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# Direct observation of electronic correlation in $C_{60}$ by double photoemission

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We report the first direct observation of electronic correlation for $C_{60}$ thin films on Cu by two-electron photoemission excited by a single photon. The energetic position of features associated with one step excitation of two electrons shows the influence of the electrostatic correlation energy between the two holes which are generated simultaneously on the same site. The correlation energy determined from this experiment for $C_{60}$ is 1.6 eV. The correlation energy is consistent with estimates derived from Auger spectroscopy.

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## I. INTRODUCTION

Correlation between electrons is a fundamental property of systems containing many electrons. The influence of correlation on the electronic structure of solids manifests itself in enhanced (or suppressed) magnetic susceptibilities of paramagnetic metals, large electronic coefficients of the heat capacity (in so-called heavy Fermion compounds), or differences between experimental and theoretical bandwidths, to name the most important aspects. However, an adequate theoretical treatment of correlation is often not possible, and in most cases correlation is handled by introducing an effective exchange-correlation potential which can be tuned to match experimental findings. In this way one may obtain a description of the electronic structure while retaining an essentially one-particle description.

Considering the experimental side, it is desirable to investigate electronic correlation in a more direct way than is offered by the approaches mentioned above. Since electronic correlation involves at least two particles, it seems a natural extension of one-particle experiments to analyze two particle states. Experiments of this type are the crucial test in atomic and molecular physics for models of the electronic structure, which are designed to include correlation effects. One way to study two particle states is to investigate the correlated emission of pairs of electrons,[1] rather than single electrons as in conventional electron spectroscopic experiments. These pairs of electrons might be generated by impact of an electron or some other energetic particle, or by photons. The advantage of photon induced pair emission is that one does not need to determine the energy loss of the incoming particle to set up the energy balance since the photon is annihilated in the process.

Two-electron photoemission is governed by a fourfold differential cross section, representing the probability for emission of two electrons with certain energies and momenta. The experiment yields a multidimensional data set, from which different subsets or sections may be selected for discussion or for comparison to theoretical models. Correlation between electrons may show up both in the energies and the angular distribution of the two emitted electrons. For atomic or molecular species, energy and momentum of the doubly charged ion can be determined, such that complete kinematic information is obtained. Therefore, in atomic physics one often studies the angular distribution of the two electrons for selected energies and geometries relative to the light polarization. For solids and surfaces, this approach is only of limited feasibility since the finite escape depth of the electrons limits the accessible angular range. Therefore, we concentrate in this study on the energetics, primarily on the sum of the two kinetic energies. From this point of view, correlation is characterized by a correlation energy $U$ defined as

$$U = E_{N-2} - E_{N-1,1} - E_{N-1,2}.$$

$E_{N-2}$ is the energy of the system with two holes on one atom, i.e., the final state generated in our experiment. $E_{N-1,i}$ are the energies of the system with only one hole on site $i$. Since single holes are in general not correlated in time or space, the correlation energy describes the energy difference between a final state with two holes generated at the same time on the same site, such that the holes interact with each other via Coulomb repulsion, and two holes which are too far apart in space and time to interact with each other, and which therefore are uncorrelated. It is this correlation energy which we determine from our experiment. The correlation energy is expected to be present in all processes leading to a two hole final state, i.e., emission of a pair of electrons from one atom or lattice site caused by the absorption of a single photon. We call these processes one step events.

A competing mechanism for generation of pairs of electrons may proceed in two steps, namely a conventional photoemission (or photoionization) event leading to a single energetic free electron, followed by an inelastic collision where part of the energy of this electron is transferred to a second electron (at a different atom/lattice site). This also leads to the simultaneous emission of two electrons from the target, and there is no way to eliminate background from such processes experimentally from the measured signal, e.g., by time resolution. This distinguishes two-electron photoemission on solids from studies on gas phase targets, where the relatively low density of the target atoms or molecules usually ensures that if two electrons are detected in coincidence they originate from the same target particle, and therefore should display the undiluted influence of electronic correlation in the double ionization event.

