Spin Blocking in the Correlated Double-Electron Capture from Metal Surfaces

C. Tusche[*]

Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany
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The resonant capture of electrons from a metallic surface into the outer shell of a helium ion creates doubly excited states in a spin singlet ($\uparrow\downarrow$) or triplet ($\uparrow\uparrow$) configuration. Here it is shown that the capture of one or two electrons can be described in a simple quantitative model, and the capture of two electrons by He^{++} proceeds in a single step. The double capture of electrons from the Fermi energy of the metal is dominated by the spin dependent electron correlation that blocks the occupation of triplet states in the ion, but creates a singlet two-hole final state at the surface, related to the concept of the exchange-correlation hole.

The many-particle electron system in a solid is typically described by independent quasiparticles. This approximation is in many cases successful since the charge of each electron is screened in a way that it looks neutral. It was already recognized in the 1930s by Wigner and Seitz [1] and Slater [2] that this screening is spin dependent. This leads to the concept of the exchange-correlation (xc) hole [3], where each electron is surrounded by a region of reduced density of electrons with the same spin orientation. A direct probe of the electron interaction is the detection of two or more electrons that were emitted in a many-body excitation, e.g., by photons or electrons [4,5]. However, direct information about the spin contribution to the electron correlation is complicated by the fact that an efficient detection of the spin of a two-electron final state is still unsolved.

A further mechanism for the excitation of the electron system at a surface is the interaction with ion beams [6–10]. During the neutralization of ions, multiple electrons are emitted from the surface or captured into the outermost shells of the ion, forming a "hollow atom" [11,12]. The spin of the electron is conserved during the charge transfer, which provides a particularly sensitive probe for surface magnetism [13–16], or spin selective ion interaction with nonmagnetic surfaces [17,18].

As electrons are excited on a short time and length scale, the neutralization can give direct access to electron correlations. For instance, Unipan *et al.* [19,20] related the population of spin singlet ($\uparrow\downarrow$) and triplet ($\uparrow\uparrow$) states of doubly excited He^{**} during the neutralization of He^{++} from a ferromagnetic sample, to the surface spin polarization. This was based on the simple assumption that two electrons would be captured independently. Busch-Wethekam-Winter [21] showed later that the interpretation was influenced by an experimental artifact: The occupation of the doubly excited states could be sensitively influenced by adsorbates, which was tentatively related to a modified work function (Φ_S). So far, a conclusive picture that

delivers quantitative information on the spin correlation of surface electrons is not available.

In this Letter, the capture of one electron by metastable $He^{*+}(2s)$ and of two electrons by He^{++} is compared, both resulting in the same doubly excited state, on clean metal surfaces with different Φ_S, and after variation of Φ_S by adsorption of cesium (Cs) or oxygen (O_2). The results provide first evidence that the capture of two electrons proceeds simultaneously without intermediate formation of $He^{*+}(2s)$. This correlated double capture creates preferentially a singlet two-hole final state in the metal, explaining previous results.

Doubly ionized He^{++}, metastable $He^{*+}(2s)$, and He^+ ions were created using a modified sputter gun [22]. In order to avoid molecular hydrogen ions in the beam, the ^3He isotope was used. Emitted electrons were collected by a hemispherical analyzer (PHOIBOS 150, Specs GmbH), in an angle of 50° with respect to the ion beam. Ions with a kinetic energy of 5–30 eV are scattered at the sample under an angle of incidence of 10°. W(100), W(110), and Ir(100) crystals were prepared by cycles of flashing in oxygen (5×10^{-8} mbar), followed by a high temperature [1700 K for Ir(100), 2400 K otherwise] flash. This procedure leads to clean, carbon free surfaces, monitored by the thermal desorption of CO [23]. Layers of Fe, Ni, and Mn were prepared by evaporation from a high-purity rod. The cleanliness of all surfaces was checked by ion neutralization spectroscopy (INS), which is particularly sensitive to trace amounts of adsorbates [24], and by Auger electron spectroscopy after the experiments. All measurements on clean surfaces were performed within less than 15 min after preparation.

