# Excited States Mapped by Secondary Photoemission

M. Bovet,[1] V. N. Strocov,[2] F. Clerc,[1] C. Koitzsch,[1] D. Naumović,[3] and P. Aebi 1[1]
[1]*Institut de Physique, Université de Neuchâtel, CH-2000 Neuchâtel, Switzerland*
[2]*Swiss Light Source, Paul Scherrer Institut, CH-5232 Villigen, Switzerland*
[3]*Département de Physique, Université de Fribourg, Pérolles, CH-1700 Fribourg, Switzerland*

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We report on angle-resolved photoemission (ARPES) experiments on Cu(110) using Mg $K_\alpha$ radiation. The secondary emission (SE) fine structure of electrons below 50 eV is found to map the *empty* band structure relevant for absolute band mapping in ARPES. The finding is based on a direct comparison of our experiments with very low-energy electron diffraction data [Phys. Rev. Lett. **81**, 4943 (1998)] recently shown to map the unoccupied states representing the photoemission final-state. This suggests a new theoretical approach to the SE process treating the outgoing electron state as the time-reversed diffraction state.

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Angle-resolved photoemission (ARPES) is a unique and widely used experimental technique to determine the electronic band structure of solid materials. For three-dimensional (3D) materials, however, ARPES suffers from an inherent difficulty with the determination of the wave vector component of the electron perpendicular to the emitting surface ($k_\perp$). Because of the electron escaping into vacuum, thereby crossing the surface potential barrier, $k_\perp$ is not conserved whereas the parallel component of the electron wave vector $k_\|$, is. Recently, a solution to this problem has been found via the very low-energy electron diffraction experiment (VLEED). [1] The authors have demonstrated that a *combination* of VLEED and ARPES allows for *absolute* band mapping, resolving the three-dimensional wave vector $\vec{k}$.

In the present article we show that the information provided by VLEED can be obtained within the ARPES experiment itself. Therefore the possibility exists for absolute band mapping within the single experiment of ARPES. The important point is to collect the very low-energy part of the energy distribution curves (EDCs) instead of the part with the highest energy, i.e., close to the Fermi level ($E_F$). In fact, the lowest energy part consists of the secondary electrons which are cut off on their low-energy side by the vacuum level.

Secondary electron emission (SEE) is a complicated, multiple stage process, involving electron excitation, relaxation, and surface transmission [2–4]. Commonly, secondary electrons have been excited with a beam of low-energy electrons ($< 1$ keV) along the normal of the crystal surface. The energy distribution curve of electrons then has a main, structureless maximum corresponding to slow secondary electrons, with a superimposed fine structure of well-defined energies (characteristic of the crystal), independent of the primary electron energy $E_p$. In order to explain the fine structure, theories of SEE traditionally emphasize electron accumulation near the critical points of the bands. In this so-called statistical approach, the electrons are emitted from Bloch's high-level states that are statistically occupied. However, comparison of SEE data with state-of-the-art band calculations shows that such theories are hardly relevant. This is because they neglect crucial ingredients of the SEE process such as electron transport to the surface and surface transmission. In particular, the group velocity vanishing in the critical points acts in fact to cancel the electron accumulation effects in the SEE spectra. There is another theory, the thermodynamic approach [5], where the emission and reflection intensities of the surface are connected. It uses simplifications to reduce the problem of calculating the fine structure in SEE by calculating low-energy electron diffraction (LEED) intensities. But the validity of the approximations are hard to verify. In fact, such a connection between LEED and SEE would be particularly interesting because recent experimental and theoretical studies have shown (see, e.g., [1]) that the LEED fine structure in the range of small energies ($\leq$ 50 eV) is governed by the energy dispersion of unoccupied high-level electronic states and reflects the band boundaries in the electron dispersion of states moving in the direction of detection. Based on the fact that photoemission (PE) final states are time-reversed LEED states [6–8], and that they are accessible by the VLEED experiment [6,8], Strocov *et al.* [1,9,10] have been developing for the last decade an experimental method to determine the electronic band structure in crystalline solids absolutely.

In this Letter, experimental ARPES spectra have been collected in the energy range of secondary electrons on Cu(110) and are compared to the results obtained by VLEED [1]. We demonstrate that the SEE fine structure in its relation to the unoccupied band structure is fully equivalent to the one of VLEED, and support this by a new model of SEE which treats the state-of the outgoing secondary electron as a time-reversed LEED state incorporating thus all the finite electron lifetime, electron transport, and surface transmission effects. This opens the possibility to measure final-state and valence band structure in one single photoemission experiment and, using the methods of determination of the final-state dispersions and lifetimes developed for VLEED, perform photoemission band mapping under full control of the three-dimensional (3D) wave vector.

