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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 2–9 keV will be shown. The data are compared with calculated sub-shell photoionization cross sections.

1. 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, 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.

2. 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].

We employed in our experiments strictly the Si(1 1 1) crystals in the range of 2–9 keV. The energy resolution delivered by this set of crystals is shown in Fig. 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

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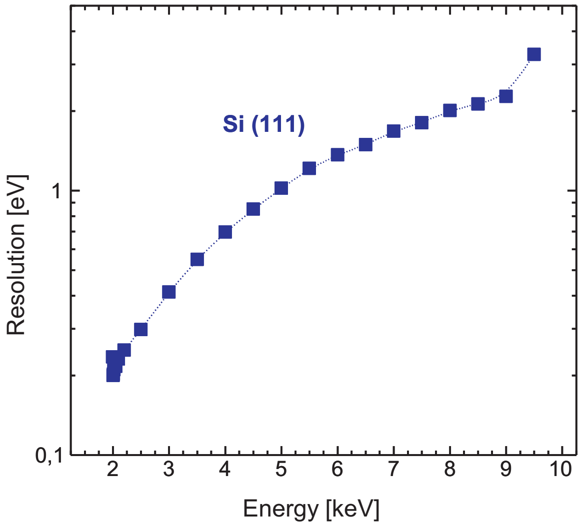

Fig. 1. The energy resolution delivered by the Si(1 1 1) DCM of the KMC-1 beamline at BESSY II.

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°. 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 setup as well as 2 different types of samples: Ni and Au films deposited in situ on a Si(1 1 1) substrate and Ni(1 0 0) and Au(1 1 1) crystals.

In the first case the KMC-1 beamline was employed as it is. The given beam spot size is 400 μm wide and 600 μm high at the focal point. In grazing incidence the beam footprint reaches a length of approximately 4–5 mm and keeps the original beam height of 0.6 mm. The lens system of the analyser has a magnification of 5 in transmission mode which means that the image formed on the entrance slit of the hemispheres will be 5 time bigger than the beam footprint area e.g. about 60–75 mm^2. The slit employed here has a height of 0.5 mm and a length of 25 mm which results in an area of 12.5 mm^2. Thus the electron analyser sees only approximately a fifth of the illuminated area on the sample. 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(1 1 1) 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 2–9 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(1 1 1) and Ni(1 0 0) 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.

2.1. 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. Fig. 2(a) and (b) displays 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 Fig. 2(b). Slices through both images are compared in Fig. 2(c) demonstrating a gain in flux density of 15 times. Fig. 3(a) and (b) shows 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 μm × 50 μm focus size obtained with the mono-capillary.

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.

3. 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]:

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

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. Eq. (1) becomes

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

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