In INS one observes electrons emitted during the Auger neutralization of He^+ [25,26]. Figure 1(a) shows measurements using 5 eV He^+ ions. These electron spectra represent the self-convolution of the surface density of states (SDOS) involved in the neutralization. The low-energy edge of the spectrum is used to monitor the surface
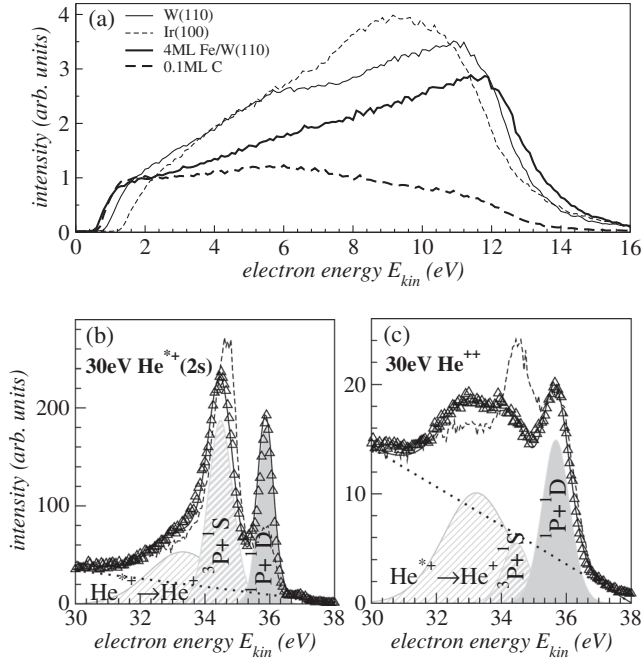
FIG. 1. (a) INS of clean W(110) or Ir(100), clean 4 ML Fe/W(110), and after adsorption of 0.1 ML of carbon. (b) Neutralization of 30 eV $He^{*+}(2s)$ ($\triangle$) at 4 ML Fe/W(110), together with a fit (solid line) of the $^3P + {}^1S$ and $^1P + {}^1D$ He KLL lines and the $He^{*+} \rightarrow He^+$ Auger deexcitation. The spectral weight changes after adsorption of 0.1 ML carbon (dashed line). (c) The same using 30 eV He^{++} ions.

by Gaussian functions, using a linear background for the high-energy tail of the Auger capture $He^{*+} \rightarrow He^*$.

Figure 1(c) shows the experiment repeated with 30 eV He^{++} ions. In contrast to $He^{*+}(2s)$, where the intensity ratio was $T/S = 2.3$, a suppressed $^1S + {}^3P$ contribution ($T/S = 0.3$) is observed. This result is in agreement with spectra shown by Hagstrum and Becker [30] and Busch-Wethekam-Winter [21], characterized by low triplet peaks. After adsorption of 0.1 ML C, the spectral weight changes. Intensity of the singlet peak is reduced for single capture. For double capture, a different effect is observed: Only the triplet peak is increased, such that T/S becomes 1.1. While carbon adsorption changes Φ_S by less than 50 meV, it has strong impact on the SDOS probed by the ion [see Fig. 1(a)].

For a quantitative understanding of the spin-dependent occupation of the excited He states, the neutralization was studied systematically on surfaces with different work functions. In a first experiment, Φ_S was varied by exposure of Cs or O_2. In order to avoid influences from a changed SDOS for very low coverages, first 0.1 ML carbon was adsorbed on the bare metal surfaces. Figure 2(a) shows the measured intensity ratio vs Φ_S, when one electron is captured. For low work functions, T/S approaches the ratio of the statistical weights [20] around 1.25, and steeply increases up to $T/S = 20$ at $\Phi_S = 5.5$ eV. Most importantly, points measured for different samples
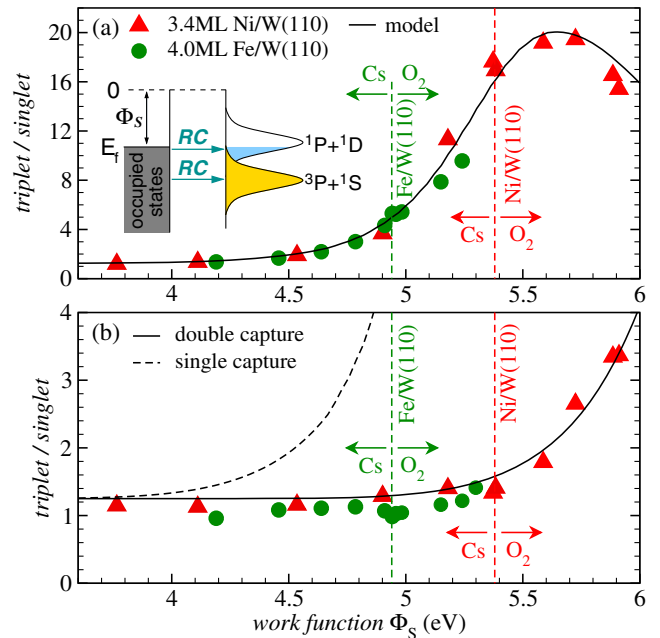
work function. Absolute values are given with respect to W(110) (5.22 eV). Electrons at the high-energy edge at 15 eV originate from the Fermi energy (E_f), and the intensity is related to the SDOS at E_f. The metals iridium and tungsten are characterized by a high density of states near E_f, related to d bands [27–29] observed as broad intensity maxima around $E_{kin} = 10–12$ eV. This is even more pronounced for the transition metals, like 4 ML Fe on W(110), due to the presence of $3d$ bands at E_f. Nonmetallic adsorbates lead to a strong decrease of the INS intensity at E_f, as shown for adsorption of 0.1 ML of carbon. The same effect is also observed for adsorption of H_2 from the residual gas [22] and oxygen or cesium.

