Two electron photoemission processes in the valence band of solids

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Abstract. We present experimental evidence on photo double ionization processes in the valence band of solids. Applying a 'Time-of-Flight' electron spectroscopy technique, we measured the energy distribution of pairs of correlated electrons emitted from clean Cu(001)- and Ni(001)- crystals upon absorption of linearly polarized photons of 45eV energy. Data were taken for normal and grazing orientation of the light wave vector with respect to the crystal surfaces. The energy sharing distributions of electron pairs emitted from the vicinity of the Fermi-level show significant differences for Cu and Ni. For interpretation of our data, we consider a direct double ionization mechanism in competition with a two step process involving single photoexcitation and a subsequent collision of the photoelectron with an additional band electron. A theoretical approach by J. Berakdar including both mechanisms is in good agreement with our data. In this theory the differences between Cu and Ni are traced back to distinct relative contributions of both mechanisms in the two metals due to the different average electron density.

1. INTRODUCTION

Two-electron photoemission processes from multi electron systems reveal most evidently the mutual coupling between the electrons of the system. For low energy VUV-photons the simultaneous emission of two electrons upon absorption of one photon, hereafter referred to as 'direct photo double ionization' can be described in first order perturbation theory for the radiation field and within the dipole approximation [1]. It was shown, that the dipol transition matrix element equals zero if the initial and final two electron wave functions are eigenstates of the same uncorrelated Hamiltonian, i.e. a Hamiltonian that does not include explicitly the electron-electron interaction potential. This finding can be taken as the formal pendant to the physical picture in which the photon is absorbed by one electron only. For the second electron to be liberated from it's binding both electrons have to be correlated, i.e. they have to be able to exchange momentum and energy by their mutual coulomb interaction. Thus experimental data on photo double ionization cross sections of multi electron systems allow for a verification of theoretical many body approaches that go beyond the single orbital approximation.

Although the most striking manifestations of electron correlation may be found in solids (e.g. the coupling of two electrons to cooper pairs leading to superconductivity), most research on photo double ionization is still concentrated on He as the most fundamental multi electron system. Here the ratio of total double- to single-ionization over a wide range of photon energies [2], as well as the differential angular and energy dependence of the two emitted electrons have been measured [3,4].

Only very recently our group has reported on the first experimental evidence of photo double ionization processes in the valence band of solids [5]. We have observed the coincident emission of electron pairs from the vicinity of the Fermi level of clean Cu (001) and Ni (001) crystals upon excitation of photons in the VUV-range. Meanwhile we have extended our measurements to different detection geometries as will be described below.

2. EXPERIMENTAL SETUP

Two position sensitive channel plate detectors (75mm diameter) were located in a horizontal plane defined by both detector axes and the normal of the crystal surface. The two detector axes included an angle of $\pm 40^0$ with the crystal normal, while the distance between each detector and the sample surface was 160 mm. Each channel plate detector had an angular acceptance within the scattering plane of $\pm 13^0$, covering a solid angle of about 2.7% of the 2π hemisphere. The energy dispersed, p-polarized synchrotron radiation from a toroidal monochromator passed through an aperture of $30\mu m$ before it hit the (001)-surface of a Cu (Ni) crystal at the incident angle α (α=angle between the light wave vector and the sample surface). Data were taken for α=90^0 and α=7.5^0. The photon beam intensity was modulated in single bunches of about 0.2 ns width and 200 ns time distance, while the mean beam intensity was adjusted to an average number of less than one photon per bunch. By measuring the time difference between a fast timing signal from a channel plate detector and a photon bunch marker signal provided by the synchrotron, the flight time of emitted electrons between the sample and each detector was measured. While the total time resolution in both channels was about 0.6ns, the energy resolution depends on the particular energy value. It varied between 0.07eV (for $E_{electron}$=5eV) and 1.6eV (for $E_{electron}$=50eV). We note that we could not take advantage of the electron detectors position resolution, as we integrated all measured emission angles over the angular acceptance of the detectors in order to achieve a reasonable statistical accuracy of our data. Correlated electron pairs, i.e. electron pairs excited by a single photon were selected from the detected single events by applying a time coincidence condition of 200ns to the two detector signals.

The experiment was performed at BESSY in Berlin.

