New Method for Absolute Band Structure Determination by Combining Photoemission with Very-Low-Energy Electron Diffraction: Application to Layered VSe_2

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We have combined photoelectron spectroscopy (PES) and very-low-energy electron diffraction (VLEED) to study the electronic band structure $E(\mathbf{k})$ of a material with complicated unoccupied upper bands, which are incompatible with the free-electron approximation. Using VLEED, we have experimentally determined these bands, and accordingly optimized the PES experiment. PES band mapping using the VLEED upper bands enabled the first consistent resolution of the lower occupied bands, in particular, the perpendicular dispersion $E(k_\perp)$, for a layered material. The combination of PES and VLEED is a powerful method to resolve even very complicated $E(\mathbf{k})$ absolutely. [S0031-9007(97)03570-9]

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The electronic band structure $E(\mathbf{k})$ is a key concept in understanding the properties of crystalline solids. Photoelectron spectroscopy (PES) gives detailed information about $E(\mathbf{k})$, but involves both occupied lower and unoccupied upper electron states. Accurate band mapping of one of these states, in particular of the dispersion perpendicular to the surface $E(k_\perp)$, requires that the other state is known. In PES, the lower bands are commonly mapped using empirical free-electron-like upper bands. This is not generally appropriate, as the upper bands of many materials are far more complicated.

The layered transition metal dichalcogenides [1] are typical examples of this. Extensive PES [2–5] and inverse PES (IPES) [6] studies have given good knowledge of the dispersion $E(\mathbf{k}_\parallel)$ parallel to the surface. However, mapping of $E(k_\perp)$ with free-electron-like upper bands have produced inconsistent results; also, additional structures due to multiple upper bands have been seen [7].

For materials with complicated upper bands, accurate PES band mapping therefore requires independent determination of the upper bands. As the photoemission final states are time-reversed LEED states [8], these bands are directly accessible by very-low-energy electron diffraction (VLEED), covering the energies about 0–35 eV relative to the vacuum level E_{vac}. Typical final state energies in PES band mapping are in this range.

VLEED band determination is based on the fact that the elastic electron reflection $R(E)$, or transmission $T(E) = 1 - R(E)$, is determined by the matching of a wave function in vacuum (plane wave superposition) to a wave function in the crystal (Bloch wave superposition $\sum_n T_n \phi_n$), under conservation of the momentum parallel to the surface $\mathbf{K}_\parallel$ [9]. $T(E)$ structures correspond to Bloch wave changes, which are associated with $E(k_\perp)$ irregularities.

Our scheme for VLEED band determination [10], recently extended to the excited-state description [11], uses an approximate *reference calculation* of $E(k_\perp)$ and the corresponding $T(E)$. The analysis is focused on the Bloch wave *partial transmissions* (PTs) $|T_n|^2$ [12]. The behavior of $T(E)$ is dominated by *coupling bands*, characterized by large PTs; the *irregularity points* (IPs) in these bands, characterized by extremal variation of $E(k_\perp)$ [11], cause the extrema in dT/dE. The experimental energies of these IPs are then directly found from the experimental dT/dE spectra. The coupling bands between the IPs are obtained by a reference *band interpolation*, or by band fitting. The procedure is simplified by neglecting the absorption $V_{\mathbf{i}}$ (*no-absorption approximation*), by which the IPs become ordinary *critical points* (CPs).

We report the first band mapping using combined VLEED and PES: The very complicated upper bands of VSe_2 were first determined by VLEED, and then used in mapping of the lower bands by PES. This enabled the first consistent $E(k_\perp)$ resolution for a layered material.

Unoccupied upper bands.—The VLEED experiment [13] was carried out with a standard four-grid LEED unit in the retarding field mode. Optimization of its operation, using explicit ray-tracing calculations [14], enabled precise VLEED measurements, with the beam diameter less than 1.5 mm. The $T(E)$ spectra were obtained by the target-current-spectroscopy technique, measuring the current absorbed by the sample. The elastic origin of the spectral structures was confirmed by their apparent $\mathbf{K}_\parallel$ dispersion.

