Angle Resolved Energy Correlated Coincidence Electron Spectroscopy of Solid Surfaces

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We report on the first measurements of the angle resolved energy distribution of correlated electrons created in single scattering events by low energy (E_p = 14–25 eV) electrons. We combined coincidence and time-of-flight techniques to measure simultaneously energies and momenta of both scattered electrons of the correlated pair. The measurements were performed in the backscattering geometry on a single crystal W(100) and a thin film of LiF. We found that the most probable energy distribution of electron pairs corresponds to a constant sum of energies of both electrons.

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The scattering dynamics of a kinetic electron with the valence electrons of a solid is an important, though difficult, subject. It is important because it underlies the interpretation of any electron spectroscopy in emission or scattering and is of fundamental interest in its own right. This problem is difficult, both theoretically and experimentally, because electron-electron scattering in the valence band is not easily distinguished from collective excitations of the electron charge density. The theoretical treatment of the scattering even requires two initial and two final states to be calculated within a realistic band structure with a largely unknown interaction potential. As a result, not much is known to date about the scattering dynamics of electrons some 10 eV above the Fermi level with the conduction electrons. In the field of atomic and molecular physics, electron scattering processes have been very successfully studied for inner and outer electron shells by using $(e, 2e)$ spectroscopy [1]. Most of the experiments with solid targets were performed in a transmission geometry, where a high energy incident electron (10–20 keV) passes through a thin film and is detected in coincidence with an ejected electron of low energy [2,3]. In the same spirit a surface experiment has been reported very recently [4], where 300 eV primary electrons at grazing incidence excite valence electrons in the near surface region. The momentum density of highly oriented pyrolytic graphite has been measured in this way. In our experiments we have used a backreflection geometry with low energy (14–25 eV) electrons at normal incidence and coincident detection of two electrons leaving the surface at a fixed angle. In previous experiments we demonstrated the existence of such correlated electron pairs emitted in coincidence [5–7]. The model of the underlying process was the elastic backscattering of a primary electron from an ion core potential, followed by its collision with an electron from the valence band with a large energy and momentum transfer. This model was corroborated by (i) the observation of a threshold energy for the primary electron which is related to the work function of the sample, (ii) the observation of a most probable angle of 60°–90° between the ejected electrons, depending on the primary energy, and (iii) the energy of the two electrons most probably to be equal. What was missing in these experiments was the determination, separately, of the energy of each of the electrons of a pair. This knowledge is crucial in distinguishing electrons created in a single-scattering event with the backscattered primary electron from electrons created in a cascade process, such as secondary electron production. In the former case the sum of the energies of the two electrons must be equal to the primary energy minus the electron binding energy, while in the latter case this balance does not need to be fulfilled. Only in the former case can the scattering dynamics of low energy electrons be studied.

In this paper we report on the first successful measurements of the energy distribution of correlated electron pairs emitted from the surface, after excitation, by a low energy primary electron. We developed a new two-dimensional time-of-flight coincidence technique which allows us to measure simultaneously energies and momenta of both electrons of a correlated pair. We applied this technique to two different materials with very different rates of low energy electron-electron scattering: tungsten as a metal and LiF as a dielectric with a wide energy gap.

The electronic setup for two-dimensional time-of-flight electron energy distribution measurements in a two-electron coincidence experiment is shown in Fig. 1. The incident electron current is pulsed with a width of less than 5 ns and a repetition rate of 2.5×10^6 pulses per second. The modulating pulse is used as the zero of the time-of-flight scale and starts both time-to-amplitude converters (TAC). When the incident electron loses its energy and exites a valence electron, one of them stops the first TAC, while the other one stops the second TAC. An additional coincidence circuit serves to reject all events not arriving simultaneously within a time window of ~200 ns. A valid event represents a point in a two-dimensional time-of-flight coordinate system. One of the coordinates of this point defines the energy of the first electron of the pair, and the second coordinate defines the energy of the second correlated electron. The detailed