ARPES EDCs have been collected at room temperature in a modified VG ESCALAB Mk II spectrometer using Mg $K_\alpha$ ($h\nu = 1253.6$ eV) photons. In order to avoid saturating the detector on the secondary electron intensity maximum, spectra were collected in the constant retarding ratio mode [11]. In this mode, the energy resolution is approximately 1% of the kinetic energy. The sequential motorized sample rotation has been outlined elsewhere. [12] The angular resolution was 1°. The Cu(110) surface has been prepared by standard sputtering ($\mathrm{Ar}^+$, 1 keV) and annealing (550 °C) cycles. Cleanness has been checked by x-ray photoelectron spectroscopy and crystallinity by LEED. x-ray photoelectron diffraction was used to determine the sample orientation *in situ* with an accuracy of better than 0.5°.

Figure 1 shows the raw data taken along the $\bar{\Gamma}$-$\bar{X}$ direction. Spectra have been taken every 2° and the scanning was stopped at 60° off-normal emission. The energy is measured with respect to $E_F$. The cutoff at low energies is due to the vacuum level ($E_V$). Electrons with lower energy cannot exist in vacuum and therefore cannot be detected. On top of the smooth background characteristic maxima are observed which disperse in energy with varying angle. In order to remove the background the first derivative of the spectra $dI/dE(\theta)$ was taken and then transformed from the emission angle $\Theta$ into $K_\parallel$ (by parallel momentum conservation equal to $k_\parallel$ in the crystal) This data is shown in a gray scale representation in Fig. 2 for both the $\bar{\Gamma}$-$\bar{X}$ and the $\bar{\Gamma}$-$\bar{Y}$ directions of the surface Brillouin zone of the Cu(110) surface. The dark and clear parts correspond to minima and maxima of the derivative, respectively. The lower part ( $< 20$ eV) was completed with a much better statistics. The region below $E_V + \hbar^2 K_\parallel^2/2m + 2$ eV was clipped as in the presentation of VLEED data in [1]. We observe various lines with a highly dispersive behavior. The (b) panel of Fig. 2 shows corresponding VLEED data [1] on the $K_\parallel$ dispersion of the current transmitted into the sample, represented in the same way.

Comparison of the above $dI/dE$ dispersion maps shows their very good agreement. In (a), the fact that the upper part ( $> 20$ eV) is independently gray scaled, let it appear with stronger contrasts than for the VLEED result. On the other hand, the good statistics of the VLEED in this energy range makes the features sharper. The region marked by arrow A illustrates well these two aspects.

Agreement is excellent except for feature $B$ which cannot be seen on Fig. 2. However, if contrast is strongly enhanced feature $B$ is also revealed in the VLEED experiment (see Fig. 3 in Ref. [1]). These very low-energy features are affected by the experimental electromagnetic environment and may depend on the setup [1]. All in all, our experimental data show that the *fine structure* of the

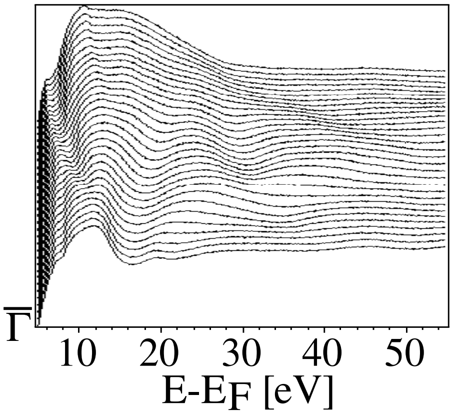

FIG. 1. Secondary electron fine structure dispersion on Cu(110): Angle-scanned raw spectra (polar angle step 2°) taken along the $\bar{\Gamma}$-$\bar{X}$ high symmetry direction. The normal emission direction spectrum is marked by $\bar{\Gamma}$.

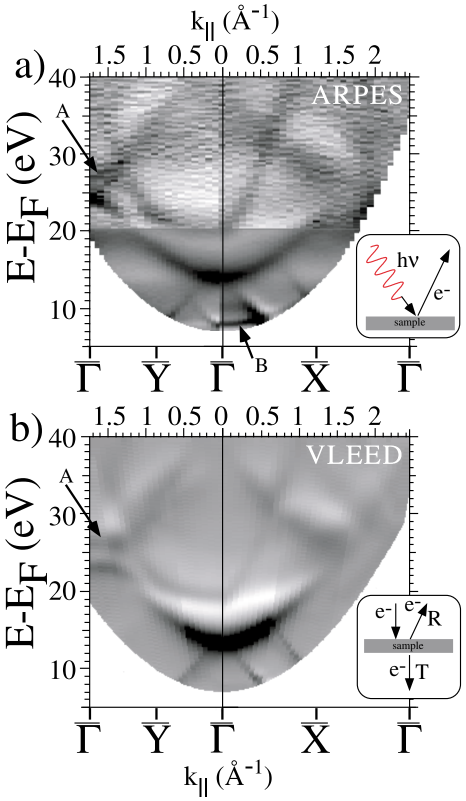

FIG. 2 (color online). Comparison of the extrema of the derivative of the secondary photoemission (a) with VLEED-results of Strocov *et al.* Ref. [1]. (b). The bottom of (a) was measured with better statistics. See text.

