Electron pair emission detected by time-of-flight spectrometers: Recent progress

Michael Huth,[1] Cheng-Tien Chiang,[1,2] Andreas Trützschler,[1,2] Frank O. Schumann,[1] Jürgen Kirschner,[1,2] and Wolf Widdra[2,1]
[1]*Max Planck Institute of Microstructure Physics, Weinberg 2, D-06120 Halle, Germany*
[2]*Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Von-Danckelmann-Platz 3, D-06120 Halle (Saale), Germany*

(Received 11 December 2013; accepted 18 January 2014; published online 11 February 2014)

We present results for electron coincidence spectroscopy using two time-of-flight (ToF) spectrometers. Excited by electron impact, the energy and momentum distribution of electron pairs emitted from the Cu(111) surface are resolved and a spectral feature related to the Shockley surface state is identified. By combining the two ToF spectrometers with a high-order harmonic generation light source, we demonstrate double photoemission spectroscopy in the laboratory that required synchrotron radiation in the past. Utilizing this setup, we report results for (γ,2e) on NiO(001) on Ag(001) excited with light at 30 eV photon energy. © *2014 AIP Publishing LLC*.
[http://dx.doi.org/10.1063/1.4864274]

Electrons in a solid form an interacting many-particle system. This leads to the emergence of effects like superconductivity, metal-insulator transition, and long-range magnetic ordering.[1,2] Understanding the electron correlation in solids is a prerequisite for a complete description as well as the design of new functional materials.

The electron correlation can be literally divided into two parts. The first ingredient is that the wave function is antisymmetric with respect to exchange of the identical electrons with half-integer spin. The second component in the electron correlation originates from the Coulomb repulsion between electrons due to their charge. The combination of these two effects leads to a reduced probability of finding one electron in the vicinity of another one, which is termed as the exchange-correlation hole.[3] An exact description of a many-electron system has to include these ingredients and these have become the important topic for modern electron spectroscopy experiments.

Electron pair emission from surfaces can reveal directly the electron correlation. The emission of electron pairs upon the excitation by a single electron (e,2e) or a single photon (γ,2e) is only possible due to the existence of electron correlation.[4] Early experiments concentrated on atomic systems with few electrons like (γ,2e) from He and (e,2e) from H and showed characteristic energy and momentum distributions of the electron pairs.[5–7] Investigations with (e,2e) on solid systems started with the work of Kirschner *et al.* which showed that for a W(001) surface pair emission from valence electrons exists.[8] Later, Herrmann *et al.* reported first experiments on (γ,2e) from metal surfaces which revealed that the electrons in a pair are emitted with a preference for unequal energies.[9] In these reports, the energy distribution of electron pairs is characterized in detail, whereas the momentum degrees of freedom were not fully explored.

In this Letter, we present momentum-resolved experiments for (e,2e) from Cu(111) valence states and for (γ,2e) from NiO(001) using a laboratory time-of-flight coincidence spectroscopy. For (γ,2e) coincidence spectroscopy on solids, a pulsed light source with photon energies higher than 20 eV is required and here we used a high repetition rate high-harmonic generation source in the laboratory.[10] Cu(111) is particularly interesting due to the formation of an electronic state near the surface with a parabolic dispersion. This Shockley surface state is one of the few systems where theoretical calculations for pair emission are available.[11,12] NiO is a *3d* transition metal oxide and while theories using *local density approximation* can successfully describe electronic properties of metals they fail to describe NiO properly. The description can be improved by the introduction of an *U* parameter to treat electron correlation more refined. Thus, for NiO, a stronger correlation between localized *d*-electrons is expected. The emission of electron pairs from the *3d*-bands by excitation with a single photon carries information about the correlation between the electrons.

