Two Electron Photoemission in Solids

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(Received 19 February 1998)

We observed the emission of correlated electron pairs from the valence band of solids following the absorption of single photons in the vacuum ultraviolet range. Applying a time-of-flight technique, we measured the energy distributions of correlated electron pairs emitted from clean Cu(001) and Ni(001) crystals. Significant differences between both metals were found. For the interpretation we suggest a single step two-electron-photoionization process and a competing two step mechanism involving a single photoionization and a subsequent electron-electron collision in the valence band. [S0031-9007(98)07072-0]

PACS numbers: 79.60.Bm, 61.80.Ba

The theoretical treatment of multielectron systems is one of the most fundamental problems in physics which still remains far from being solved. It appears most remarkable and astonishing that even nowadays—more than 70 years after the invention of quantum mechanics—a satisfying formulation of a dynamically correlated two-electron wave function of helium as the most simple multielectron system is not yet available. The basic theoretical difficulty arises from the mutual Coulomb interaction between the electrons of the system. As the exact multielectron Schrödinger equation is not separable, its solution requires approximate methods. Certainly the most common and frequently applied theoretical approach is the assumption of an effective potential created by the nuclei and all other electrons of the system, which is then used for evaluating single orbital wave functions for the electron considered. Electron correlation in the sense of the individual interaction between two or more electrons of the system is not taken into account. In spite of the unquestioned success of this approach in describing static properties of multielectron systems such as energy eigenvalues, it severely fails whenever processes are considered that are decisively characterized by the dynamic correlation between individual electrons of the system. One of the most evident manifestations of electron correlation is the simultaneous emission of two electrons from a multielectron system upon absorption of one photon, known as photo double ionization. If we imagine the process of photoionization as interaction between one photon and one electron, it is obvious that the simultaneous emission of a second electron requires a direct interaction between both electrons. This picture can be taken as the physical interpretation for the vanishing dipole transition matrix element of a simultaneous photo double ionization process, if the initial and final two-electron wave functions are eigenstates of the same uncorrelated Hamiltonian [1]. Therefore, the measurement of differential cross sections for photo double ionization processes allows an experimental verification of theoretical many body approaches to multielectron systems including electron correlation. The most investigated target in this field is He, where the process of photo double ionization was first observed by Schwarzkopf and co-workers in 1993 [2]. In the meantime the ratio of total double- to single-ionization cross sections over a wide range of photon energies [3] as well as the differential angular and energy dependence of the two emitted electrons have been measured [4,5].

In contrast to that, there is at present neither experimental evidence nor a theoretical formalism for the excitation of two electrons from the valence band of a solid upon the absorption of one photon. Nonetheless, it is in fact solids in which some of the most striking examples of electron correlation effects are found, as, e.g., the interplay between electrons in a superconductor resulting in the formation of Cooper pairs may be mentioned. In addition, the inclusion of electron correlation in band structure calculations is of general interest [6,7], as various phenomena in solid state physics as, e.g., satellite lines in single photoemission spectra cannot properly be described within pure single orbital approaches.

In a solid the interpretation of two-electron photoemission processes is in general somewhat more complicated than in free atoms, as further mechanisms in addition to that in atoms leading to the simultaneous emission of two electrons upon absorption of one photon are possible. As an example for a double step process, we consider the excitation of a photoelectron from a core level and the subsequent filling of the core vacancy by a valence electron, leading to the emission of a second valence electron via an Auger mechanism. These processes are well known, and have been widely studied in various solids [8]. As a further double step scenario for a two-electron photoemission, we suggest the combination of a single photoionization in the valence band and a subsequent collision between the photoelectron and a second band electron leading to the emission of both electrons. We point out that the theoretical treatment of this process requires the consideration of correlation between the photoelectron and the band electron.

In this paper we report on the first experimental evidence for two-electron photoemission processes from the valence band of solids. We observed the coincident emission of two electrons from the vicinity of the Fermi level of clean Cu(001) and Ni(001) crystals upon excitation by photons in the vacuum ultraviolet range.

