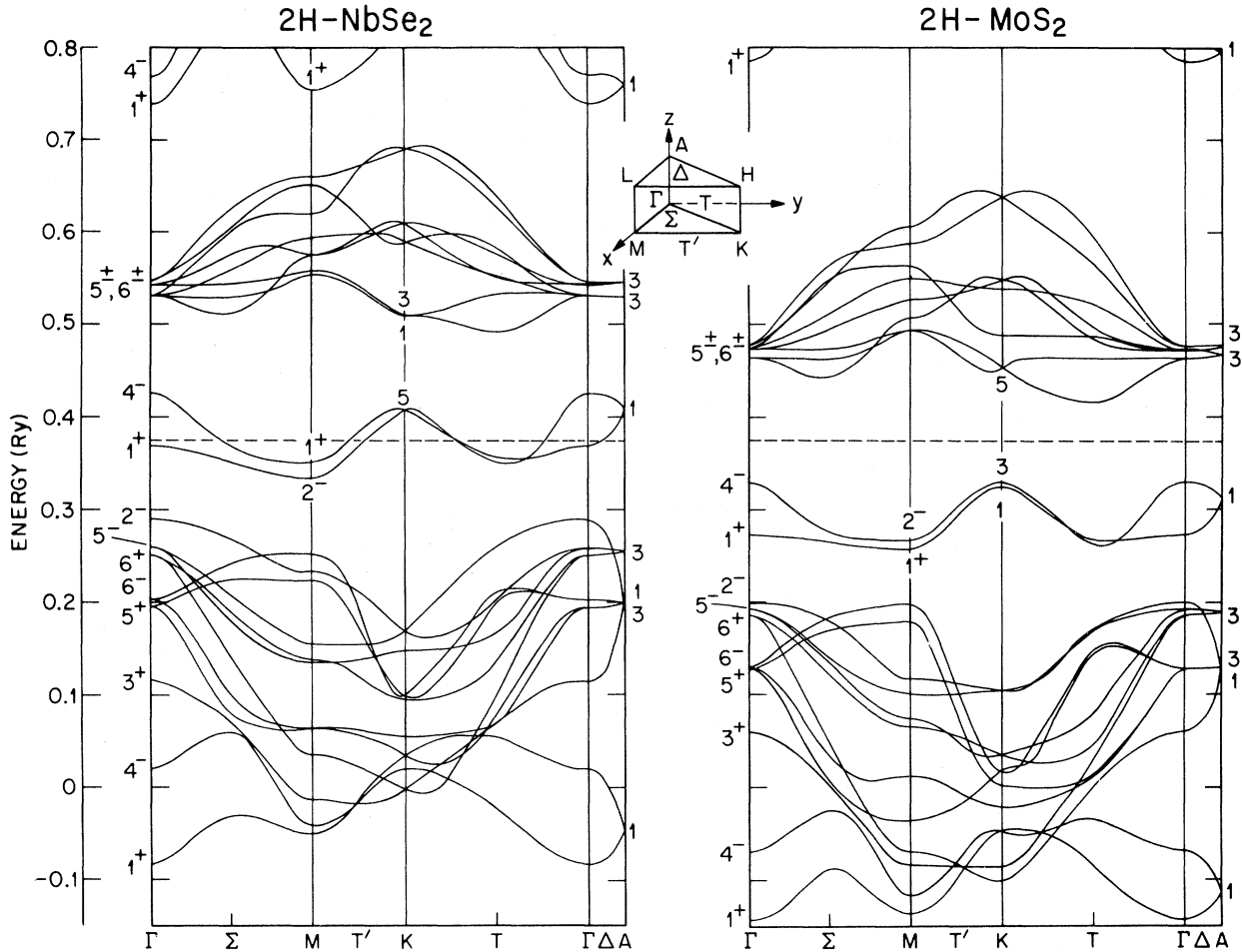
FIG. 1. APW energy bands for $2H$-NbSe$_2$ and $2H$-MoS$_2$ relative to the muffin-tin constant $V_0 = -0.931$ Ry for $2H$-NbSe$_2$.

fects between the M- and Ch-atom s-p orbitals are much stronger,[10b] and these raise the bottom of the metal $5s$-$5p$ band to energies near the top of Fig. 1. The Ch-atom s-like core levels are 14 and 15 eV below the $2H$-NbSe$_2$ and $2H$-MoS$_2$ Fermi levels, respectively.

In $2H$-NbSe$_2$, the Fermi level occurs in the lowest pair of sub-bands within the niobium $4d$ manifold. The corresponding sub-band is filled in $2H$-MoS$_2$, and this raises the Fermi level to the center of the 1.2-eV indirect band gap. In each compound, the lowest $4d$ band states have d_{z^2} symmetry at Γ; $d_{xy}, d_{x^2-y^2}$ symmetry at K, and a hybridized combination at M.