Both the one and two step mechanisms were identified in studies on Cu and Ni (100) single crystal surfaces by Herrmann *et al.*[1] The differences of the energy sharing between the two emitted electrons which have been detected for double photoemission from Cu and Ni were attributed to a different probability of the two step process relative to the one step process. Here we report our results for two-electron photoemission from $C_{60}$ films of one and 10 monolayers deposited on Cu(111). We choose this material since its valence band spectrum is richly structured,[2,3] such that the two-electron photoemission spectrum may also be expected to show structures, which can be associated with features in the single photoemission spectrum. The Cu(111) substrate was chosen since it allows one to prepare well-defined crystalline films of $C_{60}$ by evaporation.[4]

## II. EXPERIMENT

The experiment was carried out at the bending magnet beamline G1 of Hasylab, Hamburg. The spectrometer was a time of flight (TOF) instrument equipped with two spatially resolving 75 mm channelplate detectors.[1] The channelplates were positioned at a distance of 120 mm from the sample. This allowed us to collect all electrons emitted in a cone of 17° opening angle (corresponding to a solid angle of 0.28 sr, or 4.5% of $2\pi$ for each detector). The two detectors were positioned symmetrically at 40° to the light path, in the plane parallel to the storage ring. The bunch marker signal from the storage ring was used as common stop signal for the TOF detectors. The time resolution of the experiment was of the order of 0.3 ns, yielding an energy resolution of about 0.5 eV for the lowest energies. To achieve optimum energy resolution, the path difference for electrons impinging at different places on the detector is included in the analysis. The beamline G1 at Hasylab provides linearly polarized light with energies between 30 and 80 eV. The polarization plane coincided with the plane spanned by the lines from the sample to the detector centers. The common operation mode of the Doris III storage ring is a five bunch mode, which provides 200 ns dark time between light flashes. To maintain a suitable ratio between real and chance coincidences, the light intensity was reduced by placing apertures with diameters down to 50 $\mu$m in the light beam. Typical coincidence count rates were between 5 and 20 events per second, while the direct (uncorrelated) count rate was about 3000 events per second in one detector.

The sample was a Cu(111) single crystal, which was prepared in the usual way by sputtering and annealing, until it showed a sharp $1\times1$ LEED pattern. Sample cleanliness was checked by Auger spectroscopy. $C_{60}$ surfaces were prepared in thin film form by deposition on this surface from a Knudsen cell. The growth of $C_{60}$ on Cu(111) surfaces has been thoroughly investigated: Since the distance between molecules in a bulk $C_{60}$ crystal is within 2% equal to four times the next neighbor distance between Cu atoms on the (111) surface, fullerene overlayers grow in an epitaxial fashion.[4] A well ordered monolayer can easily be formed by depositing $C_{60}$, and desorbing excess material by annealing to about 300 °C. The monolayer shows a characteristic $4\times4$ superstructure in low energy electron diffraction. Deposition of additional $C_{60}$ leads to layer by layer growth. STM investigations of a $C_{60}$ monolayer on Cu(111) have revealed internal structure within the molecule.[4] This shows that the molecules are fixed, i.e., do not rotate in a quasifree manner, in contrast to a number of other substrates as well as to the surface of a bulk fullerene crystal. The reason for the freezing of the rotational degrees of freedom apparently lies in the special surface geometry of the Cu(111) surface which allows the molecule to ratchet with one if its hexagonal faces to a threefold hollow site of the surface.

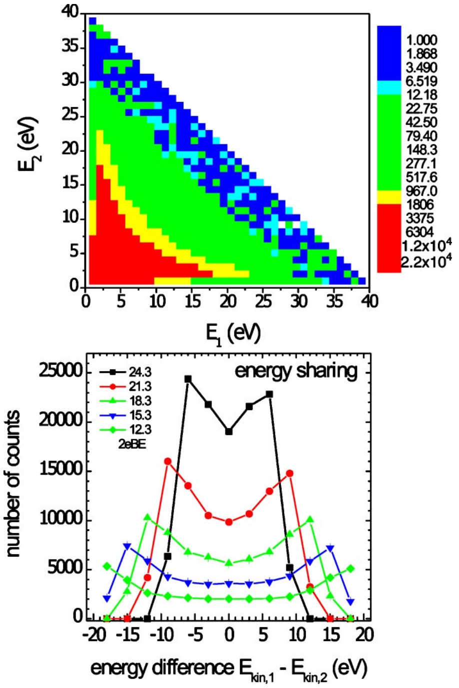

FIG. 1. (Color online) Two-electron photoemission for a monolayer of $C_{60}$ on Cu(111) measured at $h\nu=45$ at normal incidence. Top panel shows color coded distribution of double emission events as a function of the kinetic energies; lower panel shows energy sharing for 3 eV wide intervals centered at two-electron binding energies represented by different symbols.

