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Reexamination of local spin polarization at surfaces probed by hollow atoms

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The formation of doubly excited He atoms during impact of He^{2+} ions with energies from 64 to 500 eV on a clean and oxygen-covered Ni(110) surface is studied via Auger electron spectroscopy. We find that the electron spectra are affected by the adsorption of oxygen on the surface, which can be related in a clear-cut manner to shifts of the target work function. Our data are in conflict with recent work on this system where changes in the electron spectra with target temperature are attributed to a high local electron-spin polarization of the Ni(110) surface. We demonstrate that the data do not probe surface magnetism but modifications of the work function caused by surface contaminations.

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When a multiply charged ion approaches a metal surface, its neutralization proceeds in an interaction scenario that has been worked out in some detail in the past two decades [1–4]. In a simple picture, electron capture from the solid to the ion is initially dominated by resonant neutralization where conduction electrons with energy close to the work function of the target (Fermi electrons) are transferred to atomic levels of the same binding energy. Making use of a semiclassical over-the-barrier approach, one finds that levels with principal quantum number comparable to the core charge of the incident ion are initially populated [4]. For multiply charged ions, this leads to multiple capture of electrons into excited atomic states resulting in the formation of so called "hollow atoms" [5].

Recently, Unipan and co-workers [6] proposed to make use of the formation of hollow atoms during impact of multiply charged ions for probing the (short-range) magnetic order of surfaces. The method, outlined in detail in [7,8], is based on the capture of metal electrons into multiply excited levels. These levels partly decay thereafter via autoionization, and Auger electron spectroscopy can be applied to obtain information on the population of such levels. For capture of electrons with a high spin polarization P (spins are preferentially aligned parallel to each other), the occupation of atomic triplet terms is enhanced compared to singlet terms. An increase of the target temperature reduces the spin polarization, which will vanish above the Curie temperature T_C. From the ratio of the populations of triplet and singlet levels for atomic two-electron systems as a function of target temperature, information on the short-range magnetic order of the sample is then derived.

In experiments with a Ni(110) surface, 20–170 eV He^{2+} ions were scattered under near grazing angles of incidence [6–8]. For this system, the Auger electron spectra reveal two peaks at about 34.5 and 36 eV, which can be attributed to the decay of $2s^2\ {}^1S$ and $2s2p\ {}^3P$ states (termed "triplet peak") and of $2p^2\ {}^1D$ and $2s2p\ {}^1P$ states (termed "singlet peak"), respectively [9]. A prominent change of relative intensities for the peaks was assigned to the decay of singlet and triplet states with the temperature of the target. Whereas for room temperature the "triplet peak" was found to have a comparable intensity to the "singlet peak," this ratio was reversed for increasing temperatures up to above the Curie temperature (T_C=627 K). Analysis in terms of a simple spin blocking model for subsequent capture of two electrons gave $|P| = (90 \pm 7)\%$ for the local spin polarization of the surface [6,7].

Here we report on studies for $^3He^{2+}$ ions scattered with energies from 64 to 500 eV under near grazing angles of incidence Φ_{in} up to 20° from a clean and oxygen covered Ni(110) surface. The clean surface was prepared by cycles of grazing sputtering of the target with 25 keV Ar^+ ions and subsequent annealing at 580 °C for some minutes. The experiments were performed at a base pressure of some 10^{-11} mbar in an ultrahigh-vacuum (UHV) chamber which was attached via two differential pumping stages to the beam line of a small ion accelerator operated with a 10 GHz electron cyclotron resonance (ECR) ion source (Nanogan-Pantechnique, Caen, France). Electron spectra were recorded under an angle of about 15° with respect to the surface normal along the direction of the scattered ion beam with a combined lens and analyzer module 2 (CLAM2) electron analyzer (VG Scienta Ltd.). The partial pressure of oxygen was adjusted by a leak valve, and the resulting change in work function was inspected via photoemission near threshold with light from a Xe high-pressure lamp attached to a compact Jobin Yvon H10 grating spectrometer.

In panel (a) of Fig. 1, we show Auger electron spectra for scattering of 64 eV He^{2+} ions from a clean Ni(110) surface under a grazing angle of incidence of 10° for temperatures of the target ranging from 300 K (full circles) to 630 K (full triangles). The data (not corrected for background) show for all temperatures a prominent "singlet peak" at 36 eV, whereas contributions from the "triplet peak," expected about 1.5 eV lower in energy, are absent. Also subsequent cooling down of the target to 300 K (open circles) left the spectra unchanged. This observation is not in agreement with the data by Unipan *et al.* [8] for 100 eV He^{2+} ions in panel (d) and for further energies reported in [6,7] where at room temperature the "triplet peak" has a pronounced intensity, interpreted by reduced capture probabilities for singlet states owing to spin blocking. Furthermore, for higher temperatures