The experiments were performed in an ultra high vacuum chamber with a base pressure below 5×10^{-10} millibar. The Cu(111) metal surface for the (e,2e)-experiment was prepared with Ar^+ ion sputtering and annealing up to 800 K. The chamber is equipped with two time-of-flight spectrometers (Themis 1000, SPECS[13]) in coplanar geometry inclined by $\pm 45°$ with respect to the sample normal. Each spectrometer has an acceptance angle of $\pm 15°$. The detectors consist of a chevron mounted microchannel plate stack (MCP) from which the time-of-flight signal is retrieved and (x,y)-delay lines (Surface Concept) that allow to obtain the two-dimensional electron arrival position. The delay lines collect the electron cloud leaving the MCP and the charge flows to both ends of the anode. The difference of the arrival time at the ends of the anodes determines the hit position. Thus, the in-plane components of the momentum in any direction and the energy of the electrons are obtained. In the center between the spectrometers, the excitation source is mounted. Our signal processing is performed differently as compared to a typical time-of-flight photoemission spectroscopy setup that uses time-to-digital converters. The amplified time-of-flight signals are further processed to filter the coincident events on both detectors. They are fed to constant fraction discriminators for signal shaping and then to an AND logic unit that triggers data

acquisition when the time-of-flight signals arrive within a time interval of 100 ns. This logic triggers data acquisition only if coincident hits occurred. Data acquisition is carried out by a 12 channel digitizer (Aquiris DC282 ASbus2). The device samples synchronously at 2 GS/s all time-of-flight signals, the start time signal from the excitation source and both delay line detector signals. The sampled waveforms of the delay line pulses are evaluated with a dynamic threshold peak detection algorithm to calculate the hit position. The determination of the hit position is twice as successful as compared to a conventional time-to-digital converter with a fixed threshold due to the higher sensitivity. To retrieve momentum and energy of electrons, the software SIMION was used to calculate the electron trajectories in the spectrometer. This provides the conversion matrix for transformation of arrival location and time (x,y,t) to (k_x,k_y,E). In coincidence, both spectrometers analyze the three dimensional coordinates of each detected electron of the acquired electron pair.

For coincidence spectroscopy from valence states, a ToF spectrometer setting with a wide energy range is favorable because it allows to investigate the energy sharing between the electrons in a pair. A lens setting with wide energy range and acceptance angle has a high transmission which is crucial for a reasonable high detection efficiency. Such setting is comparable to a high pass energy mode of a hemispherical analyzer that reduces energy resolution. Also the performance of a ToF spectrometer depends not only on the lens setting but also on an accurate model for the conversion from the hit coordinates (x,y,t) to (k_x,k_y,E). For a reliable measurement, a precise calibration of the spectrometers for the anticipated operation mode is required. To obtain the resolution of the instrument, the excitation pulse length should be at least in the range of the time resolution of the MCP that is about 150 ps. Due to the lack of the availability of short-pulsed electron or light sources in the energy range between 25 eV and 50 eV, there were no reference data for the spectrometer performance available from the manufacturer. Here, we used the single-bunch mode at the BESSY II synchrotron radiation facility (beamline UE112-PGM1) to calibrate the angular and energy resolution of the spectrometers. As a reference feature, we analyzed photoelectrons from the Shockley surface state on a clean Cu(111) surface with a well defined dispersion.[14] With a photon energy of 17 eV, the ToF spectrometers could be set to identical settings as for coincidence measurements for valence bands. The inset in Fig. 1 shows the parallel momentum distribution of the Shockley surface state within an energy interval between E_F and $E_F - 0.1$ eV. We obtained with our coincidence spectroscopy setup in a wide energy window from 6 eV to 18 eV a momentum and energy resolution of $\Delta k_{\parallel} = 0.01$ Å^{-1} and $\Delta E = 180$ meV, respectively. A wide energy window results in a smaller ToF dispersion, therefore, these values are not representative of the ultimate resolution of the instrument. For the application of high-resolution photoemission, it has been shown that the spectrometer reaches an energy resolution better than 4.7 meV.[13]

