Momentum-transfer model of valence-band photoelectron diffraction

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Recent instrumental progress of valence-band photoemission in the X-ray range allows uncovering bulk- and surface-related electronic properties. Four-dimensional recording of energy and momentum-vector gives access to the complete spectral-density function. Systematic measurements for a number of transition metals between 15 eV-6 keV reveal unexpected strong intensity modulations due to photoelectron diffraction. Here, we present a graphical model that illustrates the role of momentum-conservation in Fermi’s Golden-Rule in an intuitive way. Intensity enhancement or reduction by factors >5 are confined to small energy- and momentum-intervals (widths 0.03 Å−1 and 200 meV). Laue-type diffraction involves the photon momentum and is intrinsic in the photoemission process, in accordance with Pendry’s final-state-model. At higher energies, Kikuchi-diffraction imprints additional modulations on valence-band-patterns and quasi-elastic background. The absence of photon-momentum transfer uncovers the extrinsic nature of Kikuchi-diffraction. For Re at 30 K and 3.4 keV the relative weight of the Kikuchi-branch is comparable to the Laue-branch, whereas at 6 keV the Kikuchi-branch prevails.
Thanks to the increased probing depth, angular-resolved photoelectron spectroscopy (ARPES) in the X-ray range is rapidly gaining importance in solid-state physics and materials research. Access to the true bulk electronic structure is an important achievement, e.g. for a detailed study of correlated and quantum materials. The potential of soft-X-ray ARPES is demonstrated in refs. 1, 2, a comprehensive overview of hard X-ray photoelectron spectroscopy (HAXPES) is given in ref. 3.

The wavelength of the excited photoelectron is smaller than the interatomic distances, giving rise to X-ray photoelectron diffraction (XPD). Core-level XPD (CL-XPD) is a powerful method probing the geometrical structure of the photo-emitting atomic layers, surface reconstruction and relaxation, as well as adsorbate sites and distances (see excellent overviews4−12). In early work angular-distributions were interpreted as being caused by photoelectron-reflection on lattice planes of the crystal12−15. A two-beam dynamical theory was applied to explain the azimuthal variations of intensities16,17. XPD cluster-models showed fair agreement for clusters down to few nm18; at higher energies a Bloch-wave approach to XPD has proven more appropriate19.

CL-XPD is well understood, but thus far, data for valence-band XPD (VB-XPD) are sparse (e.g. refs. 19−23) due to the complexity of the process. The roles of band dispersion, initial electron momentum and photon momentum in VB-XPD is not a priori clear. Early studies in the high-energy, high-temperature, low k-resolution limit revealed matrix-element weighted densities of states (MEW DOS), modulated by XPD effects19,21. The results could be interpreted analogously to CL-XPD after integrating over an energy range of a few eV23 or by the assumption of a localization of the band electrons20 as explained in orthogonalized-plane-wave approximation24. It was found that the initial-state orbital angular momentum influence the VB-XPD signal22. One-step photoemission theory made impressive progress at high energies25 and today is close to the stage of predicting VB-XPD features as shown in this article.

VB k-patterns in the hard X-ray range show a strong background from thermal-diffuse scattering, which is modulated by Kikuchi-type diffractions26. Its intensity depends on temperature and mass number of the relevant atom species and increases strongly with increasing energy and temperature, as described by photoelectron-recombination (also termed "time-reversed LEED-state"; LEED: low-energy electron diffraction) as introduced by Pendry et al.32−35.

Momentum microscopes observe a photo-transition directly in k-space, as illustrated in the k-space scheme (Fig. 2a, b) for Mo (110). In the periodic zone scheme, each Brillouin zone (BZ) contains the full set of valence bands. The spectral-density \( \rho(E_{\text{F}}, k) \) can be considered as a multitude of surfaces in 3D k-space (one for each value of \( E_{\text{F}} \)). Different energies then give different 2D-cuts (which we term energy isosurfaces) through this volume, one of which is the Fermi surface. These isosurfaces are often fragmented into isolated electron and hole pockets and appear as periodically repeated patterns, identical in all BZs. This notion is different from the conventional description in terms of E-vs.-k plots for certain high-symmetry k-directions. Energy isosurfaces are a convenient basis describing XPD for itinerant initial states because the initial k-vectors can easily be accounted for in the momentum-balance. The background patterns in Fig. 2a, b are cuts of the isosurfaces at \( E_{\text{F}} \) and \( E_{\text{F}} = 1 \text{ eV} \) in the plane of photon incidence (here [110]-plane as indicated by the dashed line in Fig. 2c).

Photon-energy \( \nu \) and photon-momentum \( k_{\nu} \) are both transferred to the photoelectron; energy- and momentum-balance have to be considered independent from each other. Energy conservation demands that all final states are located on a sphere with radius \( |k_{\nu}| \) given by Eq. (2). The \((k_{x}, k_{y})\)-schemes in Fig. 2a, b are to scale for the lattice constant of Mo. The transition at \( h\nu = 400 \text{ eV} \) leads to the fourth repeated BZ. The 4D-character of the photoemission process is evident: the photon-energy dependence for a given binding energy (Fig. 2a, for \( E_{\text{F}} \)) and the binding-energy dependence for a given photon energy (Fig. 2b, for \( h\nu = 400 \text{ eV} \)) both lead to sets of different final-state spheres.

Momentum conservation demands that the vector \( k_{\nu} \) must be added to each final-state momentum vector \( k_{\text{f}} \). This is equivalent
to a displacement of the centre C of the final-state sphere from the origin \( k = (0,0,0) \) by \( k_h \nu \). This shift of the sphere is directly visible in a \( k \)-microscope and can be quantified in the observed momentum patterns (see, e.g., Fig. 3 in ref. 29). The shift of the sphere by \( k_h \nu \) is relatively small at 400 eV but becomes substantial for hard X-rays.