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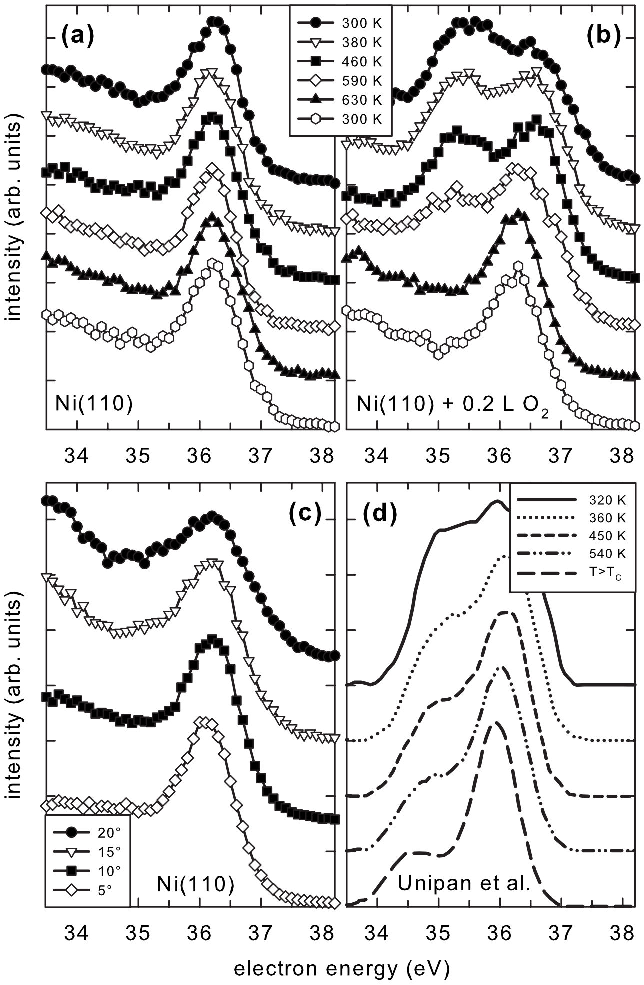

FIG. 1. Electron spectra as a function of target temperature for scattering of He^{2+} from Ni(110) under 10°. $T=300$ K, full circles: before, open circles: after heating. (a) Clean target, projectile energy=64 eV; (b) after an initial dose of 0.2 L O_2 at 300 K, projectile energy=124 eV. (c) 124 eV He^{2+} scattered from Ni(110) at $T=300$ K as a function of the angle of incidence. (d) 100 eV He^{2+} scattered from Ni(110) under 15° as a function of temperature (background subtracted spectra from [8]).

the intensity of the "singlet peak" in the spectra increases gradually up to T_C. In our experiments with a clean Ni(110) target, however, for projectile energies from 64 to 500 eV and angles of incidence from 5° to 20° [see panel (c)], we found for target temperatures from 300 to 630 K a "singlet peak" only. Also for a roughening of the target surface by sputtering and for a magnetized target, we observed the same behavior.

Different from the observations for the clean surface, we could identify prominent signatures of a "triplet peak" in our electron spectra when the target surface was exposed overnight to a pressure of some 10^{-10} mbar (no operation of cool trap). Photoemission studies near threshold revealed that the work function for the clean Ni(110) surface $W=(4.61\pm0.04)$ eV (consistent with [10]) had shifted to higher values. An O_2 dose of 0.2 L (1 Langmuir$=1.33\times10^{-6}$ mbar s) only shifted the work function to 5.0 eV. This observation motivated us to study the effects of surface contaminations on the relative intensities in the Auger electron spectra by the adsorption of O_2.

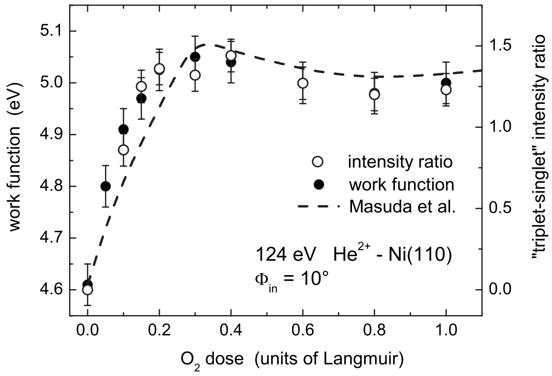

FIG. 2. Work function (full circles) and "triplet-singlet" ratio as a function of O_2 dose of a Ni(110) target. Scattering experiments were performed with He^{2+} impinging under 10° on Ni(110) at $T=300$ K. Dashed curve: work-function change from [12] adjusted to data for clean target. O_2 dose scale reduced by a factor of 2.