For the discussion of our results, instead of considering the total kinetic energy, we define a binding energy for two electrons in an analogous fashion as in conventional photoemission. The two-electron binding energy (2eBE) is given by

$$2\mathrm{eBE} = h\nu - E_{k,1} - E_{k,2} - 2\phi,$$

where $E_{k,1}$ and $E_{k,2}$ are the kinetic energies, $\phi$ is the work function, and $h\nu$ is the photon energy. The onset of the distribution of two-electron binding energies, which we call 2e-spectrum, corresponds to a final state where both electrons have been ejected from the Fermi level $E_F$, i.e., from the highest occupied level. Since each electron must overcome the sample work function $\phi$, the onset occurs at $(E_{k,1}+E_{k,2})=h\nu-2\phi$, which corresponds to $2\mathrm{eBE}=0$.

## III. RESULTS FOR $C_{60}$/Cu(111)

Figure 1 shows a typical set of two-electron photoemission data for a monolayer of $C_{60}$ on Cu(111) in the form of a color coded intensity distribution. For a given locus on the plot, the energies of the two coincident electrons are given by its coordinates. The number of events for that particular combination of energies is represented by the color of the cell. The distribution is symmetric to the line $E_{\text{kin},1}=E_{\text{kin},2}$, which reflects the symmetric geometry of our experiment. The onset of the spectrum appears at a total energy $E_{\text{tot}}=E_{\text{kin},1}+E_{\text{kin},2}\approx 31$ eV, which will be discussed further below. The lower panel of Fig. 1 shows sections through the distribution of events in the upper panel along lines of constant total energy, or equivalently along lines of constant two-electron binding energy. The abscissa is given in terms of the difference of the two kinetic energies, which represents how the available energy is shared between the two electrons. Events in which the two electrons have equal kinetic energies, $E_{\text{kin},1}=E_{\text{kin},2}$, appear in the sharing distribution at energy difference zero. The smaller the total energy, i.e., the larger the 2eBE, the more narrow is the sharing distribution, as it must be because of energy conservation. The data in Fig. 1 show a minimum for equal sharing, which develops into a broad plateau for the smallest 2eBE. To put these findings into context, we compare to the sharing distribution found for the bare Cu(100) surface which is reported in Ref. 1 for the same experimental conditions. Referring to Fig. 3(b) in that paper for a total energy of 34 eV, which corresponds to a 2eBE of 2–3 eV, one also observes a minimum for zero energy difference, with a plateau extending between $\Delta E_{\text{kin}}=-10$ to $+10$ eV. The number of events at the edges of the sharing distribution, where one-electron energy is large, the other small, are about three times as large as in the central plateau region. In comparison, the data for the $C_{60}$ monolayer for the smallest 2eBE of 12.3 eV show a wider plateau than observed for bare Cu(100), and the rate at the edges is about two times larger than in the central plateau. At even smaller 2eBE the number of events is very small, and the sharing distribution is essentially flat. So, as far as the energy sharing is concerned, the overall behavior found for $C_{60}$/Cu(111) is qualitatively similar to the results for Cu(100) reported in Ref. 1, although there are some quantitative differences.