The experiment was performed at the electron storage ring BESSY in Berlin. We measured energy and momenta of two electrons being emitted simultaneously from the (001) surfaces of a Cu and Ni sample after absorption of 45 eV photons. While the Cu sample was a pure Cu crystal, the Ni sample was produced by evaporating approximately 10 monolayers of Ni on top of the Cu(001) surface. Because of the small escape depth of electron pairs in the energy range considered here (<5 monolayers) [9], we assume the electron emission characteristics from the epitaxial Ni layer to be equivalent to that from a bulk (100) Ni crystal. Before each measurement, clean surface conditions of the particular sample were provided using standard cleaning and analysis procedures. The pressure during all measurements was in the 10^{-11} mbar range.

As our experimental setup was described before [10,11], we give only a brief illustration: The energy dispersed, p-polarized synchrotron radiation from a toroidal grating monochromator (TGM4) passed through an aperture of 30 μm diameter, before it hit the (001) surface of the Cu (Ni) sample at normal incidence. The photon beam was modulated in "single bunch" mode; i.e., the intensity was concentrated in regular bunches of 0.6 ns half-width and 200 ns time distance. The mean beam intensity was adjusted such that the average number of photons per bunch was less than one. Two channel plate detectors (75 mm diameter) were located in a horizontal plane defined by the normal of the sample surface and both detector axes (see sketch of the detection geometry in Fig. 1). Each detector had a distance of 160 mm to the sample, while the two detector axes included an angle with the light axis of ±40°, respectively.

By measuring the time difference between a photon-bunch marker signal delivered by the synchrotron and a fast timing signal from one of the channelplate detectors using a "time-to-amplitude converter," the flight time of emitted electrons between sample and each detector was determined. The total time resolution achieved in both channels was about 1.2 ns, while the energy resolution of the detected electrons depends on the particular energy value. It varied between 0.1 eV (for $E_{\text{electron}} = 5$ eV) and 3.15 eV (for $E_{\text{electron}} = 50$ eV). The fast timing signals from both detectors passed an electronic time-coincidence condition, ensuring that electron pairs were only registered, if both electrons reached the two detectors within a time window of 200 ns. As the number of photons per bunch is distributed according to Poisson statistics, a certain number of bunches contained more than one photon. Thus, in addition to correlated electron pairs, we detected a background contribution of about 15% of uncorrelated electrons, i.e., electron pairs generated by two different photons within one bunch. For subtracting this contribution from the coincidence spectra, we measured separate background runs by increasing the coincidence window from 200 ns to 1 ms, such that essentially only uncorrelated electron pairs were detected generated by different photon bunches. Before subtraction, the coincidence and background runs were normalized on the integrated single photoemission yield of both runs.

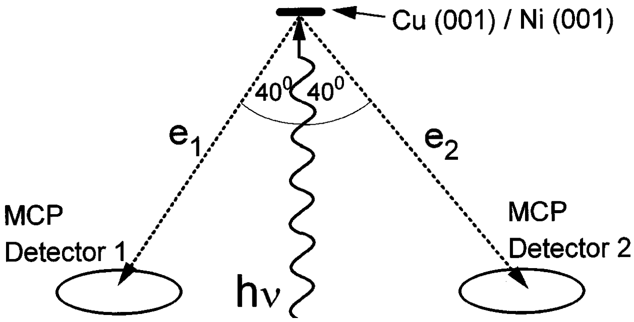

FIG. 1. Sketch of the experimental setup.

Because of the photon bunch repetition rate of $1/200\ \text{ns}^{-1}$, the maximum flight time that could be measured was 200 ns, corresponding to a minimum kinetic energy of $2-3$ eV.

In Fig. 2(a) we present a density plot of the two-dimensional time-of-flight distribution for correlated electron pairs originating from a Cu(001) surface following the absorption of 45 eV photons. The coordinate axes of the spectrum represent the flight times of the two electrons in reversed directions such that the counts in the distribution represent electron pairs with increasing velocity from the lower left to the upper right.