In panel (b) of Fig. 1, we show a set of Auger spectra recorded with a Ni(110) target initially exposed to 0.2 L of O_2 at room temperature. The spectrum for 300 K (full circles) shows indeed two peaks where the peak at the lower electron energy is attributed to the decay via autoionization containing triplet states. With increasing target temperature, the intensity of the "triplet peak" is gradually reduced, and at $T=630$ K this peak can hardly be identified in the spectrum (full triangles). Subsequent cooling to 300 K [lowest curve in panel (b), open circles] indicates that the data are not reversible for a variation of temperature. These changes in the electron spectra can be understood by effects based on desorption and dissolution processes of oxygen. Desorption and dissolution into the bulk with increasing temperature reduces the target work function [11] and leads to a decrease of the "triplet peak" as also observed in [6–8]. (Note the shift of peaks owing to a change of contact potential.) We found that already an O_2 dose of 1/20 L leads to a noticeable enhancement of the "triplet peak." Similar results can also be obtained for the adsorption of H_2 or CO_2 at a larger dose.

The close relation between the target work function and the relative intensities of the "triplet" and "singlet" peaks is demonstrated in Fig. 2. Here we have plotted the work function of the target (left axis) and the "triplet-singlet" intensity ratio for impact of 124 eV He^{2+} ions on Ni(110) under $\Phi_{in}=10°$ as a function of the O_2 dose. An adjustment of the scales for the work function and intensity ratio reveals the close relation of both quantities and shows that the work function of the target is a key parameter here. We have plotted also the work-function change as a function of O_2 dose from studies by Masuda *et al.* [12], which compare well with our results after a reduction of the scale for the O_2 dose by a factor of 2.

Further evidence for the effect of oxygen adsorption can be obtained from a direct comparison with the electron spectra of Unipan *et al.* [6–8]. In Fig. 3, we show electron spectra (subtracted with respect to background) for impact of 124 eV He^{2+} ions under $\Phi_{in}=10°$ on a clean (full circles) and on a Ni(110) surface exposed to 0.1 L of O_2 (open circles) at

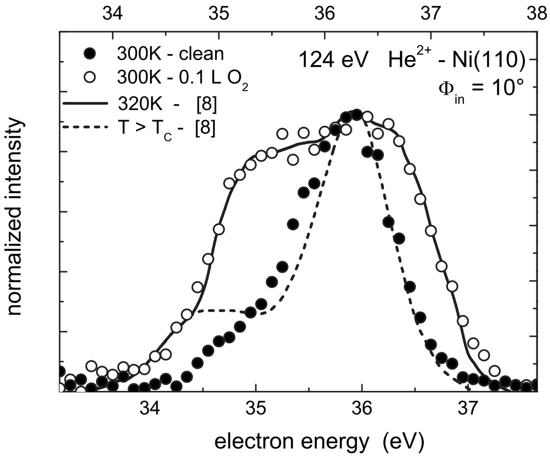

FIG. 3. Background subtracted electron spectra for scattering of 124 eV He^{2+} from Ni(110) under 10° at $T=300$ K (upper energy scale). Full circles: clean target, open circles: target exposed to 0.1 L O_2. Data from [8] for 100 eV He^{2+} scattered under 15° from Ni(110) (lower energy scale) at $T=320$ K (solid curve) and $T \geqslant T_C$ (dashed curve).

room temperature. Note the pronounced change in the electron spectra with a shift by about 0.4 eV to higher energies and a substantial increase of the "triplet peak." The energy shift is consistent with the modified contact potential between target and electron spectrometer owing to the enhanced work function of the target. A striking feature of the spectrum for the surface exposed to O_2 is the perfect agreement with a spectrum published by Unipan *et al.* [8] for 100 eV He^{2+} scattered under a comparable angle of 15° from Ni(110) (solid curve). Since our calibration of the electron energy via elastic scattering using a low energy electron gun from a low-energy electron diffraction setup is estimated to have an uncertainty with respect to the absolute electron energy of about 1 eV, we have adjusted the energy scale for the data obtained with different setups by a relative shift of 0.35 eV. We therefore speculate that the target used in the experiments by Unipan *et al.* was covered with a small amount of impurities (likely oxygen). In passing, we note that the angular dependencies (used in [7] to derive spin correlation lengths) are also observed for an oxygen covered surface.

This pronounced effect of the target work function on the intensity ratio of the "singlet" and "triplet" peaks makes it very difficult to apply the method proposed by Unipan *et al.* for probing the local magnetic order at surfaces using hollow atoms. A small amount of adsorbed species (here oxygen) leads to a considerable change of the target work function and also of the intensity ratio. This impurity driven modification competes directly with the effects based on the capture of electrons from a spin-polarized ensemble which roughly scales with $1-P^2$ for a polarization P in the case of subsequent capture [6] or with $1-|P|$ for simultaneous capture [13] of the two electrons; i.e., only for a high polarization could noticeable spin blocking effects be detected.

