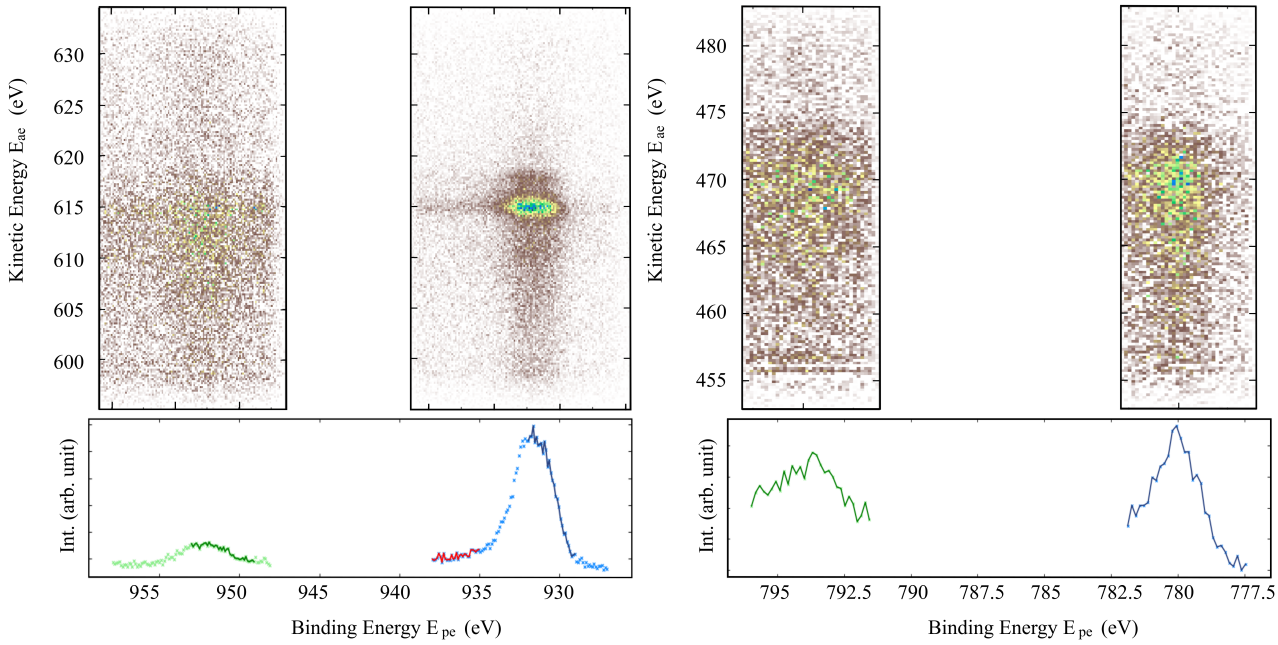
Supplementary information: The degree of electron itinerancy and shell closing in the core-ionised state probed by APECS in transition metals†

Artur Born,[a,b,c*] Fredrik O.L. Johansson,[d,e,‡*] Torsten Leitner,[a,b] Ieva Bidermane,[a,b] Danilo Kühn,[a,b] Nils Mårtensson,[a,f] and Alexander Föhlisch[a,b,c,§]

Data acquisition and treatment

In case of Cu $h\nu = 1400\,\mathrm{eV}$ photon energy was used in the presented experiment. One spectrometer was tuned to detect the $L_{2,3}VV$ Auger electron region. The other spectrometer was set up for photoelectron detection. In order to improve the energy resolution of the Auger electrons, the sample was biased with approximately 300V in order to slow down the electrons. This comes at the cost of a smaller energy window. Therefore, two measurements were done, one for the $L_{2,3}VV$ Auger electrons in coincidence with the L_3 photoelectrons and one for the $L_{2,3}VV$ Auger electrons in coincidence with the L_2 photoelectrons. Both maps and the resulting coincidence photoelectron spectra are shown in Fig. 1a. The kinetic or binding energy scales are always corrected such, that the peaks match literature values[1].