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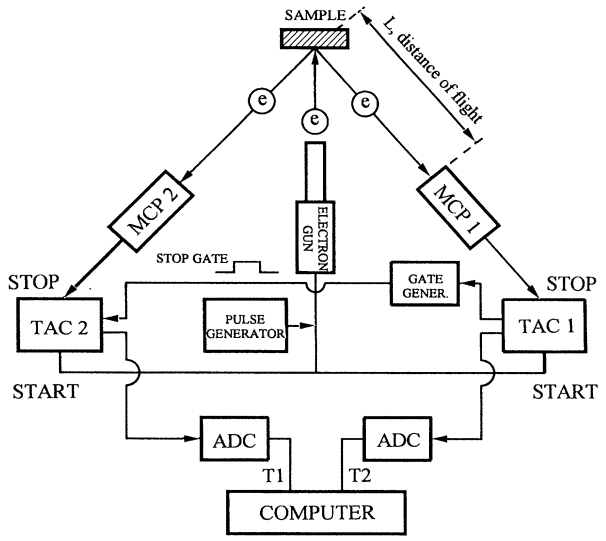

FIG. 1. Electronic setup to the two-dimensional time-of-flight electron energy distribution measurement. (TAC is time-to-amplitude converter, ADC is analog-to-digital converter, and MCP is multichannel plate.) A stop gate pulse allows the second TAC to accept a stop pulse from MCP2 only within a 200 ns gate time, generated by the stop pulse from MCP1.

description of this scheme will be given in a forthcoming paper. The main advantage of the two-dimensional time-of-flight system over a conventional two-analyzer system is its greatly enhanced true-coincidence count rate (a few counts/s vs a few counts/min [3,4]) which allows measurements even on highly reactive surfaces such as W.

The targets were a W(100) single crystal and a thin film of LiF (about 20 Å thick) evaporated *in situ* onto the tungsten substrate. The tungsten sample cleaning routine included oxygen treatment, followed by high temperature flashes to remove oxidation products. The surface cleanliness was monitored by Auger spectroscopy. The residual gas pressure during measurements did not exceed the 10^{-11} Torr range. The sample was periodically heated up to 700–1000 °C between measurements to remove adsorbed gases from the sample surface. The Earth's magnetic field inside the vacuum chamber was compensated by a factor of 100 by using a Helmholtz coils field and a Mumetal screen. The W(100) sample had been oriented in such a way that the [100] direction was in the detectors plane. The primary electron beam was normal to the sample surface, the average current being of the order of 10^{-14} A. The electrons leaving the sample were detected by two multichannel electron multipliers with a solid angle of 0.07 sr each, positioned at $\pm 45°$ relative to the surface normal.

The result for W is shown in the top panel of Fig. 2 on a 2D gray scale plot. The horizontal line and the vertical line at the lower left corner of the figure are due to accidental coincidences involving an elastically backscattered primary electron (kinetic energy $E_p = 16$ eV) in the one detector and an inelastically scattered electron in the other detector. Their crossing, due to two elastically scattered electrons, is used to define the zero of the two time-of-flight scales. Near the center of the plot, a bananalike ridge is observed which peaks near the diagonal. These are true coincidence events of two inelastically scattered electrons riding on a monotonous background. Evidently, the most likely electron-electron scattering processes are those with similar energies of the two electrons. The background in the region on the bananalike ridge includes only accidental events due to the scattering of different primary electrons belonging to the same bunch, while in the region above to the right of the ridge it has an additional component due to the multiscattering processes, that is, comprising scattering events of the electrons that previously have lost some of their energy in the cascade process. We estimate the effect/background ratio on Fig. 2 in the central part of the bananalike ridge (for the approximately equal electron energies) as 2.8:1. Converting the flight time into an energy scale reveals that the most likely energy for the two electrons is about 5.5 eV above the vacuum level. Combinations of high energy on the one axis (i.e., short time of flight) with low energy on the other axis (long time of flight) do also occur, but with less probability. The ridge is symmetrical, because the distance of flight is equal for the two detectors, and their position is symmetrical about the surface normal. It is noteworthy that, at the upper right corner, corresponding to slow electrons in both channels, the intensity is very low. This means that a coincident emission of two slow secondary electrons (1–3 eV), which dominate ordinary electron spectra, is very unlikely. The cascade process of secondary electron production, evidently, does not interfere with one-step electron-electron scattering.