SEE spectra replicates that of the VLEED spectra in detail.

Based on the observed equivalence of the SEE and VLEED fine structure, we can now trace how the SEE spectra are related to the unoccupied band structure. In the VLEED experiment an electron beam is injected into the crystal and the target current is measured as a function of the electron energy and injection angle, thereby measuring the reflection ($R$) or transmission ($T = 1 - R$) coefficient. The VLEED analysis is based on the fact that the elastic electron scattering of a crystal surface is determined by the matching of the wave function in vacuum $\Phi_v$ (superposition of plane waves) to the wave function excited in the crystal $\Phi_c$ (a superposition of decaying Bloch waves $\sum_n T_n \phi_n$). The structure of $R(E)$ displays then changes in composition of the Bloch waves—or rather those which effectively couple to the vacuum plane waves—which is related to their dispersion $E(\vec{k})$. In a simple picture we can understand this by realizing that the reflection of electrons with a given $\vec{k}_{\|}$ and energy will be maximal if (for all $\vec{k}_{\perp}$) there are no states available in the solid (i.e., it is not possible to inject electrons). It means that the reflectivity is sensing the band gap of the matching or coupling Bloch state dispersion $E(\vec{k}_{\perp})$, or, the so-called critical points (CP), where the density of states is high, of coupling bands. In quantitative terms, the inflexion points of the VLEED spectra, manifested by the extrema of their energy derivative $dI/dE$, all reflect the CPs of the bands coupling to vacuum [see [1] for detailed relation to the band structure for the case of Cu(110)]. Our experimental results demonstrate that the same relation to the band structure extends to the SEE process. Therefore, the SEE dispersion follows the one of the bulk excited states of the unoccupied band structure of coupling bands. Hence the dispersion of the angle-resolved secondary photoemission spectra ($dI/dE$) illustrates the dispersion of the CP's of the coupling bands.

The statistical theory has deficiencies to describe our results: Whereas it considers the critical points to be manifested as the SEE *spectral peaks*, we find that these points are in fact reflected by *extrema* of the SEE energy derivative. Such a contradiction highlights two fundamental deficiencies of the statistical theory: (1) Whereas it implicitly assumes that the surface transmission is equal for all Bloch waves, in fact it dramatically varies depending on their coupling properties, and even completely suppresses emission out of noncoupling ones. (2) Whereas the outgoing electron wave function is assumed propagating, the finite electron lifetime results in that it is described as decaying in time as $\Phi(\vec{r}, t) = \Phi(\vec{r}) e^{t/\tau} e^{-i(Et/\hbar)}$, where $\tau$ and $E$ are the excited-state lifetime and energy [13,14], and the wave function coordinate-dependent part $\Phi(\vec{r})$ appears as a Bloch wave exponentially decaying in space, as described by complex $\vec{k}$.

Our experimental results give a hint to a more appropriate theory of the SEE process, in particular, under photoexcitation. During the primary photoexcitation a high energy photon is ejecting an electron. In different secondary scattering processes, this photoelectron gives rise to a cascade of secondary electrons which tend to "thermalize" in scattering states where interference on the crystal potential is constructive. If such states in addition effectively couple to vacuum, the secondary electrons from them will escape into vacuum and can consequently be detected. The observed equivalence of SEE and VLEED fine structure evidences that the SEE final-state $\Phi^f_{\mathrm{SEE}}$, describing the outgoing electron, is exactly *the time-reversed LEED state* $\Phi^*_{\mathrm{LEED}}$.