3. EXPERIMENTAL RESULTS AND DISCUSSION

In fig. 1 a density plot of a two dimensional time-of-flight distribution of correlated electron pairs excited from a Ni (001) surface by 45eV photons is presented. The intensity distribution shows a sharp cutoff along a curved border line. A transformation of the electrons flight time into kinetic energy identifies the intensity cutoff as the location of data points representing electron pairs with a constant sum energy of 35eV.
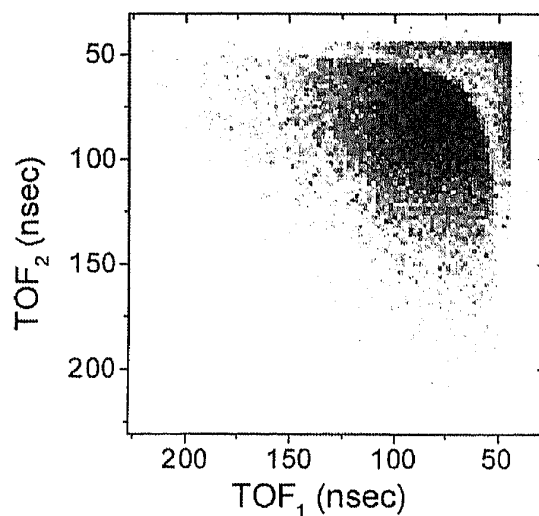

Fig. 1 Two dimensional time-of-flight distribution of correlated electron pairs excited from a Ni(001) surface upon absorption of 45eV photons.

Considering the photon energy of 45eV and assuming that the work function of an electron pair equals twice the work function of a single electron ($\Phi_{single} \approx 5eV$), our data reveal photo double ionization processes from the vicinity of the Fermi-level of Ni. As we find the same main features in the spectrum of the Cu(001) sample, the equivalent general conclusion of photo double ionization processes in the valence band of Cu is drawn.

