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Relative sub-shell photoionization cross-sections of nickel metal determined by hard x-ray high kinetic energy photoemission

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Abstract

Recently, hard x-ray high kinetic energy photoelectron spectroscopy has lead to a break-through due to its non destructive way of investigating the bulk electronic properties of materials. However, due to the relatively new development of this technique there is a lack of information concerning the photoionization cross sections at high energies. Whenever compound materials are investigated or when estimating signal levels and the feasibility of an electron spectroscopy experiment the knowledge of cross sections is essential. In the present work the experimentally determined relative sub-shell photoionization cross sections of shallow levels of nickel metal in the energy range of 2 to 10 keV will be shown. The data are compared with calculated sub-shell photoionization cross sections.

Keywords: nickel, photoionization cross section, hard x-ray high kinetic energy photoelectron spectroscopy

Introduction

Over the years photoemission spectroscopy has been one of the most versatile and most commonly used techniques to explore the electronic properties of materials. Whether investigations were aimed at the determination of the chemical environment of some species or the quantification of the elemental composition, there has always been a certain difficulty to estimate and compare the photoemission signals obtained for certain species. It has already been demonstrated that when one leaves aside the fixed experimental set-up factors such as photon flux, electron analyzer transmission, detector efficiency etc., the experimental signal is mainly determined by the quantity of the atomic species in question and its photoionization cross section [1]. In the hard x-ray regime the core level cross-sections

are decreasing rapidly, a fact that has hindered the experiments considerably. This is now compensated by the photon intensity provided by third generation synchrotron sources. In most photoemission experiments, ratios of signal intensities are followed or core level energy shifts are determined. For the analysis of such data, absolute cross section values are not essential. However, whenever compound materials are investigated, when estimating signal levels or when determining if a photoelectron spectroscopy experiment is feasible, the knowledge of cross sections is essential.

Currently, in the new emerging field of hard x-ray photoemission only calculated atomic cross section data are available [2-5]. Experimentally, a very limited amount of data is available. The starting point was the pioneering work of Kunz et al. [6] where the sub-shell photoabsorption cross-sections of shallow levels of gold (Au) were determined for energies ranging from 5 to 14.5 keV. In the present work we investigate the relative photoionization cross section of the 3s and 3p core levels of nickel (Ni) using as a reference the Au 4f 7/2 photoabsorption cross section determined by Kunz et al.[6]. In the following section we first introduce the experimental procedure before we present and discuss the results.

Experimental

The experiments were performed at the KMC-1 beamline at the BESSY II synchrotron radiation facility using the HIKE end-station. The KMC-1 beamline is equipped with 3 optical elements – a toroidal mirror and a double crystal monochromator (DCM) that enable a good preservation of the flux delivered by the dipole source [7].

Figure 1. The energy resolution delivered by the Si(111) DCM of the KMC-1 beamline at BESSY II.

We employed in our experiments strictly the Si(111) crystals in the range of 2 to 9 keV. The energy resolution delivered by this set of crystals is shown in Figure 1. We solely used this DCM in order to minimize the errors arising from the optical alignment of the beamline with respect to the experimental station.

All measurements were performed using the HIKE station and its commercially available R4000 VG Scienta electron analyzer optimized for high kinetic energy electrons up to 10 keV [8]. The energy resolution of the spectrometer was set to 0.25 eV by using a pass energy of

200 eV and a slit size of 0.5 mm. In combination with the beamline intensity these settings ensured a reasonable count rate in both cases that will be described below. The sample adjustment was ensured by a manipulator with 5 degrees of freedom, 4 axes of which are motorized (X, Y, Z and polar rotation). Finally, for each of the employed excitation energies the x-ray incidence angle was kept constant to approximately 2 degrees. In our cross section determinations the sample position was kept approximately the same with respect to the electron analyzer in order to rule out the influence of factors, which are due to the set-up geometry. The measurements were taken in grazing incidence of the x-rays and normal emission of the electrons.

In order to evaluate the reproducibility of our results we recorded the data using 2 different setting of the experimental set-up as well as 2 different types of samples: Ni and Au films deposited in situ on a Si(111) substrate and Ni(100) and Au(111) crystals.