Figure 2 shows a set of results for the 10 ML film of $C_{60}$ taken with light incidence at 35° to the surface. This was realized by rotating the sample by 35° about an axis lying in the sample surface, normal to the plane of light incidence and detector axes. The relative positions of detectors to the light incidence remained unchanged, such that one detector (referring to the central axis) is now looking at the sample surface under 75°, the other one under −5° (measured from the sample normal). The sharing distributions are very similar to the ones observed for normal light incidence. The signal around equal sharing, relative to the signal at the edges or at large 2eBE, is not significantly different from the result obtained for normal incidence. For double photoemission the signal should be largest when the combined electron momentum is parallel to the light polarization.[1] For detection symmetric to the light incidence and even sharing, the combined momentum is perpendicular to the light polarization, such that there should be no or only a small signal. This argument is based on the magnitude of the scalar product of the electric field of the light and the resulting electron momentum. In principle, considering only the excitation process, this does not depend on the orientation of the surface, and one would expect the same behavior for normal or non-normal light incidence. Indeed, we observe essentially the same double photoemission cross section and sharing distribution, however the finite emission for even sharing and symmetric emission violates this simple model. Nevertheless, one may conclude that double photoemission is largely determined by the internal structure of the $C_{60}$ molecule.

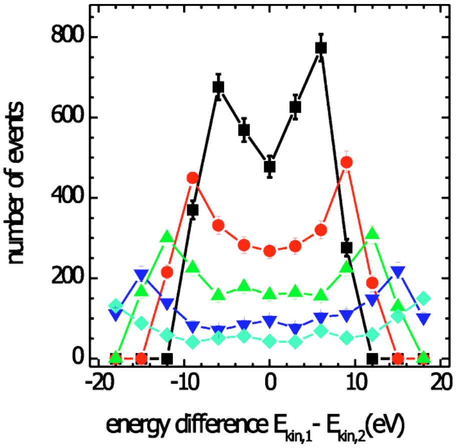

FIG. 2. (Color online) Two-electron sharing distributions for the 10 ML film for light incidence under 35° to the surface normal. The two TOF detectors are under 75° and −5° to the surface normal. The 2eBE windows for which the sharing distributions have been determined are 6–9 (diamonds), 9–12 (triangles down), 12–15 (triangles up), 15–18 (circles), and 18–21 eV (squares).

Figure 3 shows data for the 2eBE of the two electrons ejected from a monolayer of $C_{60}$ on Cu(111) and a film of about 10 layers thickness for normal incidence and detectors symmetric to the surface normal, i.e., for the conditions of Fig. 1. The spectra show the number of events as a function

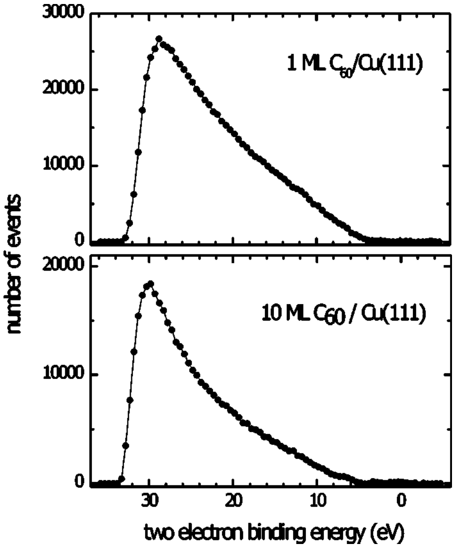

FIG. 3. Two-electron binding energy distribution from two-electron photoemission of $C_{60}$ adsorbed on Cu(111), taken at 45 eV photon energy under normal light incidence, and electron collection at ±40° to the surface. Upper panel, $C_{60}$ monolayer; lower panel, thick layer.

of the two-electron binding energy. For a photon energy of 45 eV, we find as highest sum energy 31 eV. This onset of the two-electron spectrum is consistent with the work function of $C_{60}$ of 7 eV known from other experiments. From the onset, the spectra rise toward lower total kinetic energy, and show a peak at 7 and 5.5 eV total energy for the monolayer and thick film, respectively. For the thick layer, the spectrum shows a change of slope to a steeper one around 12 eV. As the 2eBE distribution observed under non-normal light incidence, i.e., for the conditions of the sharing distribution shown in Fig. 2, is not distinguishable from that shown in Fig. 3 for the thick film, we omit to show this spectrum here.