Figure 2d–g shows 3D-views of four selected energy isosurfaces, the Fermi surface and those at \( E = 1, 2 \) and 3 eV. These surfaces have been determined experimentally as described in ref. 29; see Methods section. Clearly, the shape of the isosurfaces changes rapidly with binding energy, which is just a full-3D-view of band-dispersion. Bands with negative curvature at \( E_F \) have hole-character like the N-pocket (growing with increasing \( E_B \), compare (Fig. 2d, f)), positive curvature indicates electron-character like the octahedron centred at the \( \Gamma \)-point that shrinks with increasing binding energy. The background patterns in Fig. 2a, b are \((k_x, k_z)\)-cuts through the isosurfaces (Fig. 2d, e). In general, \( k_h \nu \) has an arbitrary direction with respect to the reciprocal lattice, and then schemes must consider full 3D \( k \)-space. The advantage of this representation is that it immediately shows all the initial \( k \)-vectors in a plane (Fig. 2a, b) or in 3D \( k \)-space (Fig. 2d–g) corresponding to a certain energy. This is an indispensable ingredient for the description of VB-XPD.

The umbrella-shaped caps of Fig. 2d–g mark the intersection areas of the given isosurface with the final-state sphere, here the NHP-plane. The band-structure pattern on the curved intersection area is observed by the momentum microscope. Thanks to the 3D-recording scheme of the ToF-microscope, all values of \( E_B \) in the energy-range of interest are recorded simultaneously. We note the analogy with the Ewald-sphere construction in electron diffraction: A diffraction spot occurs wherever the Ewald sphere intersects a reciprocal lattice point; a photoemission signal occurs wherever the final-state sphere (displaced by \( k_h \nu \)) intersects a band feature in one of the repeated Brillouin zones. The Ewald sphere does not give information on the intensity of diffraction spots or on systematic extinctions. Likewise, the intersection region of the final-state sphere with the periodic pattern of isosurfaces only shows where band features are visible in principle (obeying energy and momentum conservation). The actual photoemission intensity of a band depends on the matrix element in Eq. (1) that also accounts for the photon polarization (symmetry selection rules)31.

The 1D case of Bragg-scattering at lattice planes parallel to the surface. The proposed model of VB-XPD describes transitions from itinerant band-states to final-state plane waves (wavevector \( k_f \)) extending over many unit cells, being diffracted at the lattice.
This is the concept of Pendry’s model of the “multiple-scattering” photoemission final state\(^{22-34}\). In order to stay within the description of Fig. 2, we translate Bragg’s law to \(k\)-space. For constructive interference in normal-emission, the angle of incidence is close to normal emission, sketched as yellow circular components of the shift are |\(\nu\)| close to normal emission, sketched as yellow circular components of the shift are |\(\nu\)|. For Re(0001) in Fig. 3a, b.

The graphical expression of Eqs. (3) and (4) is shown in Fig. 3a, b. respectively. For low photon energies (\(\nu\)), the vector of the photon momentum \(\nu\) must coincide with the space \(d\) of the atom planes. In backward-scattering the path difference is twice the spacing \(d\). With the reciprocal-lattice vector perpendicular to the surface \(G\), the final-state electron momentum \(\nu\) = \(2\pi/\lambda\), we obtain the corresponding relations in \(k\)-space:

\[
\begin{align*}
d_z &= n\lambda/2 \quad k_f = nG_z \quad \text{forward} \quad \text{scattering}, \\
d_z &= n\lambda/2 \quad k_f = \nu G_z \quad \text{backward} \quad \text{scattering}.
\end{align*}
\]

Destructive interference occurs when the phase-shift difference is \(2\pi\)/2, which can be attenuated to the splitting by the vector of the photon momentum \(\nu\) must coincide with the space \(d\) of the atom planes. In backward-scattering the path difference is twice the spacing \(d\). With the reciprocal-lattice vector perpendicular to the surface \(G\), the final-state electron momentum \(\nu\) = \(2\pi/\lambda\), we obtain the corresponding relations in \(k\)-space:

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\end{align*}
\]

Vertex-band XPD in 3D \(k\)-space. Forward scattering is the most easily explained component of VB-XPD. However, it only captures a small fraction of all possible scattering processes involving arbitrary reciprocal lattice vectors \(G\) of 3D momentum space. The generalization of Eqs. (3) and (4) in 3D \(k\)-space is the Laue equation:

\[
k_f = k_f' - G.
\]

Momentum- and energy-balance demand the following five conditions: (i) the momentum of the electron in the initial anit state must be included, (ii) the photon momentum vector \(\nu\) is transferred to the photoelectron, (iii) the diffraction process itself obeys the Laue equation (momentum transfer \(G\)), (iv) the final-state energy \(\nu\) is preserved (all states lie on the same sphere, shifted by \(\nu\)), (v) the diffraction process leads to the same \(\nu\)-isosurface.

The \(k\)-space-model accounts for these conditions as follows: Energy surfaces like the experimentally determined ones in Fig. 2d-g give the complete initial \(k\)-distribution (i), which strongly depends on binding energy. Condition (ii) is fulfilled by a rigid shift of the final-state sphere by \(\nu\) with respect to \(\nu = (0,0,0)\). Final-energy-condition (iv) is fulfilled by plotting the
photo-transition on a final-state-sphere with radius $k_f$ (with the centre being shifted according to condition (ii)). Binding-energy condition (v) is fulfilled by plotting the isosurface with the correct $E_B$ as periodic pattern in the extended zone scheme, like the two cases in Fig. 2a, b.