The bandwidths along the ΓA line result from interlayer interactions. These are largest for orbitals with charge distributions that point along the z or interlayer direction. Within the $4d$ manifold, the interlayer interactions are largest for

the d_{z^2} orbitals, where the Δ bandwidth is 0.05 Ry. In the case of the Ch-atom p_z orbitals, the correpsonding bandwidths range from 0.07 to 0.13 Ry.

To illustrate the importance of hybridization effects, we now apply the Slater and Koster[11] linear-combination-of-atomic-orbitals (LCAO) interpolation method to fit the APW results for the niobium $4d$ bands in $2H$-NbSe$_2$. The LCAO d-band matrix elements are easily derived from the work of Egorov, Reser, and Shirokovskii.[12] The "effective" LCAO d-band parameters that are obtained from such a fit[10b] involve a combination of direct and indirect (i.e., via covalency effects with Ch-atom s-p orbitals) d-d interactions.

In Fig. 2 this simplified LCAO model is applied to illustrate the development of the niobium $4d$ bands in $2H$-NbSe$_2$. First, the average energies of the various $4d$ sub-bands are shown in Fig.
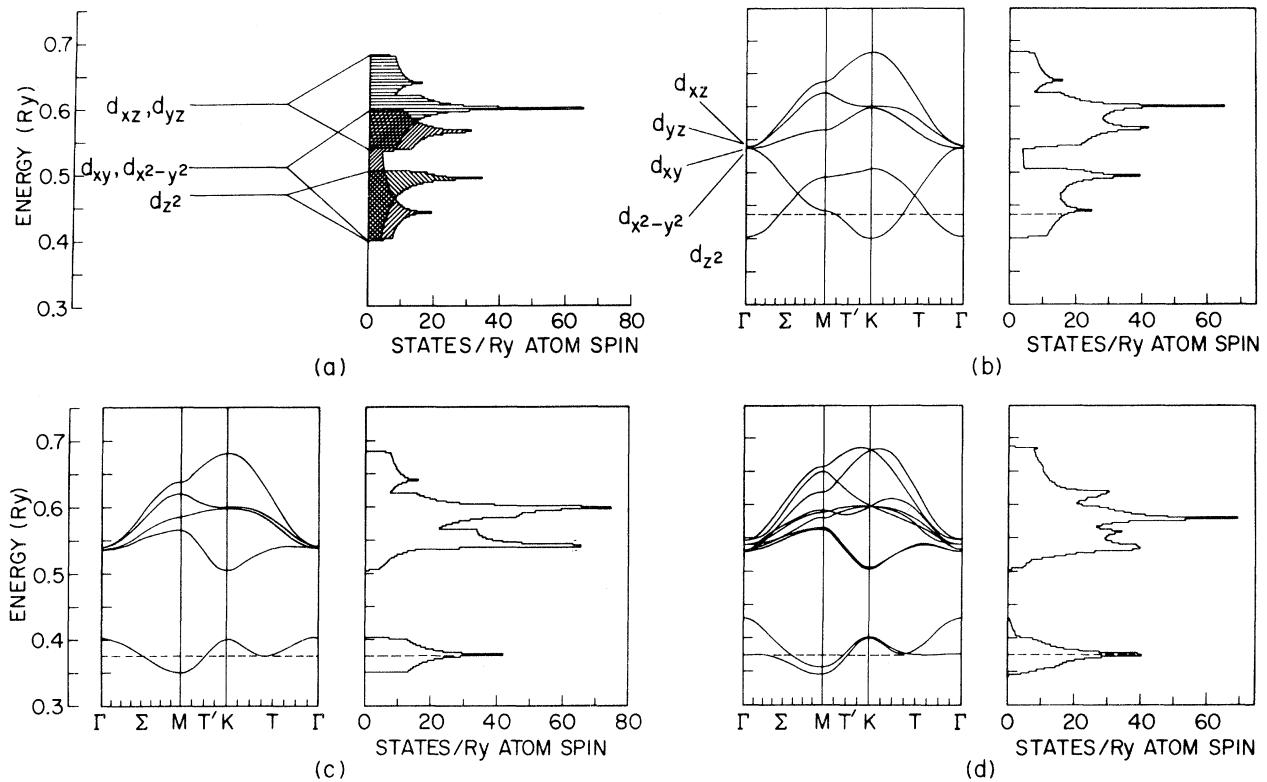
785

FIG. 2. LCAO $E(\vec{k})$ and density-of-states results for the niobium $4d$ bands in $2H$-NbSe$_2$. (a) Ligand-field levels; (b) neglecting interband hybridization and interlayer interactions; (c) neglecting interlayer interactions; (d) including interlayer interactions.

