

Correlation effects in the 5p photoemission and dichroism of atomic Europium

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The 5p dichroism of atomic Europium has been investigated by photoemission experiments and Hartree-Fock calculations.

Free Europium is an excellent test case for electron correlations in complex open shell atoms. It is furthermore very interesting due to its similarity to bulk Gadolinium. Recent photoemission experiments [1] show for the direct 5p ionization a very complicate satellite structure with strong deviations from the expected simple $5p^5 4f^7 6s^2 6p^2$ multiplet. A similar, but weaker effect is also reported by Verweyen et al for the Eu 4f photoemission [2]. Verweyen et al have shown, that the corresponding 4f dichroism pattern can be well described by a simple analytical model. But they also found a violation of the 3 parameter mode of photoionization, when extracting phase informations from the normalized dichroism pattern. This violation is attributed to strong correlation effects arising from configuration interaction.

In the case of the 5p photoemission already the analytical model for the dichroism pattern fails. For this extensive Hartree-Fock calculations have been carried out. Correlation effects have been included by configuration interaction. It is shown, that the complicated photoemission signal and the unusual behavior of the dichroism pattern are mainly due to very strong correlation between the $6s^2$, $6s5d$, $5d^2$ and $6p^2$ configurations. Including these configuration interactions a good agreement with the experimental data is found.

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Time-resolved photoelectron spectroscopy of small metal cluster anions

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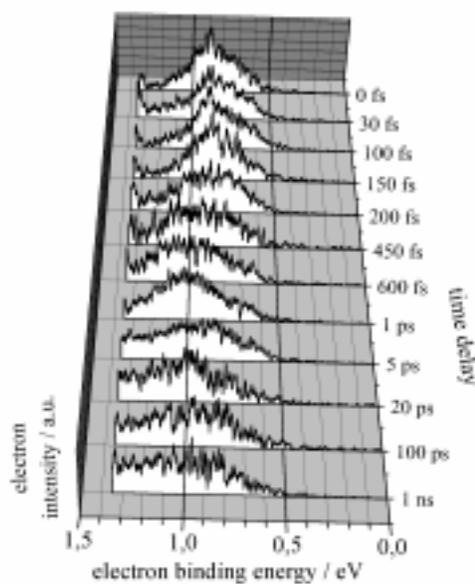
Pump-probe photoelectron spectroscopy has recently revealed ultrafast electron relaxation processes in small metal clusters in contrast to nuclear dynamics which is usually observed in pump-probe experiments on small molecules. Making use of the low electron affinity of small metal clusters we will demonstrate that negatively charged clusters are well suited for two-photon photoemission spectroscopy with femtosecond laser pulses in order to study electron dynamics of metal clusters in real time. In particular, excited electronic states in transition metal clusters like Pt_3^- , Pd_3^- and Pd_7^- show lifetimes of about 100 femtoseconds. Such an ultrashort lifetime of electronically excited states is attributed to inelastic electron scattering processes similar to those observed in bulk metals [2,3]. Further experiments will focus on the dependence of the inelastic scattering lifetime as a function of the size of the cluster and the influence by an adsorbate molecule attached to the cluster.

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FIG: Time-resolved two-photon photoelectron spectra of Pd_3^- using fs-pulses of 1.5 eV.



An X-ray Photoemission Study of the Effect of α -Irradiation on Fluorinated Tl-1223 High Tc Superconductors

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X-ray photoemission spectroscopy (XPS) has been used to investigate the effect of α -irradiation on F 1s, Cu 2p_{3/2} and Sr 2p_{3/2} binding energies of fluorinated Tl-1223 superconductors. In a recent publication [1] we have reported a detailed XPS investigation of the unirradiated samples in which we have identified the F sites. We have also reported an enhancement of the critical current density of these samples through α -irradiation[2]. In this work we try to explore the change in the electronic structure due to α -irradiation. The F 1s peak of these material started to disappear as α dose was increased, indicating that α -irradiation creates vacancies in F and hence O sites (as fluorine partially replaces O [1]). The Cu 2p_{3/2} satellite, that is typical of Cu²⁺, disappears and a low energy shoulder, that is a signature of Cu¹⁺, develops as α dose increases. Also the binding energy of Cu 2p_{3/2} was decreased with increasing α -irradiation, indicating a decrease in the average Cu valency. On the other hand, the binding energy of Sr 2p_{3/2} increases with increasing α dose up to 30 Mrad and then decreases for the sample with dose of 50 Mrad. This also indicates a decrease in the hole concentration in the Cu-O planes of fluorinated Tl-1223 because of removal of F/O from the Cu-O planes. As the irradiation dose is increased, additional F/O could be removed from the Sr/Ba-O planes which, we believe, is the reason for the decrease in binding energy of Sr 2p_{3/2} for 50 Mrad dose. These results are also consistent with our previous finding that α -irradiation enhanced the critical current density of these samples, through creating oxygen (and fluorine) vacancies that act as additional pinning centers.