In the first case the KMC-1 beamline was employed as it is. The given beam spot size is 600 microns wide and 400 microns high at the focal point an area from which the electron analyzer sees approximately a forth. As the excitation energy was scanned within the required range, the beamline focus was kept at the same position with respect to the electron analyzer. In this way the influence of the beamline dependent geometry factors on the recorded intensities in our investigation could be minimized. A thin Ni film and a thick Au film were investigated using excitations energies ranging from 2 keV to 9 keV. Both samples were prepared in situ by evaporation in ultra high vacuum (UHV). The Au film was evaporated on top of a Si(111) substrate with its natural oxide layer and the Ni film was evaporated on top of the previously prepared Au film. The thickness of the films was controlled by means of a quartz crystal microbalance. The Ni layer thickness was estimated to be 8 nm. The Au film thickness was larger than 100 nm. The thick Au sample was used as a reference and the 4f core levels of Au were at first recorded in a stepwise like manner in the 2 to 9 keV excitation energy range. Subsequently the Ni film was deposited and the 3s and 3p core levels of Ni were recorded in a similar manner. In addition to that, the Au 4f core levels originating from the gold substrate buried under the nickel film were also recorded, providing information that allowed us to check the thickness of the Ni film. A step of 1 keV in the excitation energy was employed. Moreover, for a thorough intensity calibration of the spectra, the flux delivered by the double crystal monochromator was recorded using the available ionization chamber as well as a GaAs diode that was introduced in the beam for every measurement point.

The second set of experiments were done using a refocusing parabolic X-ray capillary which provides a final beam spot which matches perfectly the expected luminosity for the electron analyzer settings. Here the investigated samples were Au(111) and Ni(100) crystals. Prior the analysis both crystals were

cleaned in UHV by Ar^+ ion sputtering until the contaminants could not be observed anymore by the lowest excitation energy provided by the KMC-1 beamline. For each chosen excitation energy the optical alignment was preserved while the Ni and Au samples were alternatively analyzed. The same core levels were recorded as in the first case described above.

X-ray Focusing Capillary

Recently the HIKE station has been upgraded with the installation of a parabolic x-ray mono-capillary for further x-ray focusing. The capillary was supplied by IfG GmbH, Berlin. Its characteristics allow us to match the light spot size with the accepted illuminated area of the electron analyzer. Figure 2 a) and b) display the Au 4f images recorded without and with the presence of the mono-capillary, respectively, using an excitation energy of 3 keV. The focused beam is evident in Figure 2 b). Slices through both images are compared in Fig 2 c) demonstrating a gain in flux density of 15 times. Figure 3 a) and b) show the beam profile measured using the knife method. A very thin Pt foil was used as a knife and driven through the focused beam along the horizontal and vertical directions. The Pt signal was followed with the electron spectrometer during the scan of the 2 axes. The results point to a $100\text{ }\mu\text{m} \times 50\text{ }\mu\text{m}$ focus size obtained with the mono-capillary.

Figure 2. The electron analyzer detector image of Au 4f core levels recorded a) without and b) with x-ray capillary at 3 keV excitation energy. The yellow rectangles depict the areas over which the intensity has been integrated in order to obtain the spectra in c).

The positive performance of the x-ray capillary across the entire energy range provided by the KMC-1 beamline introduces approximately an overall gain of 5 in the photoemission experiments.

Figure 3. Focused beam profile using the knife method a) horizontal scan b) vertical scan.

Results

It has previously been shown that in a photoemission experiment the recorded photoelectron signal intensity for a particular element and core level from a volume element extending from the surface to a depth "a" is given by the following formula [9]:

$$I = F \cdot A_0 \cdot \Omega_0 \cdot D_0 \cdot T \cdot \rho \cdot \sigma(E) \cdot P \cdot \frac{1}{\cos \theta} \int_0^a \exp\left(-\frac{z}{EAL(E)\cos \theta}\right) dz \quad (1)$$

where F is the average flux of X-rays on the sample, A_0 is the illuminated area on the sample that is viewed by the analyzer in normal emission, Ω_0 is acceptance solid angle of the analyzer, D_0 is the detector efficiency, T is the transmission function of the analyzer, ρ is the atom density, $\sigma(E)$ is the photoionization cross section and P is the factor that accounts for the anisotropy of photoemission, θ is the photoemission angle (angle formed by the emission direction and the normal to the surface), and $EAL(E)$ is the electron attenuation length of the photoelectrons in the sample. Equation (1) becomes

$$I = F \cdot A_0 \cdot \Omega_0 \cdot D_0 \cdot T \cdot \rho \cdot \sigma(E) \cdot P \cdot EAL(E) \quad (2)$$

for a bulk sample. Besides the photon flux F , there are two groups of parameters, one entirely determined by the properties and geometry of the set-up (A_0 , Ω_0 , D_0 , T , θ) and one dependent on the sample properties (ρ , σ , P , EAL). In order to derive directly the photoionization cross section from recorded intensities we would need accurate values of all the geometry factors. Since these are unknown we resort to an alternative method such as the parallel measurement of our Ni core levels and of the Au reference. By choosing the Au 4f core levels which are in the vicinity of the Ni 3s and Ni 3p in binding energy / kinetic energy, we could thus eliminate the term expressing the transmission