This picture of the SEE process is similar to the one-step theory of photoemission (see, e.g., [6–8]) which finds the photoemission intensity as a matrix element between the initial state and the time-reversed LEED state. The only difference is that whereas the photoemission intensity is built up by phototransitions from the valence states, the SEE intensity is created by cascade electron transitions from the states higher in energy. Moreover, in the SEE process modulations of this excitation term in amplitude and phase are averaged out by integration over a wide energy and $\vec{k}$ range of all contributing states at higher energies, and $\Phi^f_{\mathrm{SEE}}$ appears exactly proportional to $\Phi^*_{\mathrm{LEED}}$ (note that this requires the use of sufficiently high primary excitation energy as in our experiment). Its excitation amplitude, determined by the overlap of all higher-energy states with $\Phi_{\mathrm{LEED}}$, reduces then to the $\Phi_{\mathrm{LEED}}$ integral electron density in the crystal $\int_{\Omega} |\Phi_{\mathrm{LEED}}|^2 d\vec{r}$. In particular, if a band gap is encountered, penetration of $\Phi_{\mathrm{LEED}}$ into the crystal decreases due to stronger elastic scattering off the crystal potential. Therefore, as in the case when measuring transmission in VLEED, band gaps in the coupling unoccupied bands are manifested by minima in the SEE spectra. This fact is immediately seen in our experimental data (see Fig. 1).

Note that by scrutinizing $\Phi_{\mathrm{LEED}}$ our theoretical picture embeds the finite lifetime and surface transmission effects missing in the statistical SEE theory. Although it arrives at the same conclusions as the thermodynamical theory [5], it does not rely on severe approximations such as small variations of the effective secondary electron temperature $T_{\mathrm{eff}}$.

Compared to previous works such as [2–4] there are two main differences. First, most previous work, as for instance the recent one described and analyzed by Panchenko *et al.* [3] is done with electron excitation and mainly normal emission data is analyzed. Here, we excite with soft x rays, i.e., Mg $K_\alpha$ radiation. The use of high excitation energies with concomitant averaging over $k$ space is essential for the SEE fine structure to fully

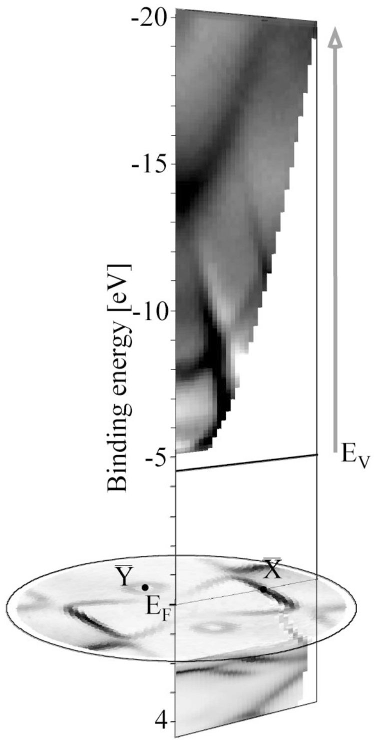

FIG. 3. Sketch of photoemission mapping possibilities, as extended now with the secondary photoemission. Above the vacuum level, unoccupied bands may be probed (arrow).

develop. Also, we present data on an extensive angle-range. Second, the previous works were based on the statistical theory. The new theoretical model we suggest is based on the excellent agreement of our fine structure data with the one of VLEED experiments, where the theoretical model is already established. Therefore, the VLEED model can be adapted to establish a new model for the secondary electrons, in particular, when excited with soft x rays. The comparison with VLEED indicates the importance of considering the inverse LEED state formalism together with its coupling strength to bulk Bloch states, which are both not considered within the statistical theory framework [2–4].

From our experimental evidence we may then draw an extended picture, as shown in Fig. 3, for what is possible from an ARPES experiment. First of all, from traditional ARPES it is possible to do Fermi surface mapping and band mapping. A section across the bulk Fermi surface oriented along the Cu(110) surface normal is plotted at zero binding energy within ($k_{\|}$) space. At positive binding energies, below $E_F$, we observe dispersing $d$ states along $\bar{\Gamma}$-$\bar{X}$ and the $sp$ band crossing $E_F$ near the $\bar{X}$ point. At higher energies, i.e., above the vacuum level we are able, as explained above, to observe the critical point dispersion of coupling bands in the empty states of the band structure.

In conclusion, we report experimental evidence for the presence of unoccupied state dispersion in the SE fine structure of Cu[110] when excited by photoemission. By comparison with the results of the VLEED method these dispersing states are identified as the dispersion of critical points of coupling states of the empty band structure. In its relation to the unoccupied band structure SEE is equivalent to VLEED. This observation leads to a new theoretical picture of the SEE process based on the time-reversed LEED description of the outgoing secondary electrons, which goes beyond the statistical theory of SEE by incorporation of the finite lifetime and surface transmission effects. In particular, the present experiments show that in the future photoemission might be able to determine the full wave vector, in analogy with the developments in VLEED, and not only be restricted to the conserved parallel component mapping. As a consequence, absolute band structure mapping, self-energy effects studies [15] could be undertaken in one, single photoemission experiment.

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