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Fully multi-channel detection of reflection (e,2e) experiments

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The (e,2e) technique can provide an exclusive information: the full spectral momentum density of bounded electrons. Yet it measures a five-fold differential cross section, thus resulting in long acquisition times. This limitation becomes more severe when applying this spectroscopy to surfaces and it cannot be overcome by increasing the flux of the primary beam, rather by using parallel acquisition, that increases by orders of magnitude the overall efficiency of coincidence apparatuses.

The implementation of fully multichannel detection on the reflection (e,2e) apparatus used to perform the pioneering momentum distribution experiment on surfaces [1] is described. By upgrading the apparatus with a novel position sensitive detector (PSD) it is possible to resolve the azimuth angle of the slow ejected electrons, hence to collect in parallel mode (e,2e) spectra that are fully differential in momentum. Angle resolved (e,2e) data on the ionization of the valence band of highly oriented pyrolytic graphite show that a momentum resolution better than 0.2 \AA^{-1} has been achieved without degrading the overall luminosity. A second PSD has been mounted on the exit of the fast scattered electron-analyzer, thus allowing parallel acquisition of different energy channels with a resolution that is ultimately determined by the associated electronics. Preliminary results relative to the newly implemented energy multichannel detector are also reported, proving that the acquisition time can be reduced by a factor of 10, while maintaining an energy resolution of the order of 1 eV.

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An Atom Specific Look at Chemical Bonding using X-ray Spectroscopies

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In the present contribution I will demonstrate how X-ray absorption and emission spectroscopies can be used to obtain unique information regarding electronic structure and its relation to chemical bonding. Two different areas will be covered, adsorption of molecules on surfaces and hydrogen bonding in water.

When a molecule is adsorbed on a metal surface by chemical bonding new electronic states are formed. The direct observation and identification of these states has been an experimental challenge. Their signature is often obscured by bulk substrate states. In the following contribution I will show how X-ray emission in spite of its inherent bulk sensitivity, can be used to investigate adsorbed molecules. Due to the localization of the core-excited intermediate state, XE spectroscopy allows an atom specific separation of the valence electronic states. Thus the molecular contributions to the surface chemical bond can be separated from those of the substrate. Furthermore, angle dependent measurements make it possible to determine the symmetry of the molecular states, i.e. the separation of pi and sigma type states. In all we can obtain an atomic view of the electronic states involved in the formation of the chemical bond to the surface.

Hydrogen bonding in water holds the key to the peculiar behaviour of liquid water and determines the chemistry of biological and geological systems. Although several experimental techniques have been widely used the hydrogen bonding networks in water are still not well understood. Using X-ray absorption spectroscopy I will demonstrate how we can learn about the changes in chemical bonding of water due to hydrogen bonding and how it is related to the structure of the liquid phase. The combination of X-ray emission and photoelectron spectroscopies provide a tool to study how the internal O sp hybridization is changed due to hydrogen bonding in ice. X-ray emission spectroscopy maps out the O2p contribution whereas high energy excited valence band electron spectroscopy is sensitive to the O2s contribution.