After the calibration of our instrument, we performed coincidence spectroscopy in the laboratory. For excitation, a pulsed low energy electron gun (Kimball EGPS-1022C) was used that was driven by a pulse generator (HP 8131A) for

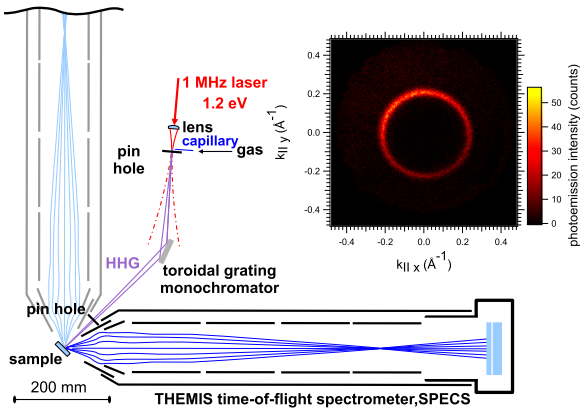

FIG. 1. Sketch of the experimental setup. The two ToF spectrometers are aligned coplanar ±45° with respect to the sample normal. Here, for (γ,2e), the HHG light source is driven by a 1040 nm laser that is focused in a gas jet. The generated high-order harmonics passes through a monochromator for photon energy selection. Inset: Parallel momentum distribution of photoelectrons from the Shockley surface state as calibration of the ToF spectrometers.

electron pulses with 2 ns length at a repetition rate of 1 MHz. A primary electron energy (E_p) of 27 eV was chosen and one expects the onset of emission at $E_{sum} = E_p - \phi = 22.1$ eV with a work function $\phi = 4.9$ eV. Hence, we chose a spectrometer setting with a wide energy range from 6 eV to 18 eV for each ToF. The primary flux was adjusted to give a count rate lower than 3000 counts/s on a single detector that results in a coincidence intensity of 2 counts/s. In Fig. 2, the energy distribution of the emitted electron pairs is displayed. The axes are the energies of individual electrons in a pair indicated as E_{left} and E_{right}. The sum energy of an electron pair is $E_{sum} = E_{left} + E_{right}$ which is constant parallel to the dashed diagonal line in the plot. Three diagonal features at different E_{sum} and an onset in intensity indicated by the dashed lines can be distinguished. The onset corresponds to the maximum energy that an electron pair can have due to energy conservation which is located at $E_{sum}^{max} = E_p - \phi$, with E_p being the primary energy and ϕ being the work function for a single electron. Events with higher energies are

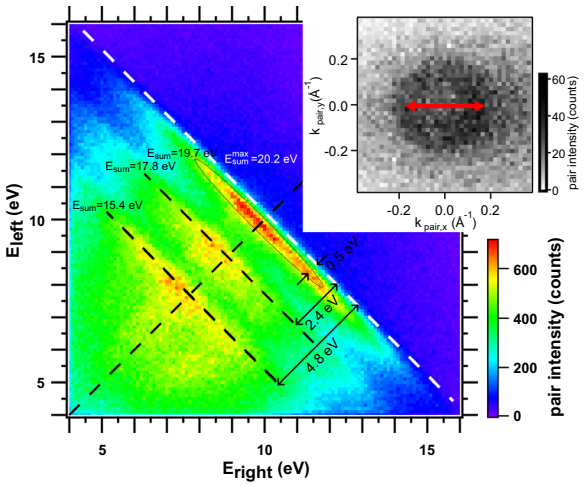

FIG. 2. 2D energy distribution obtained with $E_p = 27$ eV on Cu(111). The dashed white line marks the onset of pair emission. Three features emerge at 0.5, 2.4, and 4.8 eV below the onset. The inset shows the parallel momentum distribution for pairs between E_{sum}^{max} and $E_{sum}^{max} - 200$ meV. The corresponding state is marked with the dashed ellipse in the energy distribution.