Figure 1(b) shows the electron spectrum obtained for the single electron capture by 30 eV $He^{*+}(2s)$ ions at a 4 ML Fe film. The spectrum shows two strong peaks at an electron energy of 34.5 and 35.9 eV, that originate from the KLL Auger decay of He^{**} [30]. Each of the peaks has contributions from two excited states. The first peak corresponds to decays of the $2s^2\,{}^1S$ and $2s2p\,{}^3P$ states, and the second peak of the $2p^2\,{}^1D$ and $2s2p\,{}^1P$ states. However, the ninefold degeneracy of the ^3P state leads to a 90% triplet contribution in the first peak, while only singlet states contribute to the second. Therefore, the first peak was termed "triplet" (T), and the second peak "singlet" (S) [19,20]. For intensity evaluation the spectrum is modeled

FIG. 2 (color online). Triplet to singlet ratio observed for $He^{*+}(2s)$ ions (a) and He^{++} ions (b) vs Φ_S. Measurements for Ni/W(110) (triangle) and Fe/W(110) (circle) by adsorption of Cs and O_2 start at the initial Φ_S, indicated by the vertical lines. Solid and dashed curves represent the calculated T/S from fractional occupancies of levels near E_f (see inset).

[4 ML Fe/W(110) and 3.4 ML Ni/W(110)] follow the same curve.

The result can be understood considering that levels close to E_f get not completely filled at high work functions due to a finite overlap with occupied states [30]. Quantitatively, the $^1P + ^1D$ and $^1S + ^3P$ peaks are described by Gaussian functions. Resonant capture (RC) fills both peaks up to E_f, interpreted as a capture probability ≤ 1. This is illustrated in the inset in Fig. 2(a). The distance (d) of the capture is determined such that the Coulomb barrier between the ion and the surface drops below E_f and the ionic level. It is then assumed that the filling of the level i ($i = \{^1P, ^1D, ^1S, ^3P\}$) proceeds instantaneously, with a probability ρ_i:

$$\rho_i = (1 - \rho_0)\frac{g_i}{\sigma\sqrt{2\pi}}\int_{-\infty}^{E_f} e^{-\frac{1}{2}\left[\frac{t - E_i - \Delta E_i(d)}{\sigma}\right]^2} dt + g_i\rho_0, \quad (1)$$

with the binding energy E_i and the multiplicity g_i of level i. The distance dependent energy shift (ΔE_i) of each level by image charge interaction follows the approach from Ref. [31] with a screened Coulomb potential. When only one electron is involved in the neutralization, best results are obtained with the adiabatic description, where the metal surface reacts instantaneously to the charge transfer. When two or more electrons are transferred, and the metal cannot instantaneously fill the created hole, the diabatic model is used. For all states, a common width parameter, σ, and $\rho_0 = 5\%$ is used. The intensity ratio is then calculated from the fractional occupancies $T/S = (\rho_{1S} + \rho_{3P})/(\rho_{1P} + \rho_{1D})$, assuming a complete KLL Auger decay. This model, as shown as the solid line in Fig. 2(a), gives a good agreement over the complete range of measured work functions using a full width at half maximum (FWHM) of 1.0 eV in Eq. (1). This is an effective width that includes effects from lifetime broadening and the Fermi edge.