The remaining task is to fulfil condition (iii). It means that we search for intersection points of the final-state sphere for a given $E_B$ with equivalent $k$-points in different repeated BZs, fulfilling the Laue equation. Such cases are illustrated in Fig. 3c, where the vectors $k_f'$ and $k_f''$ reach the same band feature as vector $k_h$, but in different BZs. The red circles in insets of Fig. 3d mark the $(E_B, k)$-regions, where the final-state sphere intersects such identical points. Their distances are given by certain reciprocal lattice vectors $G$. In complete analogy to the Ewald construction, energy conservation demands that both ends of $G$ must lie on the final-state sphere, which defines the $(E_B, k)$-region where the intensity is enhanced by VB-XPD. The scheme in Fig. 3e illustrates the 3D-nature of the momentum-transfer scenario. The planar detector-screen captures the projection of the curved cap.

All vectors $G$, which are completely inside of the final-state sphere, fulfil the diffraction condition on opposite sides of the circle (Fig. 3f) and at a multitude of positions on the sphere. Each of the dotted coloured lines $G1$–$G4$ represent a certain reciprocal lattice vector that is shifted such that it touches the sphere with both ends. Since $G$ is a reciprocal lattice vector, its two ends touch identical points of the (reduced) BZ. Each $G$ corresponds to a specific $(E_B, k)$-region on the shifted sphere where the Laue condition is fulfilled. If a band feature runs through such a region, its intensity is enhanced by VB-XPD.

Figure 3g–i shows an example for Mo at $h\nu = 1200$ eV, for the Fermi energy and a $k_z$-section through the NHP-plane of the BZ (Fig. 2c). The right V-shaped region on top of the isosurface is crossed by the final-state-sphere in two different BZs (Fig. 3g, h). In turn, the intensity of this feature in the measured momentum pattern is enhanced by VB-XPD (dashed ellipse in Fig. 3i). Here it becomes clear why the VB-XPD patterns look irregular and do not reflect the lattice symmetry: The shift of the final-state sphere by $k_{hv}$ breaks the symmetry. For example, in the case of Fig. 3f, the diffraction condition on the left and right side (red line $G3$) is fulfilled for different regions of BZ.

With respect to the “continuum” of kinetic energies the situation resembles Laue diffraction using a broad-band X-ray beam. However, the band dispersion poses additional constraints that—together with the broken symmetry—make the situation quite complex. “$k$-space movies” (Supplementary Videos 1–5) illustrate this puzzling behaviour.
are the different roles of the two relevant energies, $E_{\text{final}}$ and $E_{\text{fl}}$. The former defines the wavelength of the photoelectron, which governs diffraction dynamics. The latter defines the relevant isosurface of the spectral function $\rho(E_{\text{fl}}, \mathbf{k})$ which is strongly energy dependent, giving rise to the strong diffraction modulation on the eV-scale (Fig. 1a–c). In CL-XPD $E_{\text{fl}}$ is fixed and there is no $E$-vs.-$k$ dispersion; hence, only one energy- and one momentum-condition exist.

**Experimental results for near-normal emission.** Figure 4 shows a typical example for strong intensity enhancement around the centre of the $k_x$–$k_y$ distribution (Fig. 4a, b) with maximum intensity at $E_{\text{fl}} \approx 1.8$ eV, also visible in the $E_{\text{fl}}$–$k_x$ section (Fig. 4c). In comparison, $E_{\text{fl}}$–$k_x$ and $E_{\text{fl}}$–$k_y$ sections away from normal emission show a much lower intensity and more homogeneous intensity distributions along the bands (Fig. 4d, e). Figure 4f reveals the spectral dependence of the intensity-enhancement, integrated over the rectangular area marked in Fig. 4b. The diffuse background shows horizontal “stripes” of enhanced intensity in Fig. 4d, e, which are a fingerprint of quasi-elastic thermal-diffuse scattering. Their energy position (here $\sim 1.8$ and 3.3 eV) corresponds to maxima in the matrix-element weighted density of states (MEWDOS) as discussed in refs. 19,21,23,30. The MEWDOS stripes appear inhomogeneous, which might point on a directional dependence of the diffuse scattering effect.

We analyse the transition by the quantitative scheme in Fig. 4g, with $G_{1}$ = $G_{110}$ = $G_{1110}$ = 2.824 Å$^{-1}$ and $k_{hv} = 0.23$ Å$^{-1}$ ($k_{G_{1}} = 0.09$ Å$^{-1}$; $k_{G_{110}} = 0.21$ Å$^{-1}$). The intensity enhancement confirms Eq. (3) with $k_{G} = 4G_{110}$, shifted by the small value of $k_{hv}$ away from the $\Gamma$-point of the fourth repeated BZ. Such measurements provide a metric in $k$-space for the determination of the centres and boundaries of repeated BZs and for the empirical quantities $m_{\text{eff}}$ and $V_{0}$ in Eq. (2). Precise measurement of the energies of diffraction enhancement for two high-symmetry planes can yield both parameters. From the single measurement of Fig. 4, we derive $m_{\text{eff}} = 1.03 m_e$ ($1.04 m_e$) assuming $V_{0} = 10$ eV (6 eV). Here the resulting $m_{\text{eff}}$ depends only weakly on the assumed value of $V_{0}$.