It can be seen that the intensity distribution of correlated electron pairs in the spectrum has a pronounced cutoff along a curved border line. When transforming the electrons flight times into kinetic energies—as shown in Fig. 2(b)—the intensity cutoff is converted into a diagonal line representing electron pairs with a constant sum energy of approximately 35 eV. This finding was verified by calculating the location of data points representing a constant sum energy of 35 eV in the time-of-flight distribution. As can be seen in Fig. 2(a), the calculated points, which are drawn as a dashed line, coincide perfectly with the observed intensity cutoff. Evidently, the maximum sum energy of correlated electron pairs is given by $E_{\text{sum}} = 35$ eV. Considering the photon energy of 45 eV and the work function in Cu of approximately 5 eV, a constant sum energy of $E_{\text{sum}} = 35$ eV represents electron pairs emitted from the vicinity of the Fermi level. We emphasize that coincidences between photoelectrons from core levels and subsequent Auger electrons cannot explain the intensity distribution in the spectra of Figs. 2(a) and

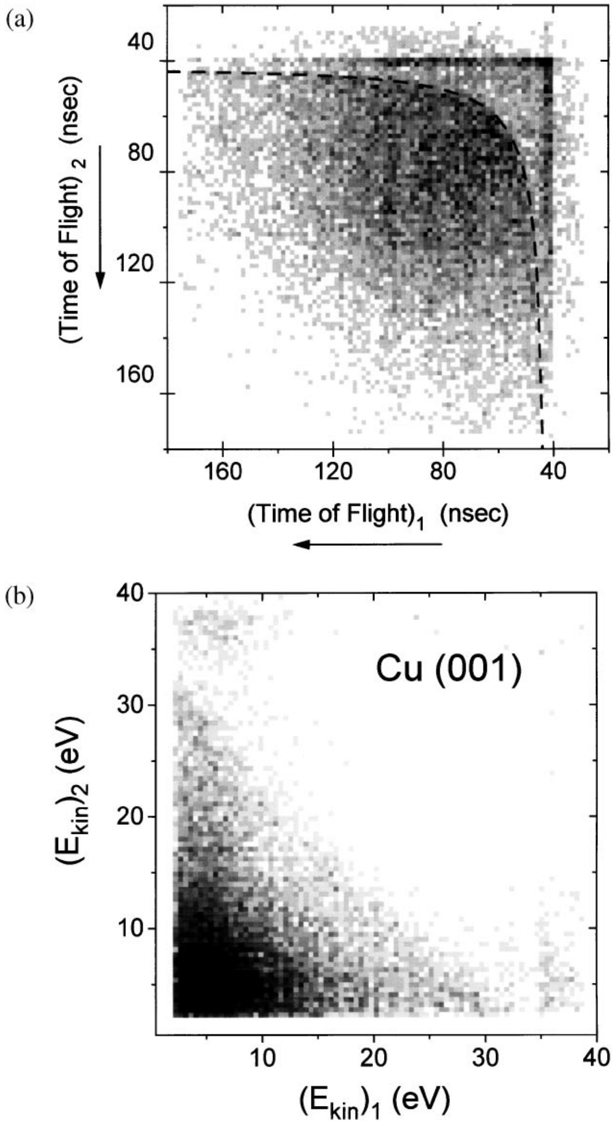

FIG. 2. (a) Two-dimensional time-of-flight distribution of correlated electron pairs from Cu(001) at 45 eV photon energy. The dashed line indicates the location of electron pairs with a constant sum energy of 35 eV. (b) Data from (a) after conversion of the electrons flight time into kinetic energy. The data points between 35 and 40 eV on both energy axes represent the background contribution from accidental single photoemission events.

2(b). Photoelectrons from core levels have discrete energies and Auger electrons from the valence band may be distributed in energy over a maximum range of about 6 eV according to the valence band width of Cu and Ni. Considering the experimental energy resolution, coincidences between photo- and Auger electrons would show up in the two-dimensional energy spectrum as isolated elliptical intensity spots, having a width of about 1−2 eV in the one direction and about 6.5 eV in the other direction.

Therefore, we interpret our data as a clear experimental evidence for the simultaneous creation of two electrons in the conduction band of Cu by the absorption of one photon. To our knowledge, this has never been measured for any solid before. As we find for the Ni(001) sample, the same main features in the two-dimensional time-of-flight and energy distributions, a similar analysis as described for Cu leads to the equivalent conclusion of a two-electron photoemission process in the conduction band of Ni being revealed in our data.

