

High-resolution Auger-Electron Spectroscopy Induced by Positron Annihilation on Fe, Ni, Cu, Zn, Pd, and Au

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Abstract. Positron annihilation induced Auger electron spectroscopy (PAES) enables almost background free, non-destructive surface analysis with high surface selectivity. The Auger-spectrometer at the high intense positron source NEPOMUC now allows to record positron annihilation induced Auger spectra within a short data acquisition time of 10-80 minutes. With a new hemispherical electron energy analyzer and due to the exceptional peak to noise ratio, we succeeded to measure Auger-transitions such as the $M_{2,3}VV$ double peak of nickel with high energy resolution. The relative Auger-electron intensities are obtained by the analysis of the recorded positron annihilation induced Auger spectra for the surfaces of Fe, Ni, Cu, Pd and Au. It is demonstrated, that high-resolution PAES allows to determine experimentally the relative surface core annihilation probability of various atomic levels.

1. Introduction

In positron annihilation induced Auger-electron spectroscopy (PAES) the sample is irradiated with low-energy positrons with a kinetic energy of a few 10 eV which is well below the threshold for impact ionization of core electrons. The implanted positrons thermalize very rapidly within a few picoseconds. Due to the low implantation energy the vast majority of the positrons diffuses back to the surface where they can be trapped in the surface potential before they annihilate together with an electron (see e.g. [1]). In contrast to conventional AES, where core electrons are removed by photo-ionization with X-rays (XAES) or by impact-ionization with keV-electrons (EAES), at PAES core electrons are removed by positron-electron annihilation for the initiation of the Auger-process. Since only the annihilation with core electrons leads to the emission of Auger-electrons the element dependent core annihilation probability is an important number to estimate the intensity of the relevant Auger transitions. Jensen et al. [2] calculated core annihilation probabilities for various materials which typically ranges between 1 and 10 %.

The completely different initiation of the Auger-transition leads to several advantages of PAES over conventional AES. The positron annihilation induced Auger-spectra show no secondary electron background in the range of higher Auger-transition energies due to the low positron energy. The annihilation of positrons, which are trapped in a surface state, with electrons in the topmost atomic layer leads to the extreme surface sensitivity of PAES. At PAES the emission of the Auger-electron is decoupled from the impact position of the positron, and hence the probed atom is neither perturbed by the impinging primary particle nor by the

detached core electron. However, the main drawback of PAES is the very long measurement time of up to a few weeks for one spectrum, if usual lab beams based on β^+ -emitters are used. For this reason, up to now only a few research groups [1, 3, 4] benefit from PAES' advantages for surface studies.

To overcome the long data acquisition times, we developed and installed a PAES-setup at the positron beam facility NEPOMUC (**NE**utron induced **PO**sitron source **MU**ni**Ch**) at the research reactor Heinz-Maier-Leibniz FRM II. Both, the high intensity of the low-energy positron beam of more than 10^7 moderated positrons per second, and a new state-of-the-art hemispherical electron energy analyzer with a large acceptance angle of up to $\pm 13^\circ$ lead not only to an enormous reduction of the measurement time but also to an improved signal-to-noise ratio. Although, the reactor-based positron source NEPOMUC delivers an intense remoderated positron beam its low-energy positron flux is in the order of 10^{-11} A. Hence, it is still six orders of magnitude lower than the electron current from conventional electron guns. However, we succeeded to demonstrate that the signal-to-noise ratio is about one order of magnitude higher at PAES than at EAES. Within this work, we present high-resolution PAES experiments on pure Fe, Ni, Cu, Zn, Pd, and Au. Besides the determination of the peak energy of the respective Auger-transitions, the relative Auger intensities are discussed in terms of core annihilation probabilities.

2. Experimental

2.1. The Auger-spectrometer at the positron beamline NEPOMUC

The positron beam facility NEPOMUC at the research reactor FRM II delivers a high-intensity 1 keV positron beam of nearly 10^9 moderated positrons per second [5]. This primary positron beam is remoderated with a tungsten single crystal in back reflection geometry for brightness enhancement [6]. The voltage of the remoderation crystal can be adjusted between 15 V and 200 V, and was set to 17 V for all presented measurements. Taking into account the positron work function of the W crystal of -3.0 eV, the kinetic energy of the remoderated beam amounts to 20 eV with respect to ground potential. The low-energy positron beam is adiabatically guided in a longitudinal magnetic field of typically 6-8 mT via a beam switch to the PAES apparatus.