This type of intensity enhancement occurs even in the VUV-range; see example for Re in Fig. 5. An intense spot of constructive interference appears in the centre of the $k_x$–$k_y$ images (Fig. 5a–c). The $E_{\text{fl}}$–$k_x$ sections (Fig. 5d–f) reveal that the enhancement is restricted to a small energy range of $\sim$200 meV. When varying the photon energy, this spot shifts in binding energy by the same amount, as revealed by the intensity profiles (Fig. 5g–i). Clearly, the constructive interference stays at fixed $E_{\text{fl}}$, because this energy is relevant for the diffraction dynamics. The change of the enhancement from band to band excludes a matrix element effect. In the vicinity of $E_{\text{fl}}$ there is a total bandgap at the $\Gamma$-point, so we cannot follow the trend up to the Fermi energy. Given the lattice constants of Re and $k_{G_{2}}$, $k_{G_{2}} = 0.20$ Å$^{-1}$ which agrees approximately with the given final state momentum. However, the final state is no longer free-electron-like, deviations from parabolic dispersion can occur and flat unoccupied d-bands can serve as additional final states.

**Experimental results of VB-XPD for arbitrary reciprocal lattice vectors.** The—at first sight puzzling—multitude of irregularly distributed regions of strong intensity enhancement observed for all materials studied so far (overview in Fig. 1) reflects the general case of Fig. 3c–i. Figure 6 shows an analysis for Mo(110) at $h\nu = 1700$ eV. With $k_{G} = 21.17$ Å$^{-1}$ this transition leads to the eighth repeated BZ; $k_{G_{2}} = 0.86$ Å$^{-1}$ shifts the sphere by 45% of the BZ radius. The diameter of the $k$-field of view in Fig. 6a is $\sim$6 Å$^{-1}$; hence, the first and fourth next BZs are visible. The $k_x$–$k_y$ cuts (Fig. 6a, b) show pronounced intensity enhancement in a small region within 200 meV from the Fermi energy, whereas no enhancement is visible in the $E_{\text{fl}}$–$k_x$ cut (Fig. 6c). Quantitative analysis by the transition scheme (Fig. 6d) reveals that the sphere crosses the identical feature for $k_{G_{2}} = 0.20$ Å$^{-1}$ (see details in Fig. 6e) and $k_{G_{2}} = 0.30$ Å$^{-1}$ (see details in Fig. 6e). Both constructive interference conditions lead to the observed intensity enhancement (dashed ellipses in Fig. 6a, b).

In the terminology of a diffraction experiment, the low- and high-index cases $G_{1110}$ and $G_{22140}$ belong to the zero-order and a higher-order Laue-zone, respectively. Due to the forward...
Fig. 5 Photon-energy dependence of valence-band photoelectron diffraction for Re(0001) between $\hbar\nu = 15$ and 16 eV. a–c Momentum distributions in the $k_x - k_y$ plane; d–f corresponding sections of binding energy $E_B$ vs. momentum component $k_x$ along the dashed lines in (a–c). g–i Binding-energy profiles of the intensities in the areas marked by rectangles in (a–c). The interference condition shifts with photon energy; steps of 0.5 eV correspond to momentum steps of only 0.04 Å$^{-1}$ along $k_z$.

Fig. 6 Analysis of valence-band photoelectron diffraction for the Mo(110) surface at $\hbar\nu = 1700$ eV. a Momentum distribution in the $k_x - k_y$ momentum plane showing an intensity enhancement in a small local region (dashed ellipse). b Section of binding energy $E_B$ vs. momentum component $k_x$ along the dashed line in (a) revealing the energetic localization close to the Fermi energy $E_F$. c $E_B$ vs. $k_y$ section showing that there is no intensity enhancement in this plane. d Quantitative analysis yielding that the final-state sphere runs through the eight repeated Brillouin zone along $k_z$ and crosses the identical feature for the Laue conditions $k'_f - k_f = G_{-110}$ (details in (e)) and $k''_f - k_f = G_{-210}$. Vectors $G$ are labelled by the Miller indices; the high index of 14 results from our choice of the $k_x$- and $k_y$-axes along crystallographic directions [110] and [110]. The photon momentum $k_{hv}$ causes a strong shift of the centre C of the sphere (details in (f)). The background pattern is the periodically repeated measured 4D array, cut at $E_F$ and $k_y = 0$ (dark is high spectral density). Full data array for 1700 eV; see Supplementary Videos 1 and 2.
characteristic of scattering at keV energies, the diffracted intensity is larger for the smaller scattering angle, i.e. the lower Miller index. Note that here we consider only a planar cut through one quadrant. There will be many more such conditions when the full final-state sphere in 3D k-space is considered.

The sequence for Mo at hν = 400 eV in Fig. 7 captures some snapshots. The way how the positions for constructive interference “travel” through (Ek, k)-space is best visible in Supplementary Videos 3–5. The cut at Ek (Fig. 7a) and the intensity profiles (Fig. 7b–d), taken in the rectangular areas marked in Fig. 7a, reveal a number of regions with locally enhanced intensities. Electron- and hole-pockets appear as oval features (Fig. 7a) with inward or outward dispersion; see cuts in Fig. 7e–l, taken along the dashed lines in Fig. 7a. Enhanced intensities appear mostly in the second BZ at negative kx and ky values and show almost “resonance-like” VB-XPD enhancements.

Proving that the interference stays fixed on the Efinal-scale like in Fig. 5 would require prohibitively long acquisition sequences in 0.5 eV photon-energy steps. In Figs. 4 and 6, high intensity in comparison with neighbouring bands and sudden intensity jumps along a band are used as criterion for VB-XPD. The enhancement in the electron ball (Fig. 7e) at the lower left rim of Fig. 7a shows a rather sharp cutoff at a binding energy of ~2 eV. Figure 7f shows the enhanced maximum of a band that stays well below Ek. Sequence Fig. 7g–j shows how the interference condition crosses the equivalent k-space object in the BZ at the bottom of Fig. 7a. The enhancement exhibits a characteristic “fine structure”. Figure 7k extends the analysis to the other side of the bottom BZ and finally Fig. 7l returns to the object of Fig. 7e, but at opposite kx and ky. The small spot in Fig. 7l appears an order of magnitude brighter as the surrounding bands. The horizontal stripes with enhanced brightness in Fig. 7a confirm the 3D-generalization of the graphical model in Fig. 3. For instance, in 3D the reciprocal lattice vector G3 responsible for the red lines in Fig. 3f yields a full cylinder touching the final-state sphere along two rings.