Figure 2(b) shows the work function dependence for doubly charged He^{++} ions, measured for the same samples. As a clear difference to above, the curve is flat with ratios close to 1.25 for work functions up to 5.4 eV. This is also reflected by the lower maximum ratio of 3.5 at 5.92 eV, indicating an increased relative probability to occupy the high energy level even at high work function surfaces, than for He^{*+} ions.

To understand this difference, one needs to look at the possible neutralization paths that can fill the doubly excited He states. It is commonly believed [19–21,30,31] that the neutralization of He^{++} proceeds through RC of a first single electron and the intermediate formation of metastable $He^{*+}(2s)$ above the surface. Then, the second electron would be captured in a second step, treated independently. As the occupation probabilities would be determined in the second step, one would expect a result similar to the
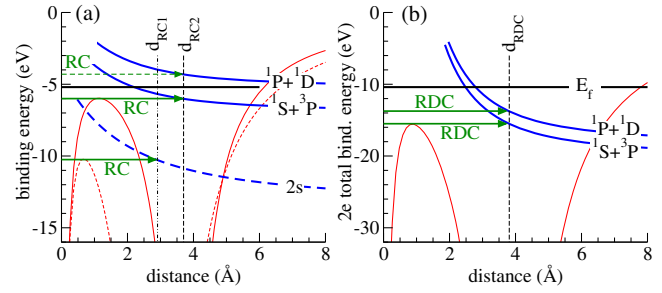

FIG. 3 (color online). Energy levels (thick blue lines) and Coulomb barrier (thin red lines) for the capture of (a) one electron into the $He^{*+}(2s)$ (dashed lines) or He^{**} states (solid lines), and (b) the simultaneous capture of two electrons.

singly charged ion. This argument was also used before by Busch-Wethekam-Winter [21] to explain a pronounced sensitivity due to the adsorption of oxygen on a nickel surface. The energy scheme for the first and second capture is shown in Fig. 3(a). The condition for the capture of the first electron to the $2s$ level is found at a distance closer to the surface than for the second capture ($d_{RC1} = 2.9$ Å vs $d_{RC2} = 3.7$ Å). Following this classical picture, a subsequent capture of two electrons on the incoming trajectory is therefore unlikely.

An alternative path to fill the He^{**} states is by simultaneous resonant capture of two electrons. This resonant double capture (RDC) becomes the dominating transition channel when the resonance condition between the occupied states and the atomic level is met at a larger ion-surface distance than for the sequential capture [32]. For a simultaneous capture, only the total energy of the electron-pair is conserved. This energy can be arbitrarily shared between both electrons, peaked at equal energies for single-step transitions, as was demonstrated for double photoionization of helium [33], or double photoemission from surfaces [34].

Figure 3(b) show that the energies for the RDC are clearly in the region of occupied metal states. The result of this model is shown as the solid curve in Fig. 2(b). A good agreement with the measured data is obtained over the complete Φ_S range, using a slightly reduced capture distance of 3.0 Å, over $d_{RDC} \approx 3.8$ Å estimated from Fig. 3(b). The slightly reduced effective distance is not very surprising as exact values of RDC transition rates are unknown. It can be concluded that the simultaneous two-electron capture is the dominant neutralization channel in the studied range of Φ_S. When Φ_S becomes sufficiently small (≤ 2 eV), however, additional neutralization channels involving the $3s$ levels or formation of He^{-**} can increase the occupation of the triplet states [35].

In a second experiment, bare W(110), W(100), and Ir(100) surfaces, and films of Fe, Ni, and Mn grown on these substrates were studied. The different film-substrate

combinations exhibit work functions in the range from 4.5 eV [Mn/W(110)] to 5.6 eV [Ir(100)]. Figure 4(a) shows the results for the single electron capture by $He^{*+}(2s)$. Error bars were derived from independent samples. Here, the qualitative behavior is similar to the Cs or O_2 covered surfaces. The detailed comparison shows that the measured points lie below the curve of the adsorbate covered surfaces, and the onset of increased T/S is slightly shifted to higher work functions.

In the model displayed by the solid line in Fig. 4(a), this is well described by a reduced FWHM of 0.7 eV, and additionally, a shift of Φ_S by 0.25 eV. For instance, at the clean metal surfaces, the effective work function seen by the ion is reduced. This can be readily understood by comparing the INS spectra in Fig. 1(a): The metals are characterized by a high INS intensity at E_f, attributed to the d states. These states contribute strongly to the ion neutralization, leading to a lower effective work function. Even for minute adsorbate coverages, states close to E_f are suppressed in the INS spectrum, and do not contribute to the electron capture.