The overall shape of the two-electron spectrum is to some extent determined by two step processes, in particular the rise of the spectrum towards low total energies. For the kinetic energies of our experiment, the inelastic mean free path for electron propagation is rather small, between 0.5 to 1 nm. Therefore, there is a large probability that a single electron originating from a conventional photoemission process undergoes a collision which leads to a loss of energy as well as to a change of propagation direction. At first sight one may expect the two step process to increase in weight relative to the one step process for larger energy loss since the number of available final states increases. This may explain the rise of the two-electron spectrum with decreasing total energy seen in Fig. 3.

In a simple picture, the probability to find a certain two-electron binding energy is expected to be related to the density of occupied electronic states. In single photoemission, the spectral intensity for a given kinetic or binding energy is given by the joint (i.e., initial and final) density of states, multiplied by the appropriate matrix element. In double photoemission, we can as a first approach start from an analogy to single photoemission. Then the spectral intensity for a particular sum energy should be given by all combinations of single photoemission events which yield that particular 2eBE. It is clear that this is represented by the self-convolution of the single photoemission spectrum. The single photoemission spectrum of $C_{60}$ has been reported by a number of groups.[2–6] It shows several features which are well understood in terms of electronic structure calculations, and can be associated with certain molecular orbitals. In contrast to the single photoemission data, the experimental 2e spectra at first sight do not show structures which appear to be related to features in the density of states. However, careful inspection suggests that at least the spectrum for the monolayer may contain some weak features. To remove background arising from two step processes and to enhance any fine structure which may be present in the 2e spectra, we subtract a smooth linear or polynomial background from the data. The results are shown in Fig. 4 for the $C_{60}$ monolayer and the thick film. Indeed, it turns out that the spectrum for the monolayer is not completely smooth, but shows some fine structure superimposed on the rising spectrum. In contrast, the spectrum for the thick film apparently does not show systematic modulations outside the statistical uncertainty.

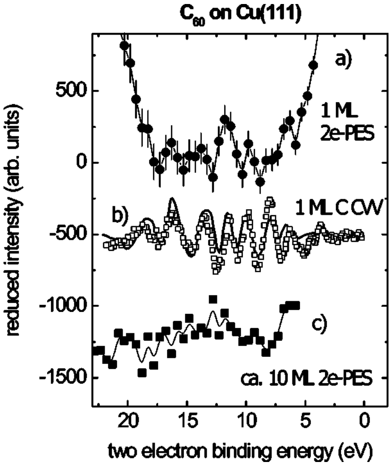

FIG. 4. Fine structure in two-electron photoemission from $C_{60}$ on Cu(111). (a) Two-electron photoemission of a $C_{60}$ monolayer on Cu(111) (filled circles, same data as upper panel in Fig. 2). To reveal fine structure, a linear background was subtracted. (b) Open squares show the carbon *KVV* Auger spectrum after subtraction of smooth background (from Ref. 3). Full line gives the self-convolution of the valence band density of states, shifted by 1.6 eV to higher two-electron binding energy. The fine structure in two-electron photoemission spectrum resembles that found in the Auger spectrum and the self-convoluted DOS. (c) Two-electron PE spectrum for a thick film of $C_{60}$ on Cu(111). After subtraction of a smooth spline the spectra oscillate around zero; for spectra (b) and (c) arbitrary offsets of −500 and −1250 were introduced to avoid overlap.

To understand the origin of the observed fine structure in more detail, we recall that a two hole final state similar to the one considered here is generated in an *XVV* Auger transition.[7] The initial state of the Auger transition is a core hole in a shell *X*, which is filled by a valence electron denoted by *V*, and another valence electron *V* is ejected, carrying away the surplus energy. Since Auger transitions are local, the two holes are generated at the same time on the same atom, or lattice site, and a genuine two hole final state is generated. As a consequence, the energy of the Auger electron is affected by Coulomb interaction, or correlation. This reasoning forms the basis of studying correlation effects in solids via *XVV* Auger spectra.[7] We suggest that the final states are identical for double photoemission and the carbon *KVV* Auger transition. Therefore, we expect to find similar features in the spectra. The carbon *KVV* Auger spectrum of $C_{60}$ is known[3] to consist of a broad rise over a range of about 20 eV,[6] which at first sight is structureless. After subtraction of a smooth background, fine structure becomes visible, as shown in Fig. 4. It turns out that there is a close correspondence between the fine structure observed in the 2e and the *CVV* Auger spectra of a $C_{60}$ monolayer on Cu(111). Closer inspection shows that while the positions of the peaks in the 2e spectrum correspond to those of the *KVV* Auger spectrum, the intensities are not the same: The peak at 12 eV is significantly stronger, and the peak at 7 eV is weaker than in the Auger spectrum. This may be caused by different weightings in the 2e spectrum. A possible interpretation is that the transition matrix elements for the various two hole final states are not identical to those in the Auger process.