Coexistence of Laue- and Kikuchi-type VB-XPD in the hard X-ray range. At hard X-ray energies, a new type of diffraction signature appears; experiments were performed at beamline P22 of PETRA III. Results for Re at Efinal = 3.4 and 6 keV (Fig. 8) reveal that a significant background is superimposed on the as-measured valence-band k-distributions. This background is higher than for Mo at 1.7 keV (Fig. 6a). At 3.4 keV (Fig. 8a–h) valence-bands are visible as circles, originating from an electron-like tube centred at the A-point, and ellipses from elongated hole-pockets at the M-points. A lattice model is shown in Fig. 8i and the BZ with its high-symmetry points are defined in Fig. 8j. At Efinal = 6 keV (Fig. 8k–m) the background is even higher, the VB-pattern looks irregular and band-structure features are hardly discernible. The most eye-catching features are pronounced dark spots (marked by crosses), two bright regions at the upper left rim (dashed ellipses) and a bright X-shaped feature (centre marked by a circled cross). Here the field-of-view (~12 Å−1) comprises 19 BZs: the central one, and two rings with 6 and 12 BZs centred around it. On this large momentum scale, we observe something new. The as-measured VB-patterns (Fig. 8a, k) are modulated by pronounced long-range structures.

The key of understanding the long-range modulations lies in the comparison of as-measured VB k-patterns with CL-XPD...
patterns. Figure 8b, l shows core-level diffractograms taken at the Re4f signal (Fig. 8g). The photon energy was increased by 41 eV in order to shift the 4f7/2-signal to exactly the same final-state energy as the valence patterns; see spectra in Fig. 8g, h. All other settings of the microscope were kept fixed so that the k-scales stay identical, for later correction. At Efinal = 3.4 keV the 4f7/2-XPD-pattern (Fig. 8b) shows a system of Kikuchi bands crossing under 120°, whose intersection region is visible as a bright hexagon centred at [0001]-direction (circled cross). Position and size of the hexagon and dark areas in the XPD-pattern (Fig. 8b) agree with the structure imprinted on the valence-band-pattern in Fig. 8a.

The Re4f XPD-pattern at Efinal = 6 keV (Fig. 8l) exhibits a rich fine structure due to the shorter wavelength of the outgoing photoelectron and the larger inelastic mean-free path. It also shows a system of Kikuchi bands, dark spots (marked by crosses) and bright regions (dashed ellipses). The centre of symmetry (k = 0) shows a bright X-shaped feature (centre marked by a circled cross). All these characteristic features are visible in the measured valence-band momentum-image (Fig. 8k) as well. The model in Fig. 8i shows the lattice planes with distance d11-20, leading to the outgoing rays forming the Kikuchi band (width 2G11-20, see double arrows in Fig. 8b, l) in the k-microscope images. The centre of the images was shifted downwards in order to reach a larger radius in the upper part.
Following ref. 26, we eliminate the Kikuchi-modulation by multiplicative correction, yielding the pixel-by-pixel ratio of the as-measured VB-patterns (Fig. 8a, k) and the core-level diffractograms (Fig. 8b, l). In the ratio images (Fig. 8c, m) the diffraction modulation is largely eliminated and the true valence-band features are clearly visible. The two VB-patterns are different because at 6 keV the final-state sphere runs through the ΓMK-plane and at 3.4 keV close to the AHL-plane of the BZ (indicated by the dotted and dashed sectional planes in the BZ (Fig. 8j), respectively). The increased noise in Fig. 8m reflects the dramatic drop in cross section with increasing energy26,37. Close inspection reveals that Kikuchi diffraction acts on both the underlying background signal and the band features themselves. Remarkably, after the division regions of local intensity enhancement due to Laue-type diffraction are still present (marked by dashed ellipses in Fig. 8d, e).

The rigid shift of the entire VB k-distribution by the photon momentum is clearly visible in the difference between the centre of the Kikuchi patterns and the centre of the VB-patterns (marked by circled cross and circled plus in Fig. 8c, m, respectively). The Kikuchi patterns are symmetric to the crystallographic ⟨0001⟩-direction at k∥ = 0 (b, l). The VB-patterns are defined on the k-scale of the band states (kx, ky), which refers to the centre (Γ-point) of the band structure (Fig. 8c, m). The transfer of k∥ shifts the origin of the (kx, ky)-scaled (circled crosses) significantly away from the ⟨0001⟩-direction (circled plusses). The curvature of the final-state sphere is clearly visible for such large k-fields. The intersection contour of the sphere with the periodic patterns of BZs runs through different k-values, as explained in Figs. 2a, b and 3c. In turn, the patterns in Fig. 8c, m are not strictly periodic because at the rim the kz-values are smaller than in the centre. The photon polarization (p-polarized with electric vector tilted by 22° against the surface normal) causes asymmetries in the photoemission signal31,38, which are still significant in the HAXPES range39.