function of the analyzer. Furthermore, by fixing the geometry of our experiments to grazing incidence / normal emission and by keeping the sample position constant with respect to the electron analyzer, the $\cos\theta$ term can be set to 1 (photoemission angle $\theta \sim 2$ degrees – see Figure 4) and the parameters A_0 , Ω_0 , D_0 will always be the same. Thus in both our cases the entire geometry dependent factors could be removed. Consequently the cross section of Ni can be expressed as follows

$$\sigma_{Ni} = \sigma_{Au} \cdot \frac{I_{Ni}}{I_{Au}} \cdot \frac{F_{Au}}{F_{Ni}} \cdot \frac{\rho_{Au}}{\rho_{Ni}} \cdot \frac{P_{Au}}{P_{Ni}} \cdot \frac{EAL_{Au}}{EAL_{Ni}} \quad (3)$$

The signal from the ionization chamber situated in the beam at all times provided satisfactory quantification of the photon flux for all our experiments. Thus the flux parameter F was separately noted for each recorded core level using the readings of that particular ionization chamber. The parameters dependent on the sample properties ρ , P and EAL were tackled in the following manner: the densities $\rho_{Ni}=9.14 \times 10^{22}/\text{cm}^3$ and $\rho_{Au}=5.9 \times 10^{22}/\text{cm}^3$ were taken from crystallographic data and were assumed to be the same for the film and crystal. The term P which accounts for the photoelectron angular distribution is known to have dipole (β) and non-dipole (γ , δ) contributions [3,4,10] and in the case of linearly polarized light is given by:

$$P = \frac{1}{4\pi} \left(1 + \frac{\beta}{2} (3\cos^2\psi - 1) + (\gamma\cos^2\psi + \delta)\sin\psi\cos\phi \right) \quad (4)$$

where ψ is the angle between the light polarization and the photoelectron emission direction and ϕ is the angle between the light direction and the plane created by the light polarization and the photoelectron emission direction. Considering the geometry of our experiment shown in Figure 4, $\psi=0$ and $\phi=90$ and equation (2) becomes $P = 1 + \beta$. The values of the β parameter for Ni and Au were taken from Trzhaskovskaya et al. [4, 10].

Figure 4. HIKE/KMC-1 experimental geometry.

Last but not least the EAL_{Ni} and EAL_{Au} were calculated using the NIST Electron Effective-Absorption-Length database [11] for each kinetic energy.

Considering that we in the first experiment chose to investigate an overlayer film of a defined Ni thickness “ t ” deposited on top of a Au substrate the photoemission signal given by eq. (1) becomes

$$I_{Ni}^l = FA_0\Omega_0D_0T\rho_{Ni}\sigma_{Ni}EAL_{Ni} \left(1 - \exp\left(-\frac{t}{EAL_{Ni}} \right) \right) \quad (5)$$

for the recorded core level intensity corresponding to the Ni overlayer and

$$I_{Au}^s = FA_0 \Omega_0 D_0 T \rho_{Au} \sigma_{Au} EAL_{Au} \exp\left(-\frac{t}{EAL_{Ni}}\right) = I_{Au}^0 \exp\left(-\frac{t}{EAL_{Ni}}\right) \quad (6)$$

for the recorded intensity corresponding to the Au substrate. I_{Au}^0 is the intensity corresponding to photoemission from the substrate without any film. In the first experiment we recorded the signals from the Ni overlayer I_{Ni}^l and Au substrate with the overlayer I_{Au}^s as well as the signal from the Au substrate with no overlayer I_{Au}^0 .

Figure 5 a) and b) show the core level spectra of Ni 3s and Ni 3p recorded as a function of excitation energy in the range from 2 to 9 keV obtained from the Ni thin film. Within the selected energy window of Ni 3p, the Au 4f core levels corresponding to the gold substrate are clearly visible at higher binding energy. Figure 5 c) displays the Au 4f core levels recorded from the Au thick film prior to the Ni deposition (no overlayer). In order to make the evolution of the core level intensities more clearly visible in Figure 5, the level of background on the low binding energy side was subtracted; the high binding energy background sides of the spectra were normalized to unity and then shifted upwards along the intensity scale.

Figure 5. a) The Ni 3s core levels of the Ni film recorded for energies between 2 and 9 keV; b) the Ni 3p core levels of the Ni film; the Au 4f core levels of the Au thick film used as substrate are visible through the Ni film; c) Au 4f core levels of the Au thick film prior to the Ni deposition.

We obtained a similar set of spectra for the Ni(100) and Au(111) crystals in our second experiment.