The dashed line indicates a line of constant total energy of the electron pair, assuming other energy losses to be absent. The locus of this line is given by

$$\frac{1}{2} m_e L^2 \left(\frac{1}{T_1^2} + \frac{1}{T_2^2} \right) = E_0, \tag{1}$$

where m_e is the electron rest mass, L is the effective flight distance, T_1 and T_2 are the flight times, and E_0 is the total (constant) energy of the electron pair. From the measured peak position of the ridge, we find $E_0 = 2 \times 5.5 = 11$ eV. Apparently, the top of the ridge fits well to this line of total constant energy. From this fit, we may determine the binding energy E_b of the ejected electron with respect to the vacuum level by equating

$$E_b = E_p - E_0 = 5 \text{ eV}. \tag{2}$$

Since the work function of W(100) is 4.6 eV, this means that the ejected electrons probably come from just below the Fermi level. This is true for any points along the ridge. In the upper-right part of Fig. 2, the ejected

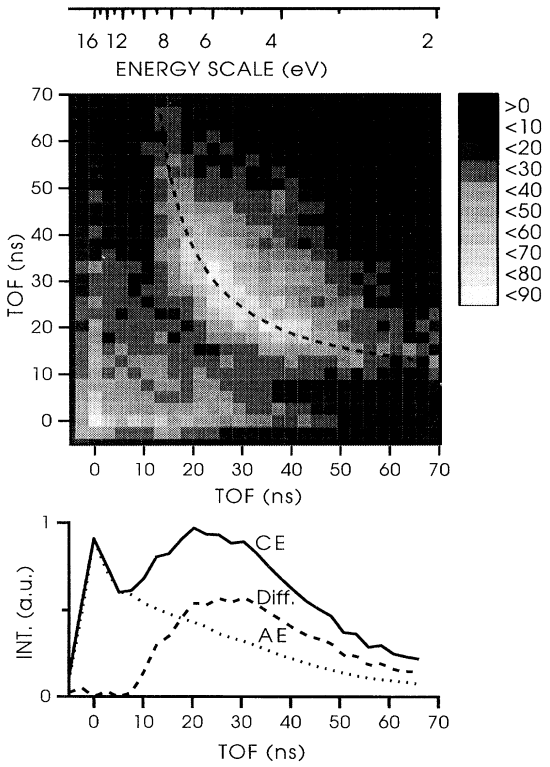

FIG. 2. Top panel: Top view projection of the 3D plot of the time-of-flight distribution of correlated electrons of W(100). Primary energy $E_p = 16$ eV. The gray scale in the image reflects the relative number of coincidence events, white being the largest value. The white grid separates channels of the time-of-flight analysis. The gray scale gives the total number of events per channel. The dashed line corresponds to the constant sum of energies of two correlated electrons equal to 11 eV. Diffuse lines along the axes in the lower-left corner correspond to distribution of accidental coincidence events. Lower panel: The full line (CE) represents the projection of the 2D time-of-flight onto the horizontal axis. Without imposing the coincidence condition, only accidental coincidences are detected, leading to the projection of shape AE. Scaling this curve to fit CE in the high energy region provides a good estimate of the background of accidental coincidences in the region of the true coincidences. These correspond to the difference curve, showing a cutoff at ~10 eV.

electron stems from deeper levels below E_F at the expense of the energy of the exciting electron. Of course, at these low energies, exchange is quite likely, which makes the meaning of "ejected electron" and "exciting electron" irrelevant. Here, we observe in a fairly direct way the electron-electron scattering dynamics in a metal.