In addition to coincident events, we measured a background contribution of electron pairs including single photoelectrons from the valence band that did not undergo considerable energy loss in random coincidence with various electron energies in the second detector. This contribution which appears in Fig. 2(a) as straight lines of increased intensity parallel to both coordinate axes is very useful, as it allows one to verify the time calibration of our measurement. Furthermore, we find for both samples a strong contribution of electron pairs with sum energies of only a few eV. We assume those electrons to originate from various energy loss processes of single photoelectrons and correlated pairs in the solid. In our further analysis we concentrate on electron pairs with sum energies close to $(E_{\mathrm{sum}})_{\max} = 35$ eV, since their kinematics results from the nearly pure two-electron photoexcitation from the vicinity of the Fermi level with almost no perturbations from energy loss processes.

In Figs. 3(a) and 3(b) we present the background corrected distributions of the energy differences between the electrons of pairs originating from an energy region between the Fermi level (E_{F}) and $E_{\mathrm{F}} - 2$ eV. Both so-called energy sharing distributions cover an energy sharing range ($E_1 - E_2$) between ±30 eV, which does not include correlated pairs in which one electron carries less than 3 eV. This restriction is a consequence of the experimental lower detection limit of 2−3 eV and does not reflect the physical probability for the appearance of such unequal sharing.

The spectra show some similar general features while significant differences are in detail. In both distributions a minimum for equal energy sharing ($E_1 - E_2 = 0$)

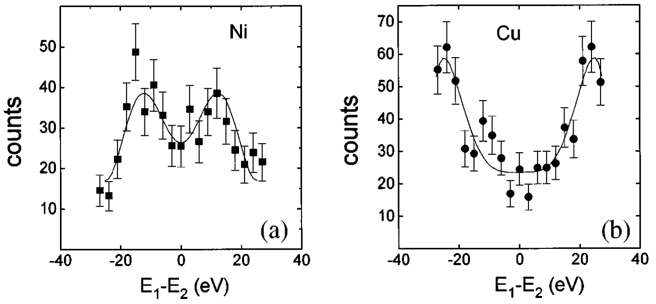

FIG. 3. (a) Energy sharing distributions of correlated electron pairs with sum energies $E_{\mathrm{sum}} = 34 \pm 1$ eV from Ni(001) at 45 eV photon energy. (The spectrum shows the distribution of energy differences between the electrons within the correlated pairs.) The solid line is a fit through the data points to guide the eye. (b) Equivalent to (a) but for Cu(001).

appears, indicating a higher probability for the two electrons of a pair to be emitted with unequal energies into the solid angles viewed by the detectors, rather than sharing their sum energy equally. However, the minimum for equal energy sharing is significantly more pronounced for Cu than for Ni.

For interpretation of this finding we refer to a very recent theoretical approach by Berakdar [1], where the single step and two step photoionization processes as described before were modeled. There it was shown that the dipole transition amplitude for the single step photo double ionization vanishes when the light polarization vector is perpendicular to the sum momentum vector of the two emitted electrons. This is the case for symmetric emission angles and equal energies of both outgoing electrons. Thus in this case the theoretical cross section of the single step photo double ionization process is zero, whereas it was also shown in Ref. [1] that the corresponding theoretical cross section of the two step mechanism remains finite.

As our detection geometry is symmetric, the minima at equal energies in the energy sharing distributions of Figs. 3(a) and 3(b) could be interpreted as a signature for the contribution of the single step photo double ionization mechanism. We note that we always measure a superposition of symmetric and asymmetric emission angles due to the high angular acceptance of our electron detectors. Therefore, the contribution of measured pairs with equal electron energies is always finite even if the cross section for symmetric emission of those pairs vanishes. Nevertheless, we find a significantly deeper minimum at equal energies in the sharing distribution of Cu than in that of Ni. Following the above interpretation, we could take this finding as an indication for a higher contribution of the two step photo double ionization process as underlying mechanism for the emission of electron pairs from the vicinity of the Fermi level of Ni than in the corresponding case of Cu.

However, we point out that only a more detailed comparison of our data with the corresponding theoretical results can provide a quantitative understanding of our findings.

We gratefully acknowledge the fruitful and stimulating discussions with J. Berakdar and the technical support provided by the staff of BESSY 1 during the beamtimes.

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