For comparison, we show in Fig. 4 a self-convolution of the density of states as measured by photoemission. Convolution of the richly structured valence band spectrum with itself yields a broad peak with a number of small features, which become better visible after subtraction of a Gaussian or a similar curve. The fine structure shows the same sequence of peaks as the 2e or Auger spectrum, however, in order to make the peak positions coincide one must shift the self-convolution by 1.6 eV towards higher 2eBE.[6] This shift is caused by electron correlation, it costs more energy to generate two vacancies on one lattice site, in this case within one molecule, than to eject two electrons independently from each other. The observation of this correlation shift demonstrates that at least a fraction of the observed double photoemission is associated with events in which two electrons are ejected from one lattice site, or in our case from within a single atom within one molecule. This is the first direct observation of the correlation energy in double photoemission from a solid target.

At the bottom of Fig. 4, we show the 2e spectrum of the 10 ML film of $C_{60}$ on Cu(111) as given in Fig. 3(b), again after subtraction of a smooth polynomial. Here, we do not find the fine structure observed for the monolayer film. This apparently indicates that the direct double photoemission (i.e., the single step process) is less likely in comparison to other processes than for the monolayer film. At present it is not clear why the relative weight of one and two step processes should change with the thickness of the fullerene layer. There is no obvious reason why the matrix element for the direct double photoemission should depend on the thickness of the $C_{60}$ film since the electronic structure does not change significantly. Furthermore, we note that in the *CVV* Auger experiment the fine structure was observed for thick films which may be considered as the surface of bulk $C_{60}$.

Finally, we turn to the abundance of double photoemission events relative to single ones, since this ratio can be extracted with relatively low uncertainty from gas phase experiments,[9,10] and has also been addressed by theoretical investigations.[11,12] In the gas phase studies, all ions are extracted into a time of flight spectrometer, and the ionization state can be inferred from the flight time. Since the positive ions are collected, the experiment does not discriminate events where one electron has very low kinetic energy, as is the case in our experiment. The total number of double ionization events relative to single ionization events was measured as a function of the photon energy. For the photon energy used here, the results are comparable to our condensed phase data since according to Reinköster *et al.*[9] only single and double ionization play a role, whereas fragmentation of the molecule for which the photon energy is in principle sufficient does not occur. At $h\nu = 45$ eV, the ratio between angle- and energy-integrated double and single ionization events is found to be $1/7$,[9] whereas Kou *et al.*[10] find a ratio of about $2/3$. Theoretical analysis[11] yields a value of about $1/10$, considering only ionization out of the highest occupied molecular orbital (HOMO). As the experimental data are for all double ionization events, irrespective of the orbital which is being ionized, the results are not comparable to the theoretical data. Nevertheless, although there appears to be a discrepancy between the experimental data outside statistical uncertainty, the relative abundances are significantly larger than found in our experiment on condensed $C_{60}$. Without restricting the energy of the ejected electrons, and taking into account the relevant solid angle we find a ratio of the order of $1/50$ for double to single events. However, this is an upper limit for the ratio of total cross sections, since the doubles rate includes a large portion of events which involve an inelastic scattering process. Restricting the comparison to events where the electrons are ejected from the HOMO, as considered in the calculations,[11,12] will yield a smaller ratio. Unfortunately, this number cannot be determined with a precision comparable to gas phase experiments because of the relatively large influence of chance coincidences and because the background of events involving inelastic collisions cannot be separated unambiguously. In any case, the relative number of events double to single ionization events is smaller for the condensed sample.