The positron beam is non-adiabatically released by a magnetic field termination out of μ -metal at the entrance of μ -metal shielded Auger analysis chamber into the electrostatic guiding and focusing unit. A tungsten shielded NaI-detector is directed toward the center of the analysis chamber, and hence allows the detection of the annihilation radiation, i.e. the positron intensity, at the sample position. An electron gun enables the measurement of conventional EAES. A movable MCP-detector with phosphor screen is used for the positron beam and for electron beam adjustment. A sample lock and a sample preparation chamber equipped with an effusion cell, an electron beam evaporator, a piezo-oscillator as thickness monitor, and an argon ion sputter gun for surface cleaning are connected to the Auger-chamber [7]. The electron spectra and hence the emitted Auger-electrons are recorded via a hemispherical electron analyzer using a MCP/CCD read-out system.

2.2. Sample preparation

For the presented measurements high purity polycrystalline samples of Fe (purity >99.99%), Ni (>99.99%), Cu (>99.999%), Zn (>99.99%) Pd (>99.994%), and Au (>99.99%) were used. First, all samples were cleaned by acetone and rinsed by deionized water. After mounting on the sample holder, the sample surface was sputtered in the UHV-sample preparation chamber with 1 keV Ar^+ -ions for typically 20-30 minutes.

2.3. Measurement

The PAES-measurements were carried out at room temperature and at a pressure of typically $< 5 \cdot 10^{-9}$ mbar inside the Auger-chamber. The kinetic energy of the incident positron beam

on to the grounded sample is defined by the remoderation stage and was set to 20 eV for all measurements. Consequently, the secondary electron background ends at about 20 eV and hence well below the energies of the expected Auger transitions. The beam intensity at the sample position was about $9(3) \cdot 10^6$ moderated positrons per second.

The typical data acquisition time for the positron annihilation induced Auger-spectra presented here was 80 minutes. The entrance slit amounted to 7 mm, and the exit slit is given by the discretization of the CCD-camera read-out which amounts to 1.6 mm. The step width of the detected electrons was set to 0.25 eV and the fixed retard ratio (FRR) of the analyzer was set to 1.0 for Ni and Au resulting in an energy resolution of $\Delta E/E = 0.025$. For all other samples the step width was set to 0.5 eV, the FRR was 0.5, and the energy resolution amounted to $\Delta E/E \leq 0.049$ for the PAES measurements presented here.

3. Results and discussion

For all samples Fe, Ni, Cu, Pd, Zn and Au Auger-spectra were recorded with PAES which are plotted in figure 1. All spectra show an exceptional signal-to-noise ratio which is in the case of Cu as high as S/N=11:1. Comparison with EAES showed that the signal-to-noise ratio at PAES is at least one order of magnitude higher. The secondary electron spectrum ends at about 20 eV. However, the background, which is still observable, is mainly attributed to detected (Compton- and photo) electrons which are produced by the annihilation radiation in the sample. In addition, scattered Auger-electron of Auger transitions at higher energy might also contribute to the background. The dark current of the MCP detector of the electron analyzer is negligible.

The double peak structure of certain Auger transitions, which is particularly clearly visible for Ni, correspond to the respective energy levels of core electrons with different total angular momentum quantum number, e.g. $p_{1/2}$ and $p_{3/2}$ for the $M_{2,3}$ levels. The spectrum obtained for Pd shows a significant second peak according to an additional Auger transition at about 80 eV. Moreover, at Au, three distinct Auger peaks emerge which were attributed to the O_{3VV} , O_{2VV} and $N_{6,7VV}$ transitions. Note, that with increasing electron binding energy of the annihilating electron, i.e. increasing energy of the Auger-electron, the peak intensity decreases due to the accordingly declining core annihilation probability.

For all spectra the peak energies were found to agree with the theoretical values. For example at Cu the experimentally determined separation of the $M_{2,3VV}$ transition was determined to 2.19(0.18) eV, which is in excellent agreement with the theoretical value of 2.2 eV [8]. However, mainly due to the large secondary background at EAES significant peak shifts of the Auger transitions could not be observed, which might be expected due to the completely different ionization process of the probed atom in both techniques.

The data shown in figure 1 was analyzed not only with respect to the absolute energy of the Auger-transitions but also with respect to their intensities. In order to estimate the relative core annihilation probabilities of the respective Auger transitions the Auger-intensities are plotted as a function of the binding energy of the annihilated electron for Fe, Ni, Cu, Zn, Pd, and Au (see figure 2).

With the following assumptions the variation of the observed Auger-intensities can be correlated to the relative changes of the core annihilation probability. Since the positron flux at the sample position is considered to remain constant the time normalized spectra can be compared directly. The deexcitation of the excited electron shells is governed by the Auger-process. This assumption is reliable since the effective core potential seen by the outer electrons is low and characteristic X-ray emission is not probable at the considered excitation energies. The different positron reflexion, which increases with higher nuclear charge, is not taken into account.