In fig. 2a and 2b we show the sum energy distributions of electron pairs from the Ni- and Cu-sample in addition with the corresponding background distributions (dashed curves) that were measured separately by removing the coincidence condition for the two fast detector signals. The background distributions are normalized to the counts of the corresponding coincidence distributions at a sum energy of 35eV as this number represents the maximum sum energy of correlated electron pairs. We assume the background contributions in the coincidence spectra to be created by random coincidence events between uncorrelated electrons in the two detectors and coincidences involving dark counts. The intensity cutoff at high sum energies in the coincidence spectrum of Cu is found to be steeper and shifted by about 2eV towards lower energies with respect to that of Ni. We interpret these different shapes to be due to the different conduction band density of states of both metals right below the Fermi-level. In Cu the density of states in the vicinity of the Fermi level consists only of a very weak contribution of s-p hybridized states, while it steeply rises at about 1.5eV below the Fermi level due to the increasing density of d-states. We assume the high energy edge of the Cu sum energy spectrum to represent photo double ionization processes from those d-states. In contrast to that the Ni density of states increases sharply immediately at the Fermi level which is revealed in the location of the high energy edge in the Ni sum energy spectrum at a value around 35eV.
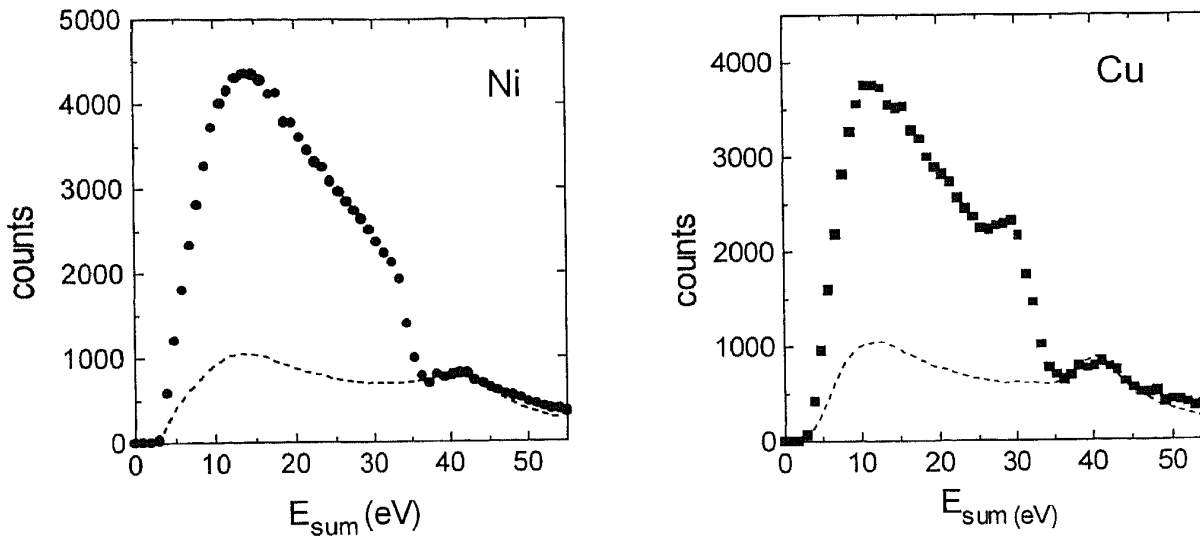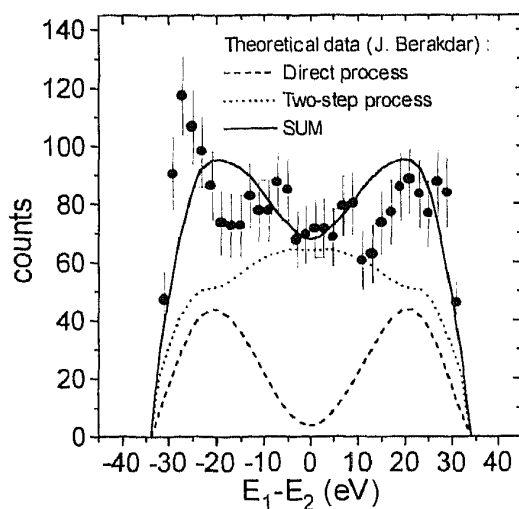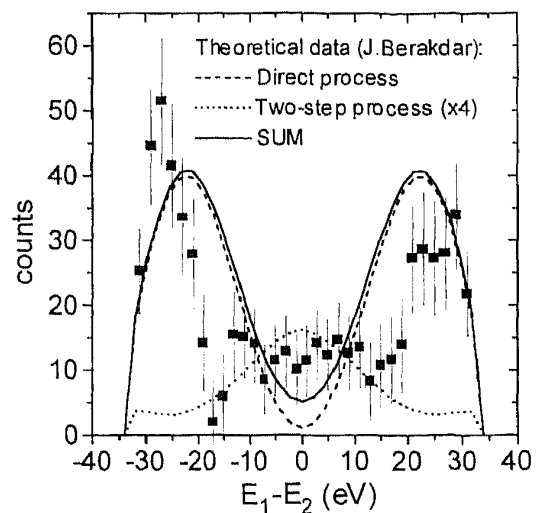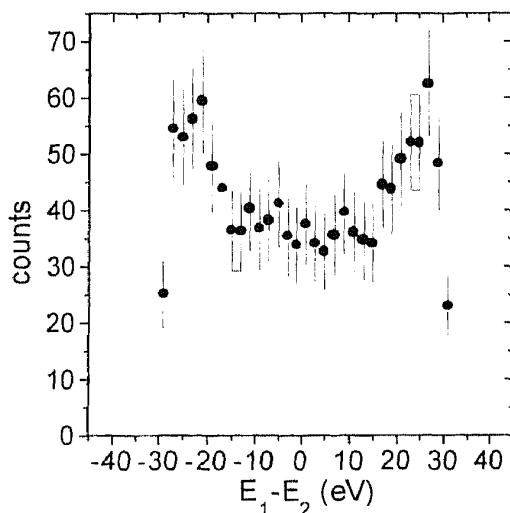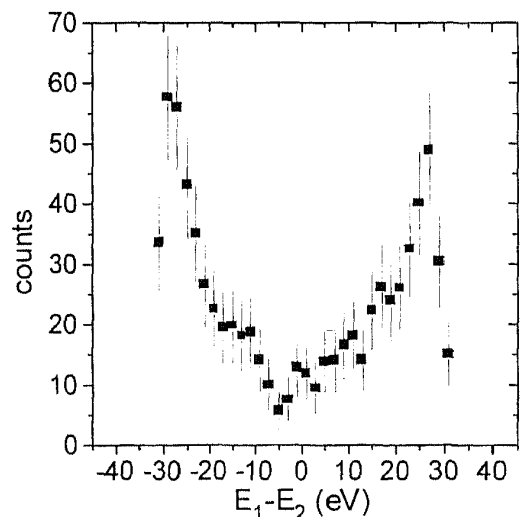