A reference calculation of $E(\mathbf{k})$ and the corresponding $T(E)$ was made in the no-absorption approximation, as reliable excited-state calculations on VSe_2 are lacking. We calculated $E(\mathbf{k})$ within the local-density approximation of the density-functional theory (LDA-DFT) using the self-consistent linearized-augmented-plane-wave (LAPW)

method. $|T_n|^2$ and the total $T(E)$ were found from the LAPW bulk Bloch waves, using a conducting-Fourier-component group velocity (CFC-v_g) approximation [15]. The absorption was simulated (1) by damping the $T(E)$ variations in proportion to $1 - \frac{V_i(E)}{V_i^0}$, where $V_i^0 \approx 3$ eV, and (2) by Lorentzian convolution with half-width $V_i(E)$. We modeled $V_i(E)$ by a linear function with a Fermi-Dirac-like step at the plasmon threshold $E_{\text{thr}} \approx 16$ eV [3], and estimated the parameters from experimental spectra: $V_i(E) = 0.3 + 0.04E + \frac{1.0}{1+e^{-(E-E_{\text{thr}})/3.0}}$, with E in eV relative E_{vac}.

The VLEED band determination started with analysis of how the reference $E(k_\perp)$, in Fig. 1(a), is connected with the reference dT/dE, in Fig. 1(b) (dashed line): We identified the coupling bands as those having substantial $|T_n|^2$. At lower energies, each of their CPs produces an extremum in dT/dE. Close to 10 eV, the increased absorption V_i causes dT/dE extrema from adjacent CPs to overlap. Above the plasmon threshold $V_i \approx 1.5$–2.5 eV, which smoothes out almost all dT/dE structure.

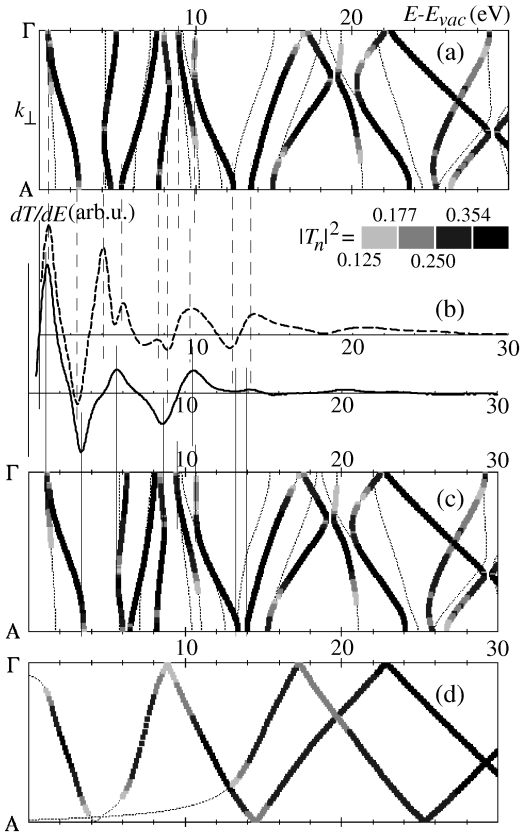

FIG. 1. VLEED band determination: (a) The reference $E(k_\perp)$ along ΓA with the PTs $|T_n|^2$ shown by gray scale, and [(b), dashed line] the normal incidence dT/dE. The corresponding CPs and the dT/dE extrema are indicated. [(b), full line] The experimental dT/dE, (c) $E(k_\perp)$ interpolated between the experimental CPs, and (d) the excited-state simulation for the principal coupling bands.

Next, the reference dT/dE was compared with the experimental one, in Fig. 1(b) (full line). In average, the experimental extrema (and the associated CPs) are at 0.7 eV higher energy, due to the self-energy correction $\Delta\Sigma$. The poor agreement between 4 and 9 eV is due to a common weakness of band calculations in this region. Everywhere else, the one-to-one correspondence between the extrema of the reference and experimental dT/dE is clear, and from their energy differences we mapped the corresponding experimental CPs. The whole bands, in Fig. 1(c), were obtained by band interpolation: we corrected the reference bands piecewise by linearly varying energy shifts to fit the experimental CPs [16].

The excited-state band smoothing was simulated: The principal coupling band branches were connected by real lines across the gaps, and the $k_\perp(E)$ were Lorentzian smoothed with half-width $V_i(E)$ in the extended zone scheme. The resulting bands, in Fig. 1(d), are exactly the upper bands required for PES band mapping [17].

A free-electron parabola $\frac{\hbar^2}{2m^*}(\mathbf{k} + \mathbf{G})^2 + V_{000}$ will fit the experimental upper bands only locally: the parameters m^* and V_{000} depend strongly on E and $\mathbf{k}_\parallel$, which makes such an approximation of the upper bands inadequate [13]. Without experimental VLEED corrections, also the smoothed calculated LAPW upper bands are inappropriate: the deviations are as large as 1.5 eV, leading in the PES band mapping to $k_\perp$ errors of up to $0.5|\Gamma A|$.

Conceptually, the main advantages of experimental VLEED bands are that they (1) are corrected from band calculation inaccuracies, and (2) include the true self-energy corrections.