Spectral properties of 1D Peierls systems

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Low-dimensional, strongly correlated materials are interesting model systems for testing fundamental concepts of many body physics. Recently, high-resolution angle resolved photoemission (ARPES) experiments on quasi-one-dimensional (1D) compounds have revealed some unexpected and complex properties. Dispersive 1D bands and underlying Fermi surfaces are observed, but the spectral lineshapes are incompatible with the usual Fermi liquid scenario, and apparently reflect the singular behavior of correlated electrons in 1D [1]. Temperature-dependent spectra bear clear fingerprints of transitions to ordered (e.g. CDW) insulating phases. Remarkably, the extrapolated leading edges, and not the measured quasiparticle energies, yield the correct gap values. We will use two typical 1D Peierls systems, $(\text{NbSe}_4)_3\text{I}$ and $(\text{TaSe}_4)_2\text{I}$, to illustrate this peculiar 1D phenomenology [2]. We will also discuss the spectral consequences of translational symmetry, namely the appearance of shadow bands, and of the competition between coexisting incommensurate potentials.

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Magnetic Dichroism in the Cr 2p Photoionization*

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Investigating the linear magnetic dichroism in the 3p photoionization of oriented free Cr atoms and comparing the results to those obtained from magnetically ordered thin layers, the strong influence of intraatomic effects on dichroism could be demonstrated [1]. Stimulated by the success of these studies we extended our investigations to the Cr 2p core level. Cr has very interesting magnetic properties ranging from the antiferromagnetism of the bulk metal to the ferromagnetic order observed for thin films. The dichroism in the 2p spectra allows for a detailed probing of the magnetic properties of 3d metal films and multilayer systems. In contrast to the 3p spectra the 2p spectra are dominated by the 2p spin-orbit splitting. We used the intense, linearly polarized photon beam provided by the HASYLAB BW3 undulator station to ionize the Cr 2p level (photon energy 700 eV). The free atoms were prepared in an oriented ground state by pumping an optical transition with circularly polarized laser radiation counterpropagating to the undulator beam. The kinetic energy of the photoelectrons was analyzed with the aid of a high resolution Scienta SES-200 electron analyzer. The results on the Linear Magnetic Dichroism in the Angular Distribution (LMDAD) in the 2p photoionization of laseroriented free Cr atoms are compared to the LMDAD in the 2p photoionization of a magnetized surface layer of Cr on Fe (110). This comparison allows us to disentangle the influence of interatomic and intraatomic interactions on the dichroic effect in the spectra of atoms bound in thin films or solids. We conclude that for the interpretation of the spectra of bound 3d metal atoms, atomic multiplet structure and satellite emission in the final ionic state have to be taken into account. One-electron models therefore cannot be justified. The results on free Cr atoms are compared to different theoretical approaches (an angular momentum coupling model for innershell ionization and Hartree-Fock calculations). Combining the results on the LMDAD with the Linear Dichroism (LD) in the 2p photoionization of laseraligned free Cr atoms critical atomic parameters, e.g. matrix elements and phases, can be extracted providing for a sensitive test of the atomic many-electron approach.

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**Photofragmentation of Carbonyl Sulfide (OCS) following Photoexcitation near C 1s, O 1s and S 2p
Thresholds**

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The study of multiple-photoionization after an inner-shell electron is ejected has been of intense interest for many years. In the present study we have examined the OCS molecule over the carbon and oxygen K-edge and the sulfur $L_{2,3}$ edges. The availability of intense photon beams allowed us to study very weak fragmentation processes, resulting in high resolution measurements of up to 18 different fragment ions at each edge. Of particular interest was the production of negative ions (C^- , O^- , S^-), which can be the result of only a few selective decay channels.

Surfaces of complex systems: amorphous materials and semiconductor nanoparticles

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The results of ab-initio simulations of the structural and dynamical properties of surfaces of complex semiconductors will be presented. In particular, we will discuss computer experiments [1] in which samples of amorphous silicon carbide and amorphous carbon were subjected to uniaxial strain until fracture occurred and two surfaces were formed. These simulations provided an unbiased way of generating models of amorphous semiconductor surfaces.

Furthermore we will discuss recent results [2] on the influence of surface reconstructions and surface termination on the structural stability and electronic properties of germanium clusters. General considerations on the importance of surface effects for the correct modeling of nanostructures will conclude the talk.