One of the characteristic features of the core level spectra of Ni metal is the occurrence of strong shake-up satellites [12]. The satellites can be described in terms of different screening channels for the core

hole state [13]. In this picture the main line corresponds to a 3d-screened $c^{-1}[3d^{10}4s]$ final state. The brackets denote that these electrons are in a rehybridized metallic state and c^{-1} denotes the core with one electron removed from level c . The satellite can instead be described as a 4sp-screened state, for which the final state is denoted in a related way as $c^{-1}3d^9[4s^2]$. Hence the satellite corresponds to a fully screened double hole state. The two holes can couple in different ways leading to multiplet split states.

Figure 6. Example of fits of a) the Ni3s data and b) Ni3p data.

The multiplet splittings of the satellite states in Ni are particularly large for a core-hole in the $n=3$ shells, since all interacting electrons belong to the same main shell. In the 3s spectrum the main satellite occurs at 6 eV from the main line with a weak satellite at 14 eV [14] (see Figures 5a) and 6a)). For the 3p spectrum there are satellites at about 7 eV and 13 eV from the $3p_{3/2}$ line [15] (see Figures 5b) and 6b)). When including the satellites in the cross section evaluation the $3p_{1/2}$ and $3p_{3/2}$ contributions can no longer be separated and for this reason we only give the total 3p cross-sections. In both our experiments, as a first evaluation step of the raw photoelectron intensities, a normalization procedure to the intensity of the incoming flux was employed. The signal from the ionization chamber situated in the beam at all times was directly used in the normalization procedure. This signal also accounted for the typical decrease of the ring current of the BESSY II storage ring. The recorded data were then normalized to the number of scans and fitted. The Ni 3s, Ni 3p and Au $4f_{7/2}$ core level areas were evaluated from the fits and introduced in eq. (3).

Figure 6 displays an example of the fits of the recorded data at 2 keV. Doniach-Sunjic shapes [16] were used in the fits. The considered Shirley background [17] was fitted iteratively with the fitting functions. To increase the reliability of the fits the spectra were recorded within extensive kinetic energy ranges [18]. The lifetime of the core hole and hence the Lorentzian contribution to the fits was estimated based

on previously published values [19, 20]. The Gaussian contribution was largely based on the total energy resolution of the experiment. The total fit error was below 5 %.

Before proceeding with the cross section calculations, the signals obtained from the Au thick film with and without the Ni cover layer allowed us to evaluate the real thickness of the Ni film (see eq. (6)). From these fits we obtain an approximate value of the Ni film thickness of 8 nm. The values of EAL of Ni that were used in the computation were calculated using the NIST database [11]. The Ni film thickness was further used in the calculation of cross sections in the case of the Ni thin film.

Figure 7 displays our final results for the cross sections for Ni 3s and Ni 3p obtained from the two experiments and compared to theoretical values by Scofield [5]. The values were computed using equation (3) including the integrated satellites intensities for both core levels. In the case of Ni 3s the integrated satellite intensity is approximately 7% of the main line while in the case of Ni 3p satellites their contribution lies at approximately 30% of the total 3p signal.

Figure 7. Our experimentally determined sub-shell cross sections for Ni film and Ni(100) crystal compared with the cross sections according to Scofield [5]. a) Ni 3s and b) Ni 3p; the Scofield values of Ni 3p were calculated by adding up the tabulated values of Ni 3p_{1/2} and Ni 3p_{3/2}.

In order to preserve the reliability of the Ni 3p cross section values obtained for the Ni film above 4 keV the satellite contribution was limited to 30% of the main line due to the increasing contribution of the Au 5p_{1/2} to the spectra (see Figure 5b)). We find a very good agreement between the two experimental cross sections, from the thin film and from the single crystal measurements, with the angular integrated cross sections calculated by Scofield [5] for the 3p electrons. On the other hand both experimental 3s electron cross sections are a factor of 2.5 smaller than the calculated values. This trend can not be due to experimental errors as that would result in similar errors for the 3s and 3p cross sections.

The main source of error in the experiment is originating from the beamline and sample alignment with respect to the electron analyzer. We estimate that the signal obtained for each excitation energy has an error of approximately 20 %.

Conclusions

In our present work we have investigated and determined for the first time the photoionization cross section of Ni 3s and Ni 3p electrons within an excitation energy range from 2 to 9 keV. We found a very good agreement between the data obtained through two very different experimental approaches which confirms the reproducibility and reliability of the data. Nevertheless, when comparing the experimentally determined cross sections with the theoretically determined ones by Scofield et al., we found a good agreement for the 3p level and a factor of 2.5 smaller values for the Ni 3s level, a tendency which is baffling.

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