The calculated values of the core annihilation probabilities show a large straggling [2] but can be very roughly approximated by the formula given in [9]: $p = 600 \cdot N(E_B) \cdot E_B^{-1.6}$ with p as

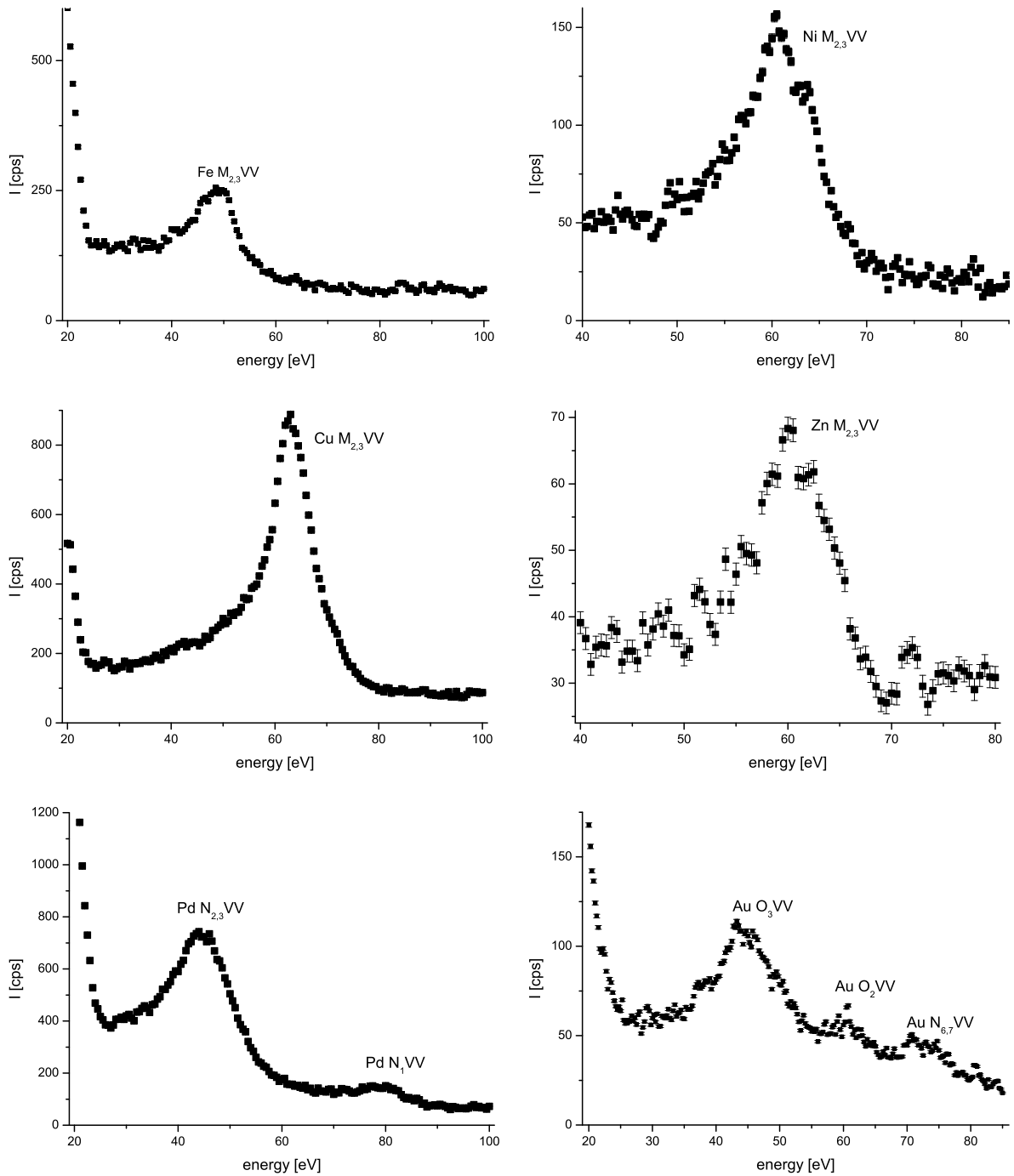


Figure 1. Positron annihilation induced Auger-electron spectra for Fe, Ni, Cu, Zn, Pd, and Au.

the core annihilation probability in %, E_B the binding energy in eV and $N(E_B)$ the number of electrons with the binding energy E_B . As shown in figure 2 the slope of the data clearly shows a trend to higher Auger intensity at lower electron binding energy which reflects qualitatively the given formula for p . This observation is attributed to the respective core annihilation probability which is lower for deeper bound electrons due to the repulsive Coulomb potential of the nucleus.