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Cation and Anion Formation of CO₂ in the Vicinity of the C 1s and O 1s Core Levels

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Mass resolved partial ion yield photoabsorption spectra of CO₂ have been recorded in the vicinity of the C 1s and O 1s core thresholds. Both anion and cation spectra have been recorded. At the C 1s edge, Ruhl and Jochims [1] have earlier observed a weak production of O⁻ at the Pi* resonance, and our experiment corroborates their finding. In the vicinity of the O 1s edge, both C⁻ and O⁻ fragments were observed, and the anion partial yield spectra reveal several electronic states that have not been observed before. Spectra from several cationic fragments which have not been observed before were also recorded, such as CO⁺⁺ and O₂⁺, in addition to spectra from stronger previously observed fragments.

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X-ray Scattering from Magnetic Surfaces and Buried Layers

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The successful realization of proposed magnetic/semiconductor, magnetic/insulator, and magnetic/metal structures will rely on maintaining the electron spin characteristics as it traverses the constituent interfaces. Therefore, the ability to characterize, understand, and ultimately control the chemical, and magnetic structure of the interfacial region remains as the critical issue to be surmounted. X-ray magnetic circular dichroism (XMCD) and X-ray resonant magnetic scattering (XRMS) have the demonstrated capability to separately determine magnetic and chemical characteristics of an interface. Data show that the interfacial chemical and magnetic roughness for both the perpendicular and the in-plane roughness are different, but related and that different aspects of the magnetic roughness control macroscopic magnetic material parameters. Furthermore, by combining XRMS and XMCD spectroscopy we can determine the chemical and magnetic distributions of each element at a multi-element (>2) interface to identify new mechanisms for interface disruption of these complex interfaces. As an example, data on the capping of La_{0.7}Sr_{0.3}MnO₃ (LSMO) layers shows that cation interdiffusion to be the source of poor interfacial spin conductance for many capping materials.

Dipolar Angular Distributions and Branching Ratio of Xenon $4d$ Photoelectrons in the Photon Energy Range of 100-250 eV*

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The Xe $4d$ photoionization process is one of the primary examples of photoionization processes to study correlation effects and spin-orbit interactions. It has been intensively examined in a broad photon energy range, and at specific photon energies a complete characterization of the $4d$ photoionization process was carried out, i.e. all the dipole transition matrix elements of both spin-orbit components were determined using spin-resolved electron spectroscopy and coincidence techniques. However, these results rely heavily on accurate partial cross section, branching ratio and angular distribution data.

In this work, measurements of the angular distributions and branching ratios of the Xe $4d_{3/2}$ and $4d_{5/2}$ photoelectrons were carried out in a wide photon energy range (100-250eV) near the Cooper with both hemispherical and time-of-flight electron spectrometers at undulator beamlines of the Advanced Light Source. Consistent results were obtained regardless the differences among our experimental techniques and data analysis. The spin-orbit branching ratios show considerable deviation from the previous published measurements [1,2] in the photon energy region of 190-200eV. Further more, for the first time, a non-negligible β difference between the two $4d$ components is observed and it changes dramatically in the vicinity of the Cooper minima. The observed β difference is a strong indication of relativistic effects. Future spin measurements and relativistic calculations are called for in order to determine the nature of the spin-orbit interactions.

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Observation of Non-Dipolar Effects of Xenon $4d$ Photoelectrons in the Vicinity of Cooper Minimum*

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The breakdowns in dipole approximation (DA) were first observed 30 years ago in soft-x-rays photon energy regime (below 5 KeV), and recent atomic gas phase studies show that there are considerable non-dipolar angular distribution effects even in the energy region below 1 KeV. For atomic systems, so far non-dipolar studies have been limited to a few n_s and n_p subshells in rare gases. Another one of the not-much-explored aspects is the study of the breakdown of the DA in the regions where dipole cross sections change dramatically. The vicinity of Cooper minimum serves an interesting candidate of such studies because the dipole matrix elements go through zero as they change the sign. Because of their multiplicity of partial waves with a higher- l state, Xe $4d$ angular distributions have been intensively studied for electron–electron correlation effects and spin-orbit interactions. Although the non-dipolar geometry were actually used in some of the previous Xe $4d$ dipolar parameter measurements [1, 2], the high-order contamination are not all unambiguous due to the drastic change of the β parameter near the Cooper minimum as well as the combined uncertainties from different measurements. Thus a setup for spontaneous dipolar and non-dipolar measurements is needed in order to disentangle the high order interactions from the dipolar ones.