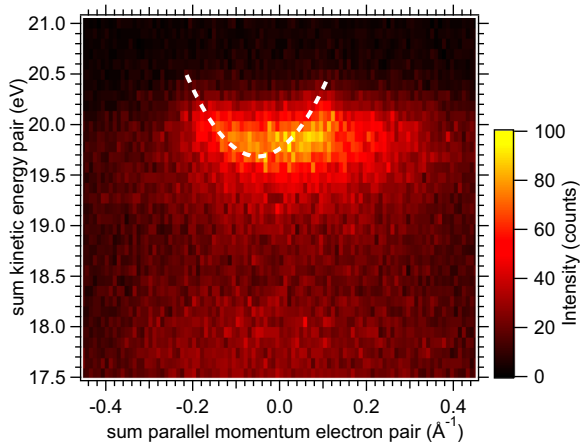

FIG. 3. Sum energy vs. sum momentum in k_x with $\Delta k_y = 0.06\,\text{Å}^{-1}$. Directly below the emission onset, a feature with parabolic dispersion appears. The offset to zero in k_x is due to a small sample misalignment.

accidental coincidences where excitations from two or more primary electrons occur. Three intensity peaks can be distinguished at pair energies 0.5, 2.4, and 4.8 eV below E_{sum}^{max}. The intensity distribution shows a maximum if the energies of the electrons in a pair are equal. Our observation is in good agreement with results from Schumann *et al.* for (e,2e) on Cu(111) excited with 29.2 eV primary electrons where also three intensity peaks were observed.[15,16] It was concluded that a theoretical framework of (e,2e) on Cu(111) starting from an effective single-particle description of the valence states is a satisfactory description. The reproduction of this result proves that the instrument is capable of coincidence spectroscopy. With our energy resolution, we could also resolve the energy-momentum dispersion of these three features. While the states at 2.4 eV and 4.8 eV below E_{sum}^{max} appear flat, the feature 0.5 eV below the onset shows a parabolic dispersion as displayed in the sum energy (E_{sum}) versus sum momentum ($k_{sum,x}$) plot in Fig. 3. It has a similar shape and size as the well-known Shockley surface state. From theoretical calculations of Giebels *et al.* for (e,2e) on a single surface layer of Cu(111) with emission at a fixed angle of 30° and excited by electrons with 30 eV energy, three intensity peaks are expected at 0.5 eV, 2.5 eV, and 5.2 eV below the onset.[11] Thus, our results with a slightly different geometry and excitation energy reveal the predicted features qualitatively. Moreover, we were also able to resolve the parallel momentum distribution of the electron pairs. The momentum distribution of the pairs can be plotted as $k_{sum,x}$ vs. $k_{sum,y}$ with $k_{sum} = k_{left} + k_{right}$. The inset in Fig. 2 shows the two-dimensional momentum distribution of electron pairs for energies between E_{sum}^{max} and $E_{sum}^{max} - 200\,\text{meV}$, which shows a circular intensity distribution with an estimated radius of $k_{\parallel} = 0.15\,\text{Å}^{-1}$.

For the (γ,2e) experiment, we used a compact high-order harmonic generation (HHG) laboratory source for pulsed excitation with vacuum ultraviolet. The setup was described previously.[10] However, here we use alternatively an all-fiber-based laser (Clark-MXR Impulse) that delivers pulses at 1.2 eV with 200 fs pulse width and up to 14 μJ pulse energy. These pulses are focused in a 4 bar Ar or Xe gas jet in a vacuum chamber to generate light pulses with energies between 13 eV and 45 eV. After the generation process, a toroidal monochromator allows to select the photon energy for excitation. The monochromator chamber has entry and exit pin holes that work as slits and allow differential pumping towards the photoemission chamber. The bandwidth of the generated light pulses is 150 meV and the repetition rate can be tuned between 200 kHz and 25 MHz.