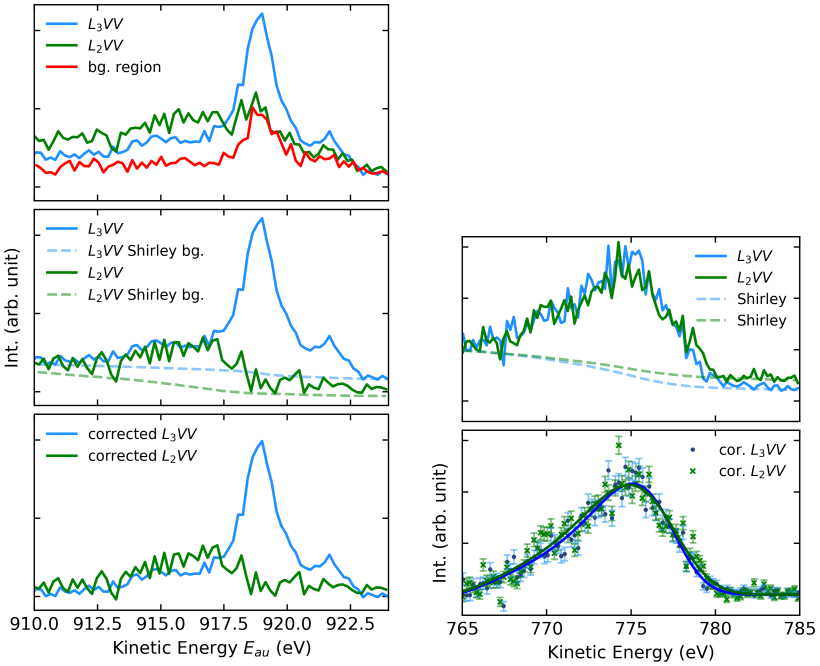
(a) Cu (b) Co

Fig. 1 L_3 and L_2 photoelectron $L_{2,3}VV$ Auger electron coincidence maps of Cu (a) and Co (b) together with the coincident photoelectron spectrum acquired by the integration of the maps along the Auger electron kinetic energy. The regions chosen for closer analysis are marked as solid color lines in the binding energy sum spectra (green, red and blue).

For later analysis Auger electrons, which were measured in coincidence with photoelectrons marked as a solid colored line in the binding energy spectra were used (green, red and blue). The resulting Auger spectra are shown in the upper panel of Fig. 2a. In blue

[a] *Uppsala-Berlin Joint Laboratory on Next Generation Photoelectron Spectroscopy, Albert-Einstein-Str. 15, 12489 Berlin, Germany*
[b] *Institute for Methods and Instrumentation in Synchrotron Radiation Research FG-ISRR, Helmholtz-Zentrum Berlin für Materialien und Energie Albert-Einstein-Strasse 15, 12489 Berlin, Germany*
[c] *Institut für Physik und Astronomie, Universität Potsdam, Karl-Liebknecht-Strasse 24-25, 14476 Potsdam, Germany*
[d] *Division of Applied Physical Chemistry, Department of Chemistry, KTH – Royal Institute of Technology, SE-100 44 Stockholm, Sweden*
[e] *Sorbonne Université, CNRS, Institut des NanoSciences de Paris, INSP, F-75005, Paris, France*
[f] *Department of Physics and Astronomy, Division of X-ray Photon Science, Uppsala University , P.O. Box 256, SE-751 05 Uppsala, Sweden*
[*] *These authors contributed equally to this work*
[‡] *fjson@kth.se*
[§] *alexander.foehlisch@helmholtz-berlin.de*

the L_3VV spectrum is shown measured in coincidence with L_3 photoelectrons. The L_2VV CK spectrum measured in coincidence with L_2 photoelectrons is shown in green . In order to prepare the analysis, the spectra have to be corrected for back scattered electrons. First of all, the background originating in the back scattered L_3 photoelectrons has to be considered, which contributes to the L_2VV CK Auger electron spectrum. This can be done by taking an Auger coincidence spectrum into account in coincidence with a region in between of the L_3 and L_2 photoelectrons. This region in shown in red in Fig. 2a and resembles the L_3VV Auger spectrum, since the only difference is that the photoelectrons lost some of their kinetic energy by inelastic scattering. Normalizing the data to the event number in the selected areas we can now subtract the background spectrum from the L_2VV CK spectrum. In the second step we also have to consider the back scattered electrons originating in the Auger main peaks and contributing to a electron tail in this spectra. This can be taken into account in a Shirley background manner. Thus, we calculated the Shirley background (dashed lines) and subtracted it from the Auger spectra. The lowest panel shows the corrected Auger spectra used for the analysis shown in the main text.



(a) Cu (b) Co

Fig. 2 $L_{2,3}VV$ Auger electron spectra of Au (a) and Co (b) in coincidence with different photoelectrons, L_3 in blue L_2 in green and background region in red. As a dashed line the Shirley background is shown. The lowest panel shows the background corrected data.

For Co the photon energy was set to $h\nu = 1150\,\text{eV}$. The same technique was used for the data acquisition. Fig 1b shows the resulting coincidence maps for the $L_{2,3}VV$ region measured in coincidence with the L_3 and the L_2 edge. The lowest panel shows the resulting photoelectron spectra. The coincidence Auger spectra corresponding to the marked as a solid line photoelectron region are shown in Fig. 2b Here we directly see that the spectra are very similar.

Thus, subtracting the L_3 back scattered spectrum as was done for Co would only lead to the increase of the noise and was not done. The Shirley background however has to be subtracted (dashed line in Fig. 2b). The resulting L_3VV and the L_2VV CK coincidence Auger spectra and the corresponding fit using the valence band (explained in detail in the main text) are shown in the lower panel. As one can see the fits have only minor differences, which are within the error bars.

In the case of Ni the data was acquired in one measurement using $h\nu = 1250\,\text{eV}$ excitation energy. The data analysis of Ni is very complex and was explained in detail and published elsewhere[2].

Notes and references

1 A. Thompson and D. Attwood and E. Gullikson and M. Howells and K. Kim and J. Kirz and J. Kortright and I.Lindau and Y. Liu and P. Pianetta and A. Robinson and J. Scotfield and J. Underwood and G. Williams and H. Winick, *X-Ray data booklet*, Lawerence Berkley National Laboratory, University of California, 2009, pp. 1–3.

2 A. Born, T. Leitner, I. Bidermane, R. Ovsyannikov, S. Svensson, N. N. Mårtensson and A. Föhlisch, *Phys. Rev. B*, 2021, **103**, 115121.