In the lower panel of Fig. 2 we show the projection of the time-of-flight matrix onto the horizontal time-of-flight axis (curve CE). This shows true coincidence events together with accidental coincidences as a background. The background in the region of true coincidences (i.e., 10 eV and lower) is determined by fitting the results of a similar measurement, but without the coincidence condition, curve AE, in the region of the high energy peak of curve CE. The difference represents the true coincidence events projected on one time-of-flight axis. We note that in the curve AE, which is similar, though not identical to, an ordinary electron energy loss spectrum, no particular feature can be identified which would correspond to the distribution of the true coincidences. This does not mean that electron-electron scattering is negligible with respect to other energy loss channels. It simply means that the phase space of our equipment is yet insufficient to detect correlated electron pairs by their true proportion. (In principle, each of the detectors with unity detection efficiency would have to cover the half-space above the sample.) We hope to solve this issue by comparison with an internal source of photoelectrons in the future.

The electron-electron scattering dynamics in a metal are expected to be clearly different from those in an insulator because of an energy gap above the occupied electron levels. As a prototype insulator, we use LiF with a band gap of about 13 eV. The electron affinity is around zero, depending on the sample. In any case, the vacuum level is close to the conduction band edge. Our sample is a thin film (about 2 nm thickness) evaporated onto W(100). At an electron energy of 18 eV, this thickness was checked to be sufficient to suppress contributions from the underlying W substrate. The angle between the detectors was 90° (±45° from the surface normal) as before. The result is shown in Fig. 3 (top panel) on an enlarged scale, with the time zero at the lower left corner. Again, we observe a well-defined ridge, though it shifted towards larger flight times, i.e., lower energy. The background from accidental coincidences is negligible. Applying the same analysis on the location and shape of the distribution of the coincidence events, we find $E_0 = 6.5$ eV by Eq. (1). From Eq. (2), we find a binding energy of $E_b = 11.5$ eV, which is close to the measured difference between the highest occupied level of LiF and the vacuum level in bulk LiF (12.9 eV, Ref. [8]). Therefore, also in this case, a kinetic electron scatters in direct collisions with valence electrons throughout the valence band. The intensity profile along the ridge is nearly constant, which is probably due to the smaller energy window compared to W, since the kinetic energy after scattering is lower. Correspondingly, the projection onto the horizontal axis in the lower panel of Fig. 3 shows a much wider distribution of coincidence events, riding on an almost negligible background of accident coincidences.

The present experiments demonstrate that energy loss processes of low energy electrons in solids are at least partly determined by direct electron-electron collisions with valence band electrons (we do not yet know at which proportion relative to dipole excitations). Our two-dimensional time-of-flight coincidence technique seems

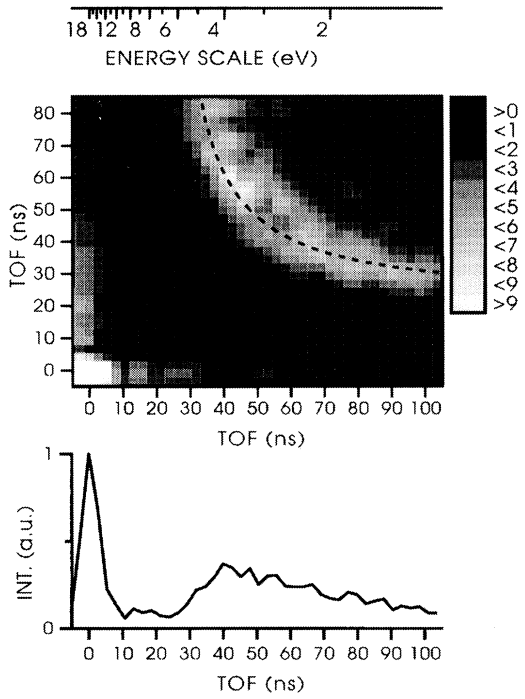

FIG. 3. Top panel: Top view projection of the 3D plot of the time-of-flight distribution of correlated electrons of a thin LiF film. The incident electron energy is 18 eV. The gray scale in the image reflects the relative number of coincidence events, white being the largest value. The white grid separates channels of the time-of-flight analysis. The gray scale gives the total number of events per channel. The dashed line corresponds to the constant sum of energy of two correlated electrons equal to 6.5 eV. Lower panel: Projection onto the horizontal axis, such as in Fig. 2.

to be a powerful new tool to study electron-electron collisions in the near-surface region of a solid. The extension of this technique to the detailed study of exchange processes by using a polarized electron source and a ferromagnetic target is obvious. Work along this line is in progress.