Discussion

We categorize the complex appearance of photoelectron diffraction into four different classes:

(i) Strong local intensity modulations (up to a factor of 5 in both directions) occur in the observed VB-patters in all spectral ranges studied (15 eV–7 keV). The signatures of this mechanism are its strong confinement in (E0, k) parameter-space to intervals down to ~200 meV and ~0.03 Å–1 and its lack of symmetry and any visible systematics. A graphical model based on Umklapp processes on the final-state energy sphere in k-space explains this type of XPD-modulation and its extremely rapid variation with energy and momentum. The missing symmetry in VB-XPD patterns reflects the transfer of photon momentum k∥ to the photoelectron, causing a rigid shift of the final-state sphere in k-space. We adopt the term Laue-type diffraction because VB-XPD deals with an energy band, similar to Laue-diffraction with an X-ray continuum.40 This mechanism is “intrinsic” to the photoemission process, as the transfer of k∥ enters into the selection of the electron-wave-vector of the final state. It has first been introduced by Pendry et al.32–35 in terms of the multiple-scattering final state (“time-reversed LEED-state”). The number of (E0, k)-regions in which the Laue condition is fulfilled increases with the number of BZs on the surface of the final-state energy isophere. For hν = 50, 400, 1700 and 6000 eV, the numbers of BZs on the surface of the sphere are about 25, 170, 708 and 2488, respectively (taking the parameters for Mo from Fig. 2).

(ii) In the hard-X-ray range another mechanism, Kikuchi-diffraction, contributes to VB-XPD and becomes dominant at energies of several keV. The signatures of this effect are the long-range modulation of the VB-patterns by Kikuchi-bands and -lines and the fact that the modulation patterns reflect the full lattice symmetry. Different from the almost resonance-like Laue-type intensity modulation, the Kikuchi-modulation acts on the entire field of view and is “extrinsic” to the photoemission process, without participation of photon momentum.

(iii) The quasi-elastic background underlying the VB-patterns also shows a pronounced Kikuchi-type diffraction signature, characterized by a strong intensity increase with increasing final-state energy and temperature (Fig. 4 of ref. 26). Although overlooked in the past, Kikuchi patterns in the background are not too surprising because such processes are also responsible for Kikuchi diffraction in scanning and transmission electron microscopy (SEM/TEM)41–43 as discussed in detail by Wang44. Unlike SEM/TEM this background extends over a continuous energy band (typically more than 10 eV) in photoemission. Stochastic quasi-elastic scattering events of VB-photoelectrons (mostly thermally induced) cause a localization of the scattered electron. The coherence with the final-state-wavefield is lost, but the scattered wave is coherent again and experiences Kikuchi-diffraction at the lattice. Unlike Laue-type diffraction, this mechanism is “extrinsic” to the VB-photoemission process, since initial coherence is lost and k∥ is not involved. We found Kikuchi-modulations imprinted on the valence-band k-distributions and their background for all single-crystalline samples studied so far (W, Mo, Re, Ir, graphite, Si, GaAs, SrTiO3, NbSe2 and other transition-metal dichalcogenides).

(iv) The fourth category of XPD-signature, well-known from previous work7,8,16,17, are the Kikuchi-patters in core-level XPD, i.e. for monoenergetic energy distributions. Recording such patterns is most important for the correction algorithm described in ref. 26. Comprehensive work in the field of electron microscopy (SEM and TEM) validated Kikuchi-diffraction as powerful tool for structural analysis41–44.

The long-range-modulations on the VB-patterns need additional discussion. If a k-randomizing scattering event (like in the classical Kikuchi-process) were involved, the bands in the intensity-enhanced regions would not stay sharp. Apparently, the high-energy Bloch waves of the photoelectrons excited in the direct transition (with well-defined k∥) experience Bragg-reflection at sets of lattice planes. This can be considered as “half” a Kikuchi-process (with missing initial scattering-step). This imprinted pattern has the same orientation, symmetry and metric as the classical Kikuchi-pattern imprinted on the background.

At this point we should have a look at the status of photoemission theories. The existing code for one-step photoemission calculations yields excellent agreement concerning band features observed with soft and hard X-rays36; it’s extension towards calculating VB-XPD by including photon-momentum and Laue-type Umklapp-processes is in progress. Measured CL-XPD patterns show excellent agreement with calculations using the Bloch-wave model between hν = 2.8–7.2 keV45. This opens a new avenue towards in situ structural analysis, simultaneously with VB-mapping. First results identifying two different sites of Te-atoms in a Si crystal, tracking an incommensurate–commensurate phase transition in TaS2 or first time-resolved pump–probe experiments46 give a glance on the potential of full-field imaging.
CL-XPD. New approaches like adapting a Bloch-wave model to VB-XPD might help to understand the experimental observations and understanding processes more quantitatively. In generalization of the analysis of Fig. 6, the appearance of VB-XPD patterns could be predicted by feeding measured 4D spectral-density functions into a suitable computer program that would automatically find all possible diffraction conditions for a given photon energy.

We can consider the Laue- and Kikuchi-scenario as two diffraction-branches with fundamentally different characteristics: The Laue-type Umklapp-process is intrinsic and happens on the final-state energy isosphere, which is shifted in $k$-space by the photon momentum $k_\text{ph}$. This diffraction branch can only be understood in a rigorous $k$-space treatment as presented in this paper. The Kikuchi signature, however, is extrinsic and governed by the orientation of the lattice planes and thus the modulation reflects the lattice symmetry. For Re at a temperature of 30 K and 3.4 keV the relative weight of the Kikuchi-branch is comparable by the orientation of the lattice planes and thus the modulation ranges are imaged with good focus in a single exposure. This instrument uses a DLD with 80 mm active area. The DLDs in both setups record count rates up to 10 MHz at a spatial resolution of $\sim 80 \mu m$ and time resolution of 30 ps, yielding 1000 countable time slices at the given pulse repetition rate of 192 ns for the 40-bunch filling pattern of PETRA III. The measured energy resolution of the combination of DLD and imaging ToF-spectrometer (0.9 m long) at a drift energy of 10 eV is 17 meV, measured in a low-energy experiment using laser excitation.