In the past, only synchrotron radiation sources operated in single-bunch mode could provide pulsed light with sufficient high repetition rate. However, coincidence experiments require long acquisition times and beamtime at synchrotron radiation sources is limited. From this aspect, this HHG light source allows ToF-based (γ,2e) spectroscopy in the laboratory. It is not suited for coincidence spectroscopy with hemispherical analyzers where for efficient spectroscopy the source repetition rate has to be in the range of the flight time dispersion of the electrons in the pair which is in the range of 10 ns. Therefore, a HHG light source with a repetition rate greater than 100 MHz would be required.[15,17,18] Here, we utilized the light source in combination with the ToF spectrometers to investigate (γ,2e) from NiO(001). On a Ag(001) crystal, 15 monolayer thick NiO(001) films were prepared by evaporation of Ni in an O_2 atmosphere of 1×10^{-6} millibar for 10 min.[19] The surface cleanliness and ordering were checked by Auger electron spectroscopy and low energy electron diffraction. The pulsed HHG light source was set to a photon energy of 30 eV, *p*-polarized, and at a repetition

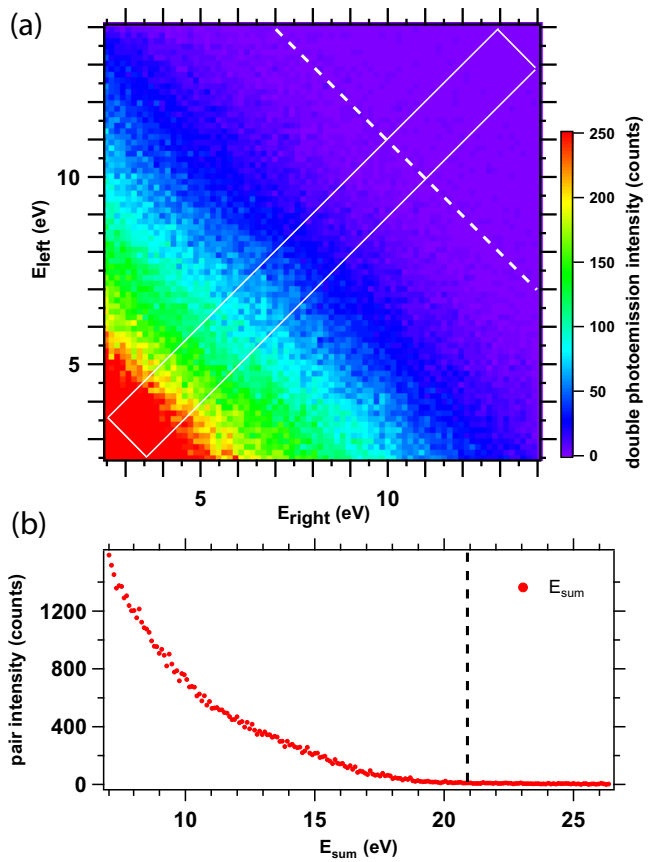

FIG. 4. (a) 2D energy distribution obtained with $h\nu = 30$ eV on NiO(001). The diagonal dashed line marks the expected onset of pair emission. The intensity does not reproduce that but increases slowly towards lower pair energies. Also no preference for a specific energy sharing can be distinguished. (b) Intensity depending on E_{sum} along the white rectangle in (a).

rate of 1 MHz. The light intensity was tuned so that the count rate on a single detector was about 1000 counts/s. The coincidence count rate was 0.2 counts/s. The two dimensional energy distribution of the electron pairs is presented in Fig. 4. As for (e,2e), the axes are the energies of the single electrons E_{left} and E_{right} and parallel to the dashed diagonal line is the sum energy constant. From sum energies of 7 to 21 eV, the intensity monotonically decreases as shown by the line profile in Fig. 4. This is in strong contrast to the (e,2e) case from Cu(111) where an onset of intensity was observed. At a fixed sum energy, the intensity is constant independent of how the energy is shared between the two single electrons. The maximum sum energy for (γ,2e) that an emitted pair can have is approximately $E_{sum}^{max} = h\nu - 2\phi$ which is indicated by the dashed line. In addition, the energy of the pair is shared uniformly between the two single electrons. To understand the observed intensity distribution, further studies using different photon energy and geometry for angle-resolved measurement as well as support from theories would be required. In a simple picture, the (γ,2e) spectrum could be approximated by the self-convoluted band structure which broadens intensity features strongly.