In our studies on the temperature dependence of the "triplet-singlet" ratio with the clean target (work function unchanged within 0.05 eV), we could not find a noticeable and reversible change of this ratio. We then conclude that the polarization P of captured electrons has to be small, since a high P would favor the population of the triplet term. This is in accord with the finding for P of some percent deduced from single electron capture into excited atomic levels and subsequent emission of circularly polarized light [14,15] as was also observed by the Groningen group [16] and for field emission of polarized electrons [17]. The high polarization $P \approx -90\%$ found in photoemission studies for Fermi electrons from a Ni(110) surface [18] does not contradict this result, since photoemission probes surface properties of the first layers, whereas electron capture for ion impact proceeds in front of the topmost surface layer only where also the theoretically predicted spin polarization is small [19].

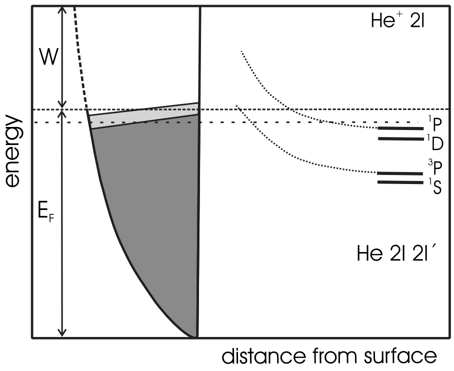

FIG. 4. Sketch for illustration of charge transfer between metal surface and He^+ $2l$. The modified density of states around the Fermi level in the rest frame of a moving ion is caused by a kinematic effect.

The observed change of the "triplet-singlet" intensity ratio with the work function of the target surface can be qualitatively understood in terms of simple microscopic concepts for electron capture by ions approaching a metal surface. In Fig. 4, we present a sketch for the energies of metal electrons and of the relevant terms for the He $2l2l'$ configuration. The vacuum level of the metal is referred to as the single ionization limit for this configuration He^+ $2l$. As proposed in previous works, the capture of the second electron for the formation of the $2l2l'$ configuration proceeds predominantly via resonant electron transfer where an electron close to the Fermi level of the metal is captured [9,20,21]. The first step, i.e., the population of He^+ $2l$, is ascribed to the formation of the He^+ $(2s-2p_z)$ Stark state on the incoming path at a distance of about 7 a.u. in front of the surface plane (jellium edge) via resonant electron capture. The capture of the second electron in order to form the He $2l2l'$ configuration is expected to proceed immediately after the first capture. Thereafter, the competition between resonant ionization to unoccupied metal states above the Fermi level and autoionization determines the decay of the doubly excited states and the intensities of the Auger transitions.

The detailed interaction scenario for the present system is an intricate problem involving hybridized excited states and complex shifts of the relevant atomic levels [22]. A detailed microscopic modeling of the interaction scenario is therefore beyond the scope of the present paper. However, in a simple picture one can conclude from the sketch in Fig. 4 that an increase of the work function of the target favors the population of terms with higher binding energies, i.e., ^1S and ^3P, which gives rise to the "triplet peak" in the electron spectra. This feature is in accord with our experimental findings. Since the relative intensities of the "singlet" and "triplet" peaks are very sensitive on the work function, our data provide important new information on this effect. Therefore, we hope that our studies stimulate detailed model calculations on this topic, where, in particular, the level shifts of the involved atomic terms will play a key role for a quantitative treatment of the formation and decay of the hollow atoms. In this respect, we note that the description of processes presented by Unipan *et al.* [6–8], based on a simple over-the-barrier approach for capture events using a not appropriate value of $W=5.05$ eV for the work function of Ni(110), ignores the formation of mixed Stark states comprising nontrivial dependences of level shifts and transition rates as a function of distance from the surface, the spin polarization induced by the presence of the projectile [23,24], and kinematic effects on the polarization. Therefore, these calculations—even though they reproduce the experiments fairly well—might not be considered as a realistic modeling for the interaction scenario.

In conclusion, we have presented evidence that the relative intensities of "singlet" and "triplet" peaks emitted from autoionizing doubly excited He atoms formed by the impact of He^{2+} ions on a Ni(110) surface show an extreme sensitivity on contaminations of the surface caused by the resulting effects of the work function on charge transfer. Our data are not in accord with the experimental results and interpretation of the work by Unipan *et al.* [6–8]. The analysis of electron spectra presented by these authors cannot be used to obtain information on the local spin polarization of the Ni(110) surface.

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