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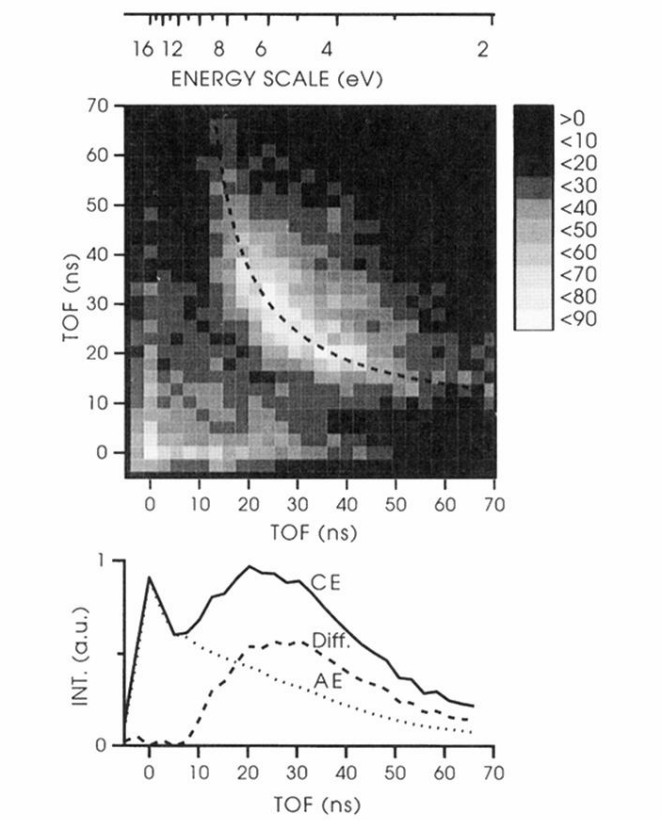

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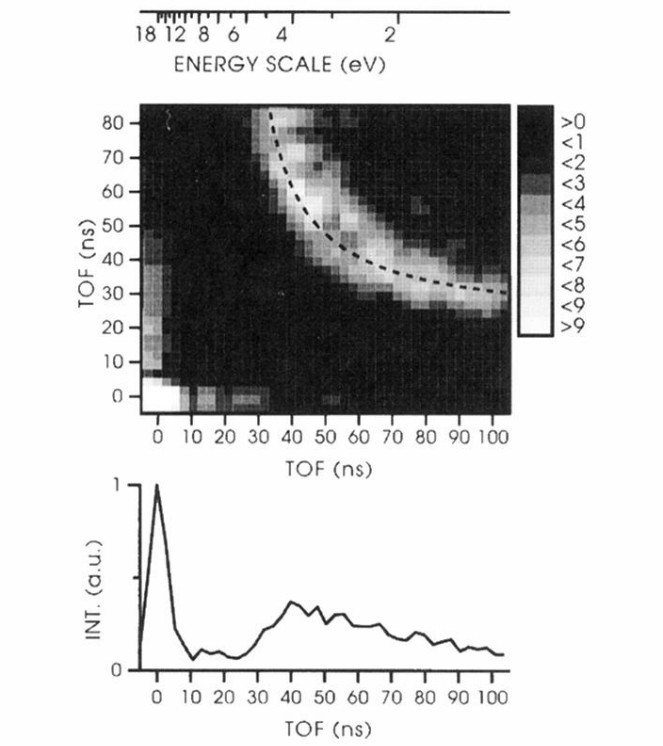

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