**Methods**

**Beamlines.** The experiments have been carried out at two beamlines (P04 and P22) of the synchrotron radiation source PETRA III at DESY in Hamburg and a UUV-beamline at BESSY II, Berlin. The hard X-ray measurements (Fig. 8) have been performed at beamline P22, which belongs to the beamlines with the highest brilliance worldwide in an energy range from 2.4 to 15 keV.\(^5\) Conditions for the present experiments were $2 \times 10^{12}$ photons/s at 4–6 keV in a spot of about 15 $\times$ 20 $\mu m^2$. Using the Si(111) double-crystal monochromator the bandwidth varies from 300 meV in the 3.4 keV range to 500 meV at 6 keV. The Si(311) monochromator crystal yields a three times smaller bandwidth. At 53.5 keV we measured 450 and 155 meV for the Si(111) and (311) crystals, respectively, and at 5.977 keV a FWHM of 62 meV using the Si (333) crystal.\(^6\) The resolving power for the (333)-crystal is $>10^4$. For the soft X-ray measurements (Figs. 1–4, 6 and 7) we used beamline P04 of PETRA III providing photons in the spectral range between 260 eV and 2 keV in a spot of $\leq 25 \mu m$ diameter. A photon bandwidth down to 30 meV at $h\nu = 1000$ eV provides an excellent energy resolution ($4 \times 10^9$) in this range. The ToF drift energy was set to 30 eV, corresponding to a detector resolution of 40 meV, matching the photon energy of the primary photon. The central task in the 3D approach is the measurement of the overall instrumental energy resolution of $\sim 50$ meV. For P22 and P04 the 40-bunch mode of PETRA III provides a pulse period of 192 ns, well matched to the 5 MHz count-rate capability of the delay-line detector. Photon pulse widths are about 50 ps rms.

For the measurements in the VUV-range (Fig. 5) we used beamline U125/10 m NIM at BESSY II, Berlin, providing VUV photons in the range from 4 to 40 eV with a very high energy resolution down to 0.5 meV. Photon flux in the single-bunch filling mode of the storage ring was up to $10^{12}$ photons/s in a spot of $\sim 100 \mu m$ diameter. The single-bunch mode of BESSY II has a pulse rate of 1 MHz.

**Instruments.** All results except those in Fig. 8 have been obtained with the ToF momentum microscope described in ref. 27. It combines the electron-optical imaging column\(^2\) developed at the Max Planck Institute (Halle, Germany) with the ToF-recording technology of the Mainz group.\(^3\) Figure 1a shows the recording geometry. The instrument exploits a general principle of optics: in the Fourier plane of the objective lens (back focal plane) a momentum image ($k$-image) is formed, which is a key feature for low-energy electron microscopy.\(^22\) The subsequent zoom lenses project this $k$-image on the entrance plane of the image microscope (field-of-view detector (DLD)). For each selected time-of-flight in the low-energy drift section of the microscope column is recorded, exploiting the time structure of the synchrotron radiation. ToF is converted into kinetic energy and calibrated at the Fermi edge yielding the binding energy $E_B$. A size-selectible field aperture in an intermediate real-space image plane facilitates the selection of well-defined source areas on the sample surface down to the $\mu m$-range. The measured $k$-field of view has a linear momentum scale up to a diameter of $\sim 7 \AA^{-1}$; for larger fields a significant field curvature appears (a well-known effect for wide-angle lenses). The deterministic part of the Coulomb interaction between the valence electron and the core electrons of the secondary electrons was corrected employing the concept described in ref. 56.

For the investigation of the long-range Kikuchi-type diffraction patterns taken with hard X-rays from beamline P22 (results in Fig. 8), we used a ToF $k$-microscope with new optics, optimized for high initial kinetic energies up to $>8$ keV. Its novel type of objective lens can image large $k$-field diameters up to $\sim 70 \mu m$, comprising many Brillouin zones in parallel. The small photon footprint of $\sim 20 \times 30 \mu m^2$ causes a large depth of focus of the $k$-images. In turn, large energy ranges are imaged with good focus in a single exposure. This instrument uses a DLD with 80 mm active area. The DLDs in both setups record count rates up to $\sim 5$ MHz at a spatial resolution of $\sim 80 \mu m$ and time resolution of 30 ps, yielding 1000 countable time slices at the given pulse-repetition rate of 192 ns for the 40-bunch filling pattern of PETRA III. The measured energy resolution of the combination of DLD and imaging ToF-spectrometer (0.9 m long) at a drift energy of 10 eV is 17 meV, measured in a low-energy experiment using laser excitation.

**Data recording.** Valence-band 3D data arrays $I(E_B, k_x, k_y)$ were recorded with acquisition times of typically 20 min at P04 and about 1 h at P22. The acquisition of core-level XPD patterns like in Fig. 8 is faster. The two momentum coordinates ($k_x$, $k_y$) are observed by full-field $k$-imaging and many binding energies $E_B$ are taken simultaneously in a single exposure by recording the time coordinate (referenced to the photon pulse) of each individual counting event in the DLD. The sample is mounted on a He-cooled hexapod manipulator for precise six-axis adjustment. Most data have been recorded at sample temperatures around 30 K. The circularly polarized (at P04) or p-polarized photon beam (at P22) impinges at 22° with respect to the sample surface (Fig. 1a).

The high parallelization of data acquisition and the high brilliance of the beamlines compensate for the strong decrease of photoemission cross-section with increasing photon energy towards the hard X-ray range (Fig. 1 in ref. 26). Count-rates exceeding $10^8$ counts per second in an interval of $\sim 15$ eV are obtained in the valence range at all photon energies used. When recording core-level signals, a proper attenuation of the X-ray beam was necessary in order to avoid excessive count rates.