The experimental upper bands were now used to optimize the PES experiment for accurate band mapping. From the experimental upper, and the calculated lower bands [18], we constructed the structure plot in Fig. 2: For every photon energy $\hbar\omega$, the plot shows the lower band energies $E_i - E_F$, for which a direct transition to an upper band is possible. The corresponding photoemission peaks have amplitudes proportional to the lower band

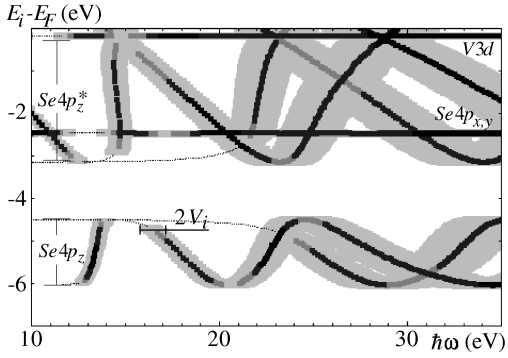

FIG. 2. Photoemission structure plot from the experimental VLEED upper bands, and LAPW lower bands. Of the amplitude factors, $|T_n|^2$ are shown by the gray scale of Fig. 1.

one-dimensional density of states $\frac{dk_\perp}{dE_i}$, to the matrix element $|M_{fi}|^2$, and to the PTs $|T_n|^2$. The peak broadening [19] is shown by shading; it is $2V_i$ horizontally if the hole lifetime is neglected. Vertical cuts of the plot correspond to energy distribution curves (EDCs), taken for $\hbar\omega = \text{const}$.

For *$k_\perp$-resolved band mapping* [13], the EDC peaks should be (1) clearly resolved from adjacent peaks, and (2) sufficiently narrow, compared to the bandwidth, that variations of amplitude factors $\frac{dk_\perp}{dE_i}$, $|M_{fi}|^2$, or $|T_n|^2$ within the peak widths do not shift the peaks from the $k_\perp$-conserving positions. According to these criteria, the plot suggests that the Se $4p_z$ band can be mapped using $16 \leq \hbar\omega \leq 20$ eV and, less accurately, $20 \leq \hbar\omega \leq 24$ eV; the Se $4p_z^*$ band using $15 \leq \hbar\omega \leq 23$ eV. To obtain sufficient $k_\perp$ sampling of these bands, $\hbar\omega$ should be changed in steps finer than 0.5 eV. Close to and above the plasmon threshold, the increasing V_i broadens the peaks, which may shift them from the $k_\perp$-conserving positions, or even merge them. Band mapping here is less accurate, or even impossible. Note that this detailed recipe for an appropriate PES experiment would not be available without the VLEED study, and that it differs significantly from common practice due to the complicated upper bands.

Occupied lower bands.—The PES experiment was done at the MAX-lab synchrotron radiation facility, Lund, Sweden. We measured normal emission EDCs, changing $\hbar\omega$ in 0.25-eV steps in the band mapping region below $\hbar\omega \approx 25$ eV, and in 0.5-eV steps above. The EDCs were scaled by normalizing the intensities between spectral peaks, and rendered to a gray scale intensity map $I(E_i, \hbar\omega)$, in Fig. 3. This map in fact combines the EDC mode with the constant-initial-state mode (cuts along $E_i = \text{const}$), and the constant-final-state mode ($E_i + \hbar\omega = \text{const}$) in one single representation. One easily recognizes some irrelevant peaks: core level peaks excited by higher-order-diffraction light as straight ascending lines, and inelastic secondary-electron-emission (SEE) peaks as descending lines with $E_i + \hbar\omega = \text{const}$. The remaining peaks are due to the lower bands, in agreement with Fig. 2: The two dispersionless peaks are due to the Se $4p_{x,y}$ and V $3d$ bands, and the dispersive peaks due to the Se $4p_z$ and Se $4p_z^*$ bands. The intensities differ from $|T_n|^2$, or even vanish, mainly due to $|M_{fi}|^2$ variations.

Of the dispersive peaks, not all are reliable for band mapping, as found from the plot in Fig. 2. For the Se $4p_z$ band, the peaks below 18 eV are reliable, except where they overlap with SEE features. From 22.5 to 24.5 eV they are less reliable because of increased broadening, and above 24.5 eV inappropriate because of merging of peaks from two upper bands. For the Se $4p_z^*$ band, the peaks below $\hbar\omega = 23.5$ eV are reliable, from 23.5 eV to 25 eV less reliable, and from 25 to 30 eV inappropriate. Above 30 eV, peaks corresponding to two upper bands are resolved, and may be used for band mapping, although they are less reliable because of large broadening. Here it is very clear how multiple upper bands produce spectral peaks corresponding to different $k_\perp$; such effects are often ignored in PES analysis.