In this work, measurements of angular distributions of the Xe $4d_{3/2}$ and $4d_{5/2}$ photoelectrons were carried out in a wide photon energy range (100-250eV) near the Cooper minima with time-of-flight (TOF) spectrometers [3] at the undulator beamline 8.0 of the Advanced Light Source (ALS). By comparing relative partial cross sections obtained spontaneously at the non-dipolar and dipolar geometry, a set of substantial non-dipolar parameter ζ values were observed in the vicinity of the Cooper minimum.

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Electronic and Atomic Structure of Sn/Ge(111) and Sn/Si(111)

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The Sn/Ge(111) surface has attracted a lot of interest recently because of the $\sqrt{3}\times\sqrt{3}$ to 3×3 transition that occurs at low temperature [1]. The Sn/Si(111) surface has not been studied as much since no such transition has been reported for this system. We have performed detailed studies of both Sn/Ge(111) and Sn/Si(111) by PES and LEED. We find that both systems exhibit very similar electronic structures, but Sn/Si(111) fails to show any low temperature phase transition down to 70 K, which was the lowest temperature in our study. However, in similarity with Sn/Ge(111), the Sn 4d spectra from Sn/Si(111) show two major components and the angle resolved valence band spectra show two surface state bands both at RT and 70 K. These features have been associated with the 3×3 phase in the case of Sn/Ge(111) [2]. A puzzling difference is that Sn/Si(111) keeps its $\sqrt{3}\times\sqrt{3}$ reconstruction also at the low temperature although it exhibits the electronic characteristics of a 3×3 phase. Based on the electronic structure one can expect that also the Sn/Si(111) surface will show a phase transition but at a significantly lower temperature compared to the Sn/Ge(111) surface. The Sn 4d core-level spectra show an interesting difference between Sn/Ge(111) and Sn/Si(111) which will be discussed in terms of the two different types of 3×3 phases that were recently reported for Sn/Ge(111) [3]. We also present a combined LEED and PES study which will resolve an ongoing controversy about the Sn 4d line shape of the $\sqrt{3}\times\sqrt{3}$ and 3×3 surfaces of Sn/Ge(111).

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Radiative and Relativistic Effects in the Decay of Highly-Excited States in Helium

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A recent experimental study[1] measured a significant fluorescence yield of the He($2lnl'$) photoexcited resonances, showing major qualitative differences from non-relativistic predictions. We present a further theoretical analysis of these states, and perform R-matrix multichannel quantum defect theory calculations to extract fluorescence and ionization cross sections, giving results in excellent agreement with new, higher-resolution measurements. The principal effect of the spin-orbit operator has been quantified as an oscillatory perturbation below threshold, causing strong mixing between all seven $2lnl'$ $J=1$ resonance series, and redistribution of fluorescence and ionization cross sections at regular intervals. These results should be applicable for highly-excited states in general, whenever there are multiple interacting Rydberg series, and emphasize that careful consideration of radiative and relativistic effects is necessary to characterize threshold spectra

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The use of Auger Photoelectron Coincidence Spectroscopy to Deconvolute the M₄₅ Auger AES of Palladium*

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Palladium (Pd) has a complex Auger spectrum. It is difficult to fully describe the M₄₅ Auger spectra of its surface atoms because of the many possible cascade processes placing intensity in this energy region. Weightman et. al. [1] fitted the Auger peak as the sum of "atomic-like" terms and we used this model as a starting point for our investigation. We compared Weightman's model to Auger photoelectron coincidence spectroscopy (APECS) data and found intensity in the M₄₅ APECS spectra that could not be accounted for. APECS data differs from regular singles data because it is able to separate the M₄₅ and M₅₄₅ components of the Auger peak completely. In the singles data, these peaks and their associated backgrounds interfere making it difficult to assign intensities. By applying Cini-Sawatzky theory to the convoluted one-electron density of states we created new model curves for each component of the Auger peak. The experimental APECS data was then fitted using these components and the final model was compared to a high resolution AES spectrum. There was a good fit between this model, the APECS data and high resolution AES data. The model also provided evidence for an M₄₅-M₅₄₅-N₄₅ Coster-Kronig process.