Fig. 2   Sum energy distribution of electron pairs emitted from Ni and Cu upon absorption of 45 eV photons. The dashed curves in both spectra show the measured background distributions of random coincidences. While the error bars in the background measurements are negligible, the size of the symbols used for the coincidence spectra represents the average statistical error.

The sum energy spectra of both metals show a strong contribution of electron pairs with sum energies below $(E_{sum})_{min} = (E_{sum})_{max} - 2\Delta E_V$, where ΔE_V describes the valence band width which is approximately 6eV for both metals. We assume those electron pairs to originate from various energy loss processes of single photoelectrons and electron pairs in the solid. In the following we concentrate on electron pairs emitted from the vicinity of the Fermi level, as they result from nearly pure two electron photoexcitation mechanisms with negligible perturbation from energy loss processes.

In general the interpretation of photo double ionization processes in solids is more complicated than those in free atoms since further mechanisms in addition to the direct mechanism as discussed in the introduction can lead to the simultaneous excitation of correlated electron pairs by single photons. The photo ionization of core levels in succession with the Auger filling of the core vacancies is one example for a two step mechanism [6]. While the energy characteristics of photoelectron - Auger electron coincidences allows to separate these processes from photo double ionization events in the valence band, we suggest a combination of a single photo emission in the valence band with a subsequent collision between the photoelectron and a second band electron as a further two step mechanism that can -within our experimental approach- not be distinguished from the direct photo double ionization mechanism. In order to gain further insight in the mechanisms underlying our data, we refer to a very recent theoretical approach to photo double ionization by J. Berakdar including the direct [1] and the above two step mechanism [7].

Fig. 3a Ni(001), $\alpha=90^0$

Fig. 3b Cu(001), $\alpha=90^0$

Fig. 3c Ni(001), $\alpha=7.5^0$

Fig. 3d Cu(001), $\alpha=7.5^0$

Energy sharing distributions of electron pairs emitted from Ni and Cu with sum energies between 33eV and 35eV at different photon incidence angles α. The theoretical curves [1,7] in the figs. 3a and 3b indicate the different model mechanisms for photo double ionization: dashed curve = direct process, dotted curve = two step process, full curve = sum of direct and two step process. The calculations are performed for the fixed sum energy $E_{sum}=34eV$. In fig. 3b the theoretical curve for the two step process is increased by the factor 4.

In the figs. 3a and 3b we present the experimental energy sharing distributions of electron pairs originating from Ni and Cu with sum energies between 33eV and 35eV for normal photon incidence ($\alpha=90^0$) in addition with the corresponding theoretical curves. As revealed in the figures, theory and experiment are in good general agreement but show some discrepancies in detail. We assume these deviations to be a consequence of the approximate assumptions used in the model as discussed below. In particular we emphasize that the model does consider the detected range of scattering angles within the scattering plane, but does not account for the experimental range of sum energies as the calculation is performed for $E_{sum}=34$ eV only. Further calculations including the full range of sum energies have to show whether an increased conformity between the experimental and theoretical curves can be achieved. However, both the theoretical and the experimental energy sharing distributions of the two metals show an intensity minimum for equal electron energies, which is significantly more pronounced for Cu than for Ni. According to the theoretical curves, the minima at $E_1-E_2=0$ are signatures of the direct photo double ionization mechanism (dashed curves), while the two step process (dotted curves) generates an intensity maximum at equal electron energies for both metals. The direct sum of the two (theoretical) contributions is normalized to the experimental data, whereas the relative weight of both mechanisms is a result of the calculation. Thus based on this theoretical approach the different shapes of the Ni- (fig. 3a) and Cu- (fig. 3b) energy sharing distributions can be interpreted as a result of the different contributions of the direct and the two step mechanism.