For explicit mapping of the occupied bands, we used the EDC peaks in the specified regions, avoiding where they overlap with core level or SEE peaks, and obtained $k_\perp$ from the corresponding experimental VLEED upper bands in Fig. 1(d). Figure 4 shows the experimental points imposed on the LAPW bands. The points from the reliable regions are black, while those from the regions with large broadening are gray.

All experimental points from the reliable regions show strikingly consistent dispersions for both the Se$4p_z$ and the Se $4p_z^*$ bands. This consistency is in strong

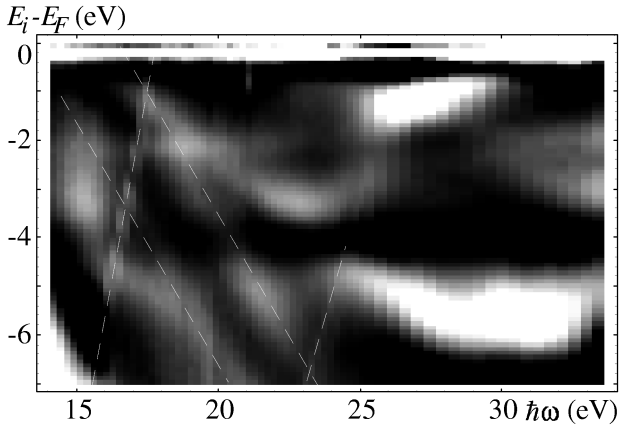

FIG. 3. Experimental photoemission intensity map. The contrast is increased by subtracting a smooth background.

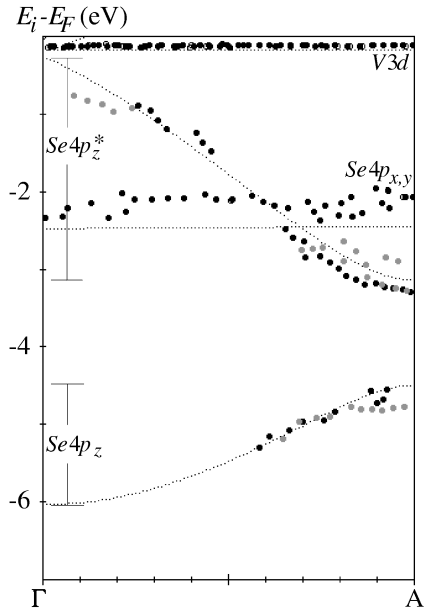

FIG. 4. PES band mapping using the experimental VLEED upper bands, imposed on the LAPW bands.

contrast to results for similar layered materials, obtained with free-electron-like upper bands, although empirically adjusted [2,5]. We stress that our results are free from any adjustable parameters, as the upper bands were determined in an independent VLEED experiment. Clearly, proper upper bands are crucial for consistent band mapping.

The gray points, corresponding to the less reliable regions, are apparently shifted towards the band interiors. This is expected, as the larger broadening of the EDC peaks induces peak asymmetry close to the band edges, which effectively shifts the peaks from their direct transition positions.

In conclusion, for the first time, a combination of VLEED and PES was applied to resolve $E(\mathbf{k})$ of a material with very complicated upper bands. The key point is that the VLEED experiment not only gave the proper upper bands, including the self-energy corrections, but also enabled optimization of the PES experiment for accurate mapping of the lower bands. The PES data, measured in accordance with this, were represented in an intensity map, which provided clear identification of the spectral structures. Mapping of the lower bands, from the direct transition PES peaks and the VLEED upper bands, gave consistent $E(k_\perp)$ in a layered material, for the first time.

Conceptually, we have proven that by combining VLEED and PES one can determine $E(\mathbf{k})$ (1) absolutely, without limiting approximations, and (2) completely, covering both upper and lower bands. One can perform the VLEED experiment using a standard LEED or IPES unit in the PES vacuum chamber, and interpret the data using a simple enchancement of any standard LDA-DFT band calculation. The combination of VLEED and PES extends accurate band mapping to many materials with complicated upper bands, in particular nonmetals. Similarly, VLEED can enchance IPES.

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[16] The noncoupling bands with $|T_n|^2 \approx 0$ do not reveal their CPs, and are therefore positioned less accurately; however, these bands give negligible contribution in PES too.
[17] VLEED band determination may be largely refined, particularly in the band smoothing simulation, if based on at least an empirical excited-state calculation [11].
[18] The analysis does not depend critically on a particular shape of the lower bands: Any curves suffice, which monotonously connect the band edges at Γ and A.
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