*Work supported by the Australian Research Council

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Observation of the unoccupied electronic states of monolayer graphite by multi-photon photoelectron spectroscopy

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Although the unoccupied band structure of graphite has been the subject of extensive theoretical and experimental studies, there remains a controversy about the location of the lowest unoccupied σ^* band, which has high electron densities in the interlayer region. There are also great interests in the formation and the properties of a single layer of graphite on transition metal surfaces in comparison with other carbide surfaces. In addition, probing the difference of the electronic band structures of single- and multi-layered graphite provides useful information on interlayer interactions. Multi-photon photoelectron spectroscopy of monolayer graphite on a Pt(111) surface was measured for clarifying these points.

The experiments were performed with a mode-locked Ti:Sapphire-seeded regenerative amplifier system. Three-photon photoemission was measured with the second harmonics (2.95 eV, 140 fs) generated with a KDP crystal. The energy distributions of photoelectrons were measured by a time-of-flight energy analyzer. A Pt(111) sample was cleaned by Ar ion sputtering and repeated cycles of heating at 870 K in 1×10^{-7} Torr of oxygen and flashing to 1100 K. The graphite layer on Pt(111) was prepared by the flashing the sample to 1100 K after exposed to C₂H₄.

On the clean Pt(111) surface three-photon photoemission from the occupied *sp*-derived surface state and the $n=1$ image-potential state have been observed. On the graphite covered Pt(111) surface three new peaks appeared in a normal emission spectrum. The intensities of the three new peaks increase with the coverage of graphite while those of surface and image-potential states decrease. The final electron energies of the three new peaks are 7.55 eV, 6.93 eV, and 6.19 eV with respect to the Fermi energy and increase with the polar angle of photoemission. Photon energy dependence showed that the higher two peaks shifted with photon energy ($\Delta E_{\text{kin}} = \Delta h\nu$) and the lowest peak shifted twice as much as the photon energy ($\Delta E_{\text{kin}} = 2\Delta h\nu$). The peaks of 6.93 eV and 7.55 eV are assigned to the $n=1$ and $n=2$ image-potential states on the graphite layer, respectively. The binding energies of 0.83 eV for $n=1$ and 0.21 eV for $n=2$ are derived with the work function of the graphite layer 4.81 eV. The third peak is tentatively assigned to the unoccupied surface state which is located at 0.29 eV above the Fermi energy. The surface state is thought to be originated from the occupied surface state of clean Pt(111) which shifted by the change of the work function.

X-ray photoelectron diffraction on silicon carbide and aluminium nitride epitaxial films: polytype structure and polarity *

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Angle-scanned X-ray photoelectron diffraction (XPD) is used to determine the polytype and polarity of silicon carbide and aluminium nitride films grown by molecular beam epitaxy.

Silicon carbide can exist in various polytype structures differing in the Si-C stacking sequence along one direction, e. g., cubic 3C, hexagonal 4H and 6H, rhombohedral 15R. These polytypes show different electronic and optical properties. The growth of heterostructures and superlattices of different SiC polytypes is studied to get new materials with adjustable bandgap and other interesting properties. Silicon carbide and aluminium nitride are polar crystals with Si and C face or Al and N face, respectively, of the bulk-terminated surface.

We have shown for the first time that XPD is a suitable technique to determine the polytype of SiC films as well as the polarity of AlN films. For high-energy photoelectrons excited by Mg or Al K radiation, the Si 2p as well as the C 1s diffraction patterns are different for the various SiC polytypes and are dominated by their bulk structure. Full-scan diffraction patterns and polar scans were measured on the most common polytypes and the polar faces of SiC and AlN. These patterns can be used as fingerprints for the identification of the structure of unknown single-crystalline films.

The diffraction patterns of the polytypes can be well described by single-scattering cluster calculations (SSC). Due to the large escape depths of the considered photoelectrons and the size of the unit cells, a large cluster radius of 2.5 nm with some 5000 atoms is necessary to simulate the fine structure of the polytypes. Such big clusters are difficult to handle in multiple-scattering cluster theory. We have investigated the influence of surface structures and atomic stacking on the diffraction pattern. The differences between the Si 2p and the C 1s diffraction patterns as well as between Al 2p and N 1s patterns measured on a given polytype are due to different elastic cross sections.

Due to the good correspondence between experiment and theory it seems to be possible to predict the XPD pattern of SiC and AlN films with any crystal structure by SSC. This is important for monitoring epitaxial growth of the polytypes in molecular beam epitaxy and was applied on in situ grown heterostructures of silicon carbide polytypes.