## IV. DISCUSSION

For the interpretation of the data it is of course important to consider how much of the observed 2e signal is to be attributed to the $C_{60}$ overlayer, and which fraction arises from the substrate. From the small escape depth for electrons with kinetic energies as in our experiment, about 1 nm, we conclude that the probing depth in the two-electron experiment is of the order of 0.5 nm, which is comparable to the diameter of the $C_{60}$ molecule. Also, the 2e spectra of Cu(111) show quite a different shape from those of the $C_{60}$ films.[13] This suggests that the contribution of the substrate to the observed data is small. The fine structure which we demonstrate to be present indeed shows that the substrate contribution is negligible due to the small escape depth.

In the present analysis we have put the emphasis on the influence of the correlation energetics of the two emitted electrons, rather than on their angular distribution. As a first approach to understand the spectral properties of the double photoemission spectrum, we have drawn on the analogy between two-electron photoemission and Auger spectroscopy. As far as the final state is concerned, this analogy appears to be very close. This is evident in the close similarity of the fine structure observed in both types of spectra. However, there are also some differences which cannot be described within this simple model, specifically the magnitude of the features in the two-electron spectrum in comparison to the Auger result. In the Auger transition, the initial state is core ionized, and one of the valence electrons fills the core vacancy. In contrast, in double photoemission, the system is initially in the ground state, and both valence electrons are emitted into continuum states. This means that when one considers *all* particles, both initial and final states are quite different. Only the state in which the sample is left behind is identical in both experiments. In the Auger case, the overlap between the valence electron wave function of that of the core hole plays a role, while in the 2ePE case the overlap with the continuum wave function is important. The core state is described by a localized atomic wave function, which if expressed in terms of plane waves is an infinite series containing all wave vectors. In contrast, in double photoemission both electrons involved in the final state may be described by a plane wave with just one wave vector, or more realistically by a time reversed LEED state. Furthermore, in the 2ePE experiment the two continuum electrons may interact not only with the remaining target, which is known as post collision interaction in Auger spectroscopy, but also with each other. This aspect is not present in a simple Auger transition since there is only one continuum electron. It remains to be seen whether the spectral shapes can be described in a model taking the specific nature of the experiment into account. Of course, the present data represent only a small subset of all possible events since the angular acceptance is limited by the apparatus used, but as explained above, even with a larger solid angle of the detection the finite scattering length unavoidably imposes severe limits on experimental studies of the angular distribution. However, if we keep in mind that the angular distribution in studies on atomic or gaseous species did not show any strong features, we propose as a working hypothesis for the time being that the spectral results shown here will not change significantly if a wider angular range can be studied.

The relative magnitude of the features which reflect the self-convolution of the density of states is very small in our experiment. One might take this as a measure for the probabilities of the one step and two step processes, as the two step process should show a spectrum derived from the single photoemission spectrum, convoluted with the secondary loss spectrum. However, we point out that also the Auger spectrum shows only a very weak modulation which corresponds to the measured self-convoluted density of states. For the Auger spectrum, to date no reason is known for why the modulation is as weak as observed in experiment. Therefore, the small magnitude of the self-convolution structure in the two-electron spectrum is probably not solely due to the low cross section for the one step process relative to the two step process.

According to Berakdar,[8] electronic correlation as manifest in the correlation energy is a static property, while the influence on the dynamics of the correlation is reflected in the momentum distribution. Specifically, the angular distribution of the two emitted electrons may be affected by correlation. Experiments to investigate this aspect have been performed in the gas phase, where energy and momentum of one of the electrons was fixed, and the angular distribution of the second emitted electron was measured. Because of energy conservation and the effective absence inelastic scattering for gas phase targets, the energy of the second electron is fixed. In principle, it is possible to address angular correlation for double photoemission using our present experimental apparatus, however, the finite acceptance of the channelplate detectors provides access only to a rather limited range of momenta.

We have reported the direct observation of the electronic correlation energy in a solid by two-electron photoemission. The data show structures which coincide with the self-convolution of the density of electronic states, shifted by about 1.6 eV to higher energy. The shift is caused by the correlation energy between the two holes created simultaneously on one site.

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