A qualitatively different result is found for doubly charged He^{++}, shown in Fig. 4(b). While the intensity ratio is constant up to $\Phi_S = 5.4$ eV, this ratio is centered around $T/S = 0.3$, clearly smaller than above. Literally, this means that the singlet peak has a higher intensity than
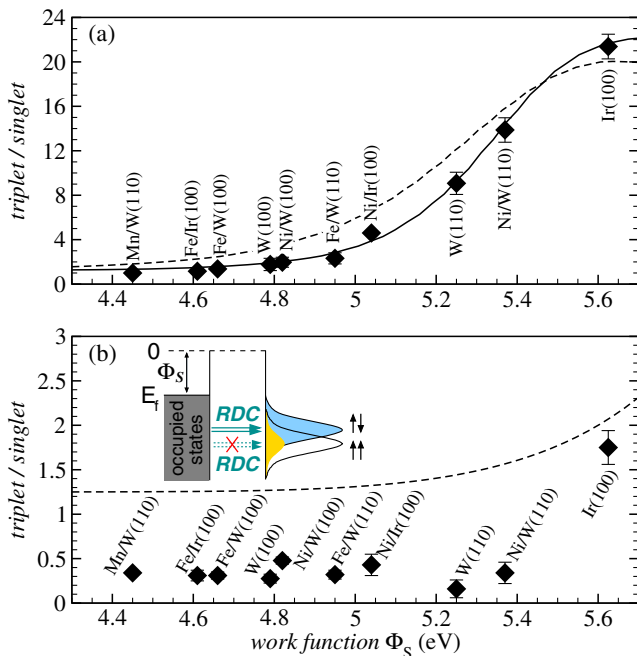

FIG. 4 (color online). Triplet to singlet ratio vs surface work function measured on various metals as indicated by the labels, using singly charged $He^{*+}(2s)$ (a) and doubly charged He^{++} (b). Occupation of triplet states is blocked during RDC (see inset). The solid line shows the calculated T/S from the model (see text), and dashed lines show curves from Fig. 2.

the triplet peak [also see inset in Fig. 4(b)]. This is in line with the observation in Fig. 1(c), where carbon adsorption leads to an increase of the triplet component, not affecting the high-energy peak close to E_f.

To understand this result, one needs to remember that only the triplet peak contains contributions of states with parallel spins. In general, the spin of the electron is conserved during capture from the surface [13–16]. It is therefore concluded that the double capture creates preferentially a singlet two-hole final state at the surface, and blocks the ^3P component, when both electrons originate from the high SDOS at E_f. This is the case for the clean metal surfaces, where the capture probability is peaked close to E_f. As we learned from the single capture, adsorption modifies the SDOS such that the pronounced d-electron contribution at E_f is strongly reduced. This is directly observed in the reduced INS intensity at E_f, which corresponds to a situation where two electrons interacting with the ion are separated by several eV on the energy axis. Only in that case, electrons with parallel spins are found. A significant difference between ferromagnetic (Fe and Ni) or nonmagnetic surfaces is not observed. Ir(100) is an exception, as Φ_S is already in a range where the singlet occupation is reduced.

An antiparallel spin correlation in the multielectron interaction is not surprising. For instance, antiparallel spins were previously observed for two surface electrons involved in the Auger capture by spin polarized He^+ [17]. This was later explained by a spin dependent screening induced by the polarized ion [36,37]. The latter is not applicable for He^{++} ions. However, spin dependent screening of electrons is a dynamic process present in any electron gas. The concept of the xc hole describes that for any given first electron, the probability to find a second electron with the same spin drops to zero at the same place [2]. In general, the farer both electrons are separated in phase space, e.g., in energy, the less pronounced is this correlation. Capturing two electrons from this correlated electron gas, both originating from the Fermi energy, therefore can explain the absence of the triplet component.

In summary, the electron capture to doubly excited He^{**} states can be understood in a quantitative model, that predicts the relative occupations in dependence on the surface work function. For the first time, evidence was given that two electrons are captured simultaneously in an resonant transfer. On bare metal surfaces, this correlated double capture from states close to the Fermi energy creates a singlet two-hole final state at the surface, and blocks the occupation of triplet states. These findings explain previous experiments on the neutralization of doubly charged He ions. The double electron capture may provide an experimental access to spin dependent electron correlation at metal surfaces, and can complement multielectron emission spectroscopies.

* tusche@mpi-halle.mpg.de

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