2(a). These correspond to the ligand-field levels of an isolated NbSe$_6$ trigonal prism.[10c] The relative splittings and order of these levels agree with that predicted by Huisman et al.,[9] though Goodenough[8] assumes a reversed order for the two lowest levels. Neglecting interband hybridization, the widths of the various sub-bands are shown by the density-of-states histograms. The actual $E(\vec{k})$ and total density-of-states curves are presented in Fig. 2(b). In Fig. 2(c) the effects of interband hybridization are included, while Fig. 2(d) illustrates the changes that are caused by interlayer interactions. Similar results are obtained for $2H$-MoS$_2$, which has the same crystal structure in the two-dimensional limit.

These results demonstrate that the lowest pair of d sub-bands in these $2H$-MCh$_2$ compounds consists of strongly hybridized combinations of d_{z^2} and d_{xy}, $d_{x^2-y^2}$ orbitals rather than the nonbonding d_{z^2} orbitals, as most of the earlier models[1,7,9,13] propose. We note that the 1-eV hybridization gap is larger than and not related directly to the ligand-field splitting between the d_{z^2} and d_{xy}, $d_{x^2-y^2}$ levels, as Goodenough[8] and Huisman et al.[9] assume.

The $2H$-NbSe$_2$ Fermi level falls near a slightly broadened two-dimensional logarithmic singularity in the density of states. The calculated value for the band density of states, $N(E_F) = 3.0$ states per eV spin Nb, agrees well with the empirical value of 2.8 states per eV spin Nb that is derived from superconductivity[14] and heat-capacity[15] data. The sharpness of this density-of-states peak at the Fermi level provides an attractive explanation for the fact that the group VB $2H$-MCh$_2$ compounds become unstable at temperatures where $kT \sim 0.01$ eV.[16] As Labbé and Friedel[17] have shown in the case of the A15 compounds, the existence of fine structure in the density of states near the Fermi energy can lead to a Jahn-Teller–type distortion which splits the density-of-states peak and reduces the free energy of the system at low temperatures.

The important contribution of the recent PE data[2-6] is to resolve the question of whether the $2H$-MoS$_2$ semiconducting gap is 0.2[1] or 1.4 eV.[9] As a result of these PE studies, it is now generally agreed that this gap is at least 1 eV in the

group VIB 2H-MCh$_2$ compounds,[3,5,6] which agrees with the present APW-LCAO results. Williams and Shephard[6] estimate from their PE data that the occupied 4d bandwidths in 2H-NbSe$_2$ and 2H-MoS$_2$ are less than 0.7 and 1.5 eV, respectively. These are only slightly larger than the calculated widths of 0.5 and 1.0 eV, respectively. These data[4,6] suggest valence p bandwidths of 5–7 eV, which agrees well with the calculated widths of 5.1 and 4.7 eV.

The main discrepancy between the PE data and the present APW results concerns the magnitude of the gap between the M-atom d and the Ch-atom p bands. The PE results indicate that these bands overlap by 0.1–0.2 eV, whereas the APW calculations predict an 0.6–0.7-eV gap. This is certainly the least-reliable aspect of these first-principles calculations. In similar calculations for the transition-metal oxides,[10] it was found that the corresponding p-d gap was overestimated by 1–3 eV. It is believed that these errors are due largely to a lack of self-consistency in the potential and the approximate treatment of exchange and correlation effects.

Finally, it is noted that if the 3p-4d band gap in 2H-MoS$_2$ is reduced by 0.7–0.9 eV, the 3p-4d band overlap of 0.1–0.2 eV will be less than the 4d valence bandwidth of 1.0 eV. As a result, the top of the 2H-MoS$_2$ valence band is still expected to consist of d_{z^2} orbitals at the zone center (Γ_4^-). This is consistent with the results of electron paramagnetic resonance studies in p-type 2H-MoS$_2$ samples.[18] Furthermore, it suggests that the A and B excitons that are observed in the 2H-MoS$_2$ transmission spectrum near 2 eV[1] involve d-to-d[9] rather than the previously assigned p-to-$d^{1,7}$ or d-to-p[6] transitions.

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Nonlocal Pseudopotential for Ge

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Photoemission studies have shown that although energy bands calculated from a three-parameter local pseudopotential agree well with experiment for Si, similar calculations disagree with experiment for Ge by amounts of order 0.5 – 1.0 eV for many states in the valence band. All these discrepancies can be removed through the introduction of one additional parameter describing the effects of 3d core states in Ge.

For many years it has been customary to interpret optical spectra and derive energy bands of semiconductors from local pseudopotentials. The number of parameters needed to specify a satisfactory local pseudopotential is small (approximately three per element making up the crystal),