We could consider the momentum- and energy-resolution at high energies in the several-keV range. The band features appear sharp up to the maximum photon energy used (here 6 keV). With increasing binding energy the reduced lifetime of the photo-hole leads to a broadening of the band features. At $E_B$ this broadening vanishes but at $E_B \sim 5$ eV the hole lifetime is 12.5 fs corresponding to 50 meV, being in the order of the overall instrumental resolution mentioned above. We do not observe a final-state broadening or smearing of $k$-resolution with increasing energy. This is most likely connected with the fact that the reciprocal space is a periodic pattern of BZs. Thus, except for the matrix elements that depend on photon energy, these patterns should be equivalent for direct and inverse counting to low- or high energy repeated Kikuchi-like patterns. The $k$-resolution argument is even in favour of high $k$-resolution at very high energies, because more and more unit cells contribute to the observed signal. Given the present experimental conditions we did not expect to observe recoil effects\(^22\); this issue is subject of ongoing experiments.

**Determination of the Fermi surface and other energy isosurfaces.** Iso-surfaces like those in Figs. 2 and 5 are determined as follows (for an explicit example, see ref. 29). From the 4D spectrum of the real-space sample $\rho(E, k_x, k_y)$ from which all energy isosurfaces, the electron velocity distribution at the Fermi surface and any other energy surface can be easily derived by simple algorithms. The lens optics is set to acquire 3D data arrays $I(E_B, k_x, k_y)$ with momentum slices of diameter $\sim 20\%$ larger than the BZ in a binding-energy range of $\sim 6$ eV width. A typical binning size for such measurements is 18 meV, yielding 230 momentum slices. Acquisition of such a 3D data array takes 10–20 min. The third momentum component $k_z$ is varied by appropriate setting of the photon energy, as explained in Fig. 2a. For the isosurfaces of Mo and Re we took 20 equally spaced 3D arrays, covering the full selected BZ in detail. A sufficiently small step size for $k_z$ accounts for the fact that for Mo and Re the isosurfaces are fragmented with several isolated electron and hole pockets (Fig. 2c–f). The $k$-slices of all 3D arrays are concatenated along the $k_z$-axis forming the 4D array, being the discretized experimental mapping of the so-called removal part of the spectral function $\rho(E_B, k)$, with intensities being weighted by the corresponding matrix elements. In the small photon energy range the remaining part of the spectral function $\rho(E_B, k)$ is a constant. All other energy surfaces are defined analogously. The Fermi velocity or any other group velocity
$v_{\theta}(k)$ is oriented perpendicular to the corresponding isosurface and is given by the gradient of $E(k)$ in $k$-space at the energy of interest.

**Sample preparation.** The refractory metal crystals W, Mo, Re, Ir were cleaned by repeated cycles of heating in oxygen followed by desorption of the surface oxide by a flash at high temperature. The base pressure during the experiment was $4 \times 10^{-10}$ mbar. Prior to the soft X-ray measurements the surface quality was verified by LEED. Layered samples like graphite and the transition-metal dichalcogenides were cleaved in UHV prior to transfer to the microscope chamber. No traces of impurities, as judged, for example, by C 1s and O 1s spectra, were present in the spectra. Since it is operated in the shielding hatch at P22 all lens voltages, the data acquisition system and all mechanical adjustment parameters (hexapod, frame position, apertures of the microscope) are fully remotely controlled.

**Data availability**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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**References**

1. Fadley, C. S. & Nemsak, S. Some future perspectives in soft- and hard-X-ray photoemission. *J. Electron. Spectrosc. Relat. Phenom.* 199, 408–423 (2014).

2. Strocco, V. N. et al. k-resolved electronic structure of buried heterostructure and impurity systems by soft-X-ray ARPES. *J. Electron. Spectrosc. Relat. Phenom.* 236, 1–8 (2019).

3. Wicke, J. C. (ed.) *Hard X-ray Photoelectron Spectroscopy (HAXPES)*, Springer Series in Surface Sciences, Vol. 59 (Springer International Publishing, Switzerland, 2016).

4. Fadley, C. S., Van Hove, M. A., Hussain, Z. & Kaduwela, A. P. Photoelectron diffraction: new dimensions in space, time, and spin. *J. Electron. Spectrosc. Relat. Phenom.* 75, 273 (1995) and references therein.

5. Woodruff, D. P. & Bradshaw, A. M. Adsorbate structure determination on surfaces using photoelectron diffraction. *Rep. Prog. Phys.* 57, 1029 (1994).

6. Westphal, C. The study of the local atomic structure by means of X-ray photoelectron diffraction. *Surf. Sci. Rep.* 50, 1–106 (2003).

7. Winkelmann, A., Fadley, C. S. & Garcia de Abajo, F. J. High-energy photoelectron diffraction: model calculations and future possibilities. *N. J. Phys.* 10, 113002 (2008).

8. Fadley, C. S. X-ray photoelectron spectroscopy: progress and perspectives. *J. Electron. Spectrosc. Relat. Phenom.* 179, 2 (2017).

9. Woodruff, D. P. Surface structural information from photoelectron diffraction. *J. Electron. Spectrosc. Relat. Phenom.* 178–179, 186 (2010).

10. Osterwalder, J. in *Handbook on Surface and Interface Science*. 20. Herm. G., Tran, T. H., Higashiyama, K. & Fadley, C. S. Multiple photoelectron diffraction and direct transition effects. *Phys. Rev. Lett.* 68, 1204 (1992).
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Author contributions
G.S. and H.-J.E. wrote the paper and coordinated the project. K.M., S.B., D.V., M.E., O.F., S.C. and B.S. set up and carried out the experiment and prepared the samples. All authors discussed the results and contributed to the writing of the manuscript.

Competing interests
The authors declare no competing interests.

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