To summarize, we present a double ToF spectrometer setup for coincidence spectroscopy which was calibrated and applied for (e,2e) from Cu(111). The energy distribution of pair emission from Cu(111) shows three intensity peaks with a preference for equal energy sharing between two electrons. The electron pair momentum distribution shows a parabolic dispersion for the state 0.5 eV below the intensity onset. This is in agreement with previous (e,2e) studies on Cu(111) and demonstrates the capability of the instrument for coincidence spectroscopy. In combination with a high repetition rate HHG light source, we achieve (γ,2e) experiments in the laboratory. Results for (γ,2e) on NiO(001) excited with 30 eV photon energy are shown. The two dimensional energy distribution of the electron pairs yields an increase in intensity towards lower sum energies and a broad and structureless energy sharing between electrons. Our work extends spectroscopy on electron pair emission with momentum resolution and initiates (γ,2e) experiments in the laboratory.

We would like to thank H. Engelhardt, R. Neumann, F. Weiss, R. Kulla, and the BESSY II staff for valuable technical support. This work was partially funded by the DFG through SFB 762.

[1]P. Monthoux, D. Pines, and G. G. Lonzarich, Nature **450**, 1177 (2007).
[2]J. Berakdar, H. Gollisch, and R. Feder, Solid State Commun. **112**, 587 (1999).
[3]J. C. Slater, Rev. Mod. Phys. **6**, 209 (1934).
[4]J. Berakdar, Phys. Rev. B **58**, 9808 (1998).
[5]C. Gazier and J. R. Prescott, Phys. Lett. A **32**, 425 (1970).
[6]L. Avaldi and A. Huetz, J. Phys. B: At., Mol. Opt. Phys. **38**, S861 (2005).
[7]L. Malegat, Phys. Scr. **T110**, 83 (2004).
[8]F. O. Schumann, C. Winkler, and J. Kirschner, Phys. Rev. Lett. **98**, 257604 (2007).
[9]R. Herrmann, S. Samarin, H. Schwabe, and J. Kirschner, Phys. Rev. Lett. **81**, 2148 (1998).
[10]C. T. Chiang, A. Blättermann, M. Huth, J. Kirschner, and W. Widdra, Appl. Phys. Lett. **101**, 071116 (2012).
[11]F. Giebels, H. Gollisch, and R. Feder, J. Phys.: Condens. Matter **21**, 355002 (2009).
[12]H. Gollisch, N. v. Schwartzenberg, and R. Feder, Phys. Rev. B **74**, 075407 (2006).
[13]M. H. Berntsen, O. Götberg, and O. Tjernberg, Rev. Sci. Instrum. **82**, 095113 (2011).
[14]S. Hüfner, *Photoelectron Spectroscopy* (Springer, Berlin, 2003).
[15]F. O. Schumann, R. S. Dhaka, G. A. van Riessen, Z. Wei, and J. Kirschner, Phys. Rev. B **84**, 125106 (2011).
[16]F. O. Schumann, C. Winkler, and J. Kirschner, Phys. Rev. B **88**, 085129 (2013).
[17]M. Volkel and W. Sandner, J. Phys. E: Sci. Instrum. **16**, 456 (1983).
[18]O. Kugeler, S. Marburger, and U. Hergenhahn, Rev. Sci. Instrum. **74**, 3955 (2003).
[19]S. Grosser, C. Hagendorf, H. Neddermeyer, and W. Widdra, Surf. Interface Anal. **40**, 1741 (2008).