The variation of the experimentally determined relative differences of the Auger intensities is influenced by several aspects. The amount of positrons that leave the surface epithermally or moderated (provided a negative positron work function, e.g. at Cu or Ni) would vary a little at the different elements but their contribution to different surface core annihilation probability would be low. The positronium formation probability at the surface is expected to be similar at metal surfaces but might change drastically if oxygen is absorbed at the surface. This cannot be excluded although each sample was cleaned by Ar sputtering immediately before the PAES measurement. Therefore, a possible surface contamination would lead to a lower measured Auger intensity due to both, a larger positronium formation probability and to less unscattered Auger-electrons from the metal. In addition, influences due to differences in the surface topology can not be considered. In order to estimate the influence of the surface structure such as steps, adsorbates or defects on an atomic scale, a complementary tool such as scanning tunneling microscopy would be very helpful.

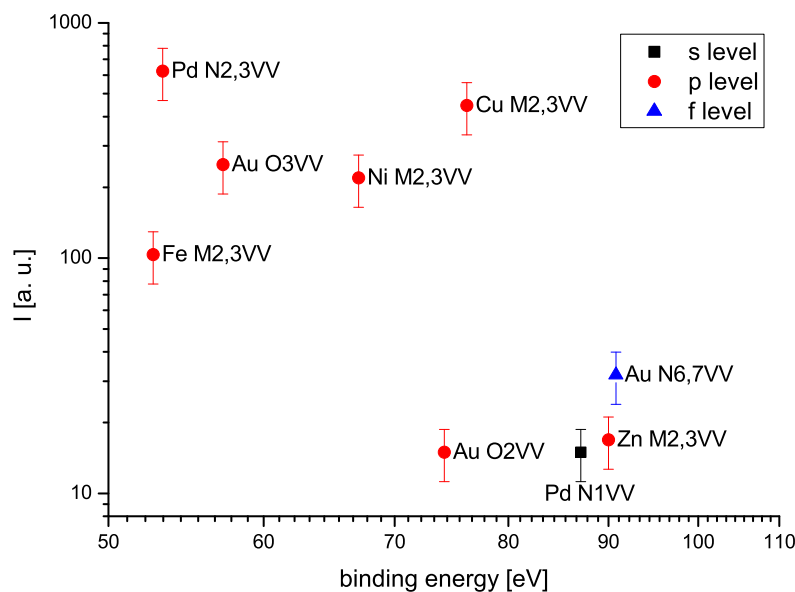


Figure 2. The relative Auger intensities obtained from the spectra shown in figure 1 as a function of the binding energy of the annihilated electron for Fe, Ni, Cu, Pd, and Au.

4. Summary and Outlook

Within the present work we demonstrated that PAES studies of surfaces can be performed within a measurement time of approximately one hour using the high-intensity low-energy positron beam at NEPOMUC. In these measurements on pure metallic surfaces the substructure of the Auger transitions, and e.g. at Au three distinct Auger peaks, could be observed due to the high resolution of the applied electron analyzer with high peak-to-noise ratio. It was shown that

the Auger intensities recorded with PAES allows the estimation of the relative core annihilation probabilities experimentally in spite of influences such as positron reflexion, surface topology or possible surface contamination. In order to anneal possible surface defects introduced by Ar sputtering it is planned to implement a heatable sample holder. In addition, future studies will be focused on sub-monolayer layers on metallic substrates in order to benefit from the high surface sensitivity and the elemental selectivity of PAES.

References

- [1] A. Weiss, R. Mayer, M. Jibaly, C. Lei, D. Mehl, and K. G. Lynn. *Phys. Rev. Lett.*, 61:2245, 1988.
- [2] K. O. Jensen and A. Weiss. *Phys. Rev. B*, 41(7):3928–3936, 1990.
- [3] R. Suzuki and T. Ohdaira and T. Mikado and H. Ohgaki and M. Chiwaki and T. Yamazaki *Applied Surface Science*, 100-101:297 – 300, 1996.
- [4] C. Hugenschmidt, J. Mayer, and K. Schreckenbach. *Surf. Sci.*, 601:2459–2466, 2007.
- [5] C. Hugenschmidt and B. Löwe and J. Mayer and C. Piochacz and P. Pikart and R. Repper and M. Stadlbauer and K. Schreckenbach. *Nucl. Instr. Meth. A*, 593(3):616–618, 2008.
- [6] C. Piochacz, G. Kögel, W. Egger, C. Hugenschmidt, J. Mayer, K. Schreckenbach, P. Sperr, M. Stadlbauer, and G. Dollinger. *Appl. Surf. Sci.*, 255(1):98 – 100, 2008.
- [7] J. Mayer, K. Schreckenbach, and C. Hugenschmidt. *Phys. Status Solidi C*, 4:3928–3931, 2007.
- [8] J. Mayer, K. Schreckenbach, and C. Hugenschmidt. *Phys. Status Solidi C*, 11:2468-2470, 2009.
- [9] P. Coleman. *Positron Beams and Their Applications*. World Scientific, 2000.