In the above theoretical concept different approximations enter in the approaches for the direct [1] and the two step mechanism [7] of photo double ionization. For the direct process, the two electron initial state is approximated by a (singlet) symmetrized direct product of two electron jellium single particle states with parabolic dispersion relation for the single particle states, where the total energy is given by a sum of the single particle energies. The final state is described by a time-reversed propagation of the asymptotic final state mediated by the Møller Operator, where the asymptotic final state is represented by two independent plane waves. The Møller Operator contains the electron-electron interaction potential V_{ee} and the retarded Greensfuction G_{ee}, where the potential term is represented by the electronic interaction potential V_{ee} only. For V_{ee} a screened Coulomb potential with a screening constant according to the Thomas-Fermi model is taken. Beyond the collective screening effect no further coupling of the electrons to the solid as diffraction at the lattice, excitation of phonons, plasmons, excitons, or elastic and inelastic collisions are considered in the final state. These neglects might contribute to the above deviations between the experimental and theoretical data.
However, using those approximations the evaluation of the dipole transition matrix element leads to the following general expression [1]:

$$M_{if} = \varepsilon \cdot (\mathbf{k}_1 + \mathbf{k}_2) \cdot L(\varepsilon, \mathbf{k}_1, \mathbf{k}_2, \mathbf{q}_1, \mathbf{q}_2)$$

Here ε describes the light polarization vector, k_1 and k_2 are the momentum vectors of the two outgoing electrons and L is a complex function of ε and the electronic momenta in the initial and final state. In the case of normal photon incidence ($\alpha=90^0$), the light polarization vector is parallel to the sample surface. Thus for equal energies of the outgoing electrons and symmetric detection geometry with respect to the surface normal (which is the case in our experiment), the sum momentum vector of the two outgoing electrons is perpendicular to ε, such that the transition matrix element vanishes. As a consequence, the theoretical contribution of the direct photo double ionization mechanism for normal photon incidence shows a minimum at equal electron energies (figs. 3a and 3b). According to the same selection rule one has to expect a maximum of the direct photo double ionization contribution if ε is perpendicular to the sample surface, which is approximately the case at grazing photon incidence. In contrast to that, the corresponding experimental energy sharing distributions at grazing photon incidence ($\alpha=7.5^0$) as shown in the figs. 3c and 3d, do reveal minima at equal electron energies. As theoretical data for this experimental geometry are not yet available, it can only be speculated that this finding could be due to different shapes and different contributions of the two step process to the energy sharing distributions at

grazing photon incidence with respect to the case at normal incidence. Preliminary calculations seem to confirm this supposition [7].

The theoretical approach to the two step mechanism of photo double ionization is fully based on single orbital wave functions for the initial and final states. The cross section of this process is basically described by the cross section of a single photoexcitation in the valence band of the particular solid multiplied with the cross section for a scattering process of the photoelectron with another valence electron, leading to the emission of two electrons with the final momenta k_1 and k_2 [7]. Similar to the approach for the direct process, no further interactions of the electrons with the solid are taken into account.

The relative weight of the two model mechanisms depends sensitively on the valence electron density of the particular solid. In both processes, the valence electron density enters in the density of the initial states, but also in the effective (screened) interaction potential between the two outgoing electrons. As a result of the above theoretical approaches, the cross section of the two step process shows a stronger dependence on the valence electron density than that of the direct process [7]. Therefore the higher theoretical contribution of the two step processes in Ni with respect to Cu as revealed in the figs. 3a and 3b can be interpreted as a consequence of the higher valence electron density in Ni than in Cu.

As a summary we point out that our experimental data on photo double ionization processes in the valence band of Cu(001) and Ni(001) crystals are in good quantitative agreement with a theoretical approach based on a direct and a two step ionization mechanism as discussed above. The minima at $E_1=E_2$ in the energy sharing distributions of electron pairs originating from the vicinity of the Fermi level of Ni and Cu at normal photon incidence can be understood as the experimental manifestation of a selection rule for the orientation of the light polarization vector and the sum momentum vector of electron pairs emitted through the direct ionization mechanism. As for the same experimental geometry the two step mechanism creates a maximum at equal electron energies, the more pronounced minimum in the energy sharing distribution of Cu with respect to Ni indicates a weaker contribution of the two step process in Cu than in Ni. According to the above theoretical approach, this is mainly attributed to the different valence electron densities of the two metals.

Acknowledgments

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