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FRAGMENTATION OF KCl MOLECULES INDUCED BY PHOTOABSORPTION IN LOW ENERGY REGION

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The fragmentation of the evaporated KCl molecules was studied by using synchrotron radiation in low energy region. Measurements were done at the beamline 52 in MAX – laboratory in Lund, Sweden. This beamline is equipped with a normal incidence monochromator and uses radiation from a bending magnet. The beamline delivers reasonable photon intensity in the energy region of 5 to 30 eV. The use of these low energy photons means that only the outermost molecular orbitals of KCl, formed from K 3p and 4s, and Cl 3s and 3p atomic orbitals are affected. The measurements were performed using a time-of-flight ion mass spectrometer for recording the total and partial ion yields as a function of photon energy and the ion mass spectra at selected photon energies. The time-of-flight (TOF) spectrometer used in these measurements was Wiley-McLaren [1] type ion mass spectrometer, build in the University of Oulu [2]. In addition to ion measurements also some electron spectra of KCl were measured using the Scienta SES-100 hemispherical analyzer.

In the total yield spectrum of KCl some interesting peaks were seen. These peaks occur at photon energies 19.3, 21.2, 21.9 and 29.9 eV, and are due to the ionisation and excitation from the molecular valence orbitals followed by possible molecular dissociation of monomers and dimers into Cl^+ , K^+ , KCl^+ and K_2Cl^+ -ions. In order to find out the character of the processes corresponding these peaks, a number of TOF -spectra at various on- and off-resonance energies, as well as partial yield spectra were recorded. Also some photoelectron spectra were recorded at these energies.

The contribution of different ions at resonances is reported and the role of the molecular Auger effect to explain the ion formation is discussed.

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Soft x-ray fluorescence and photoemission study of ion beam mixed ferromagnetic Co/Pt multilayered films

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An ion beam mixing of ferromagnetic Co/Pt multilayered films, which are known as the perspective material for new generation of data-storage devices [1], was carried out for the purpose of enhancing their magnetic and magneto-optical properties, and the electronic structures and physical properties were investigated. For this study, [Pt(4.5nm)/Co(3.5nm)]x8 multilayered films were, first of all, prepared on Si(100) substrates by alternating electron-beam evaporation, and then were ion beam mixed with 80 keV Ar ions in a high vacuum. The electronic structures of the samples were studied by using soft x-ray fluorescence (SXF) and synchrotron-radiation photoemission spectroscopy (PES), and the magnetic moments were measured by magnetic circular dichroism (MCD). In addition, x-ray diffraction and cross-sectional transmission electron microscopy (TEM) were employed to confirm the atomic structures before and after ion beam mixing. The experimental results from SXF and PES measurements show that ion beam mixing process changes the spin-hybridization between Co 3d and Pt 5d electrons and the exchange interaction, which are strongly correlated with magnetic behaviors of ferromagnetic thin films. This behavior has a good agreement with a significant enhancement in the magnetic moment after the ion beam mixing with respect to those of the unmixed Co/Pt multilayered films and even a stable equiatomic CoPt alloy, confirmed by MCD.

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Spin-resolved APS for K-, L- and M-line emissions of Ni*

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Appearance potential spectroscopy (APS) spectra are measured near 1s, 2p and 3p core electron excitation energies for ferromagnetic Ni with spin polarized electrons. Spin resolved spectra for Ni 2p_{3/2} were explained by a one electron approximation with parameterized Auger matrix elements[1]. Though the aspects of spin integrated spectra for 2p_{1/2} are very similar to that for 2p_{3/2}, our spin resolved spectra can not be explained by the above approximation. The spectra for 1s do not show a clear appearance potential and only slight primary electron spin dependence were obtained near 1s electron excitation threshold energy. The approximation involves only unoccupied density of states. The results of 2p_{1/2} and 1s indicate the importance of the role of a core hole for the APS spectra. The spectra for 3p show an entirely different aspect from those for 2p. This may be caused by the many body effect for which the soft x-ray emission intensity is resonantly enhanced (i.e. resonant inverse photoemission)[2]. The variation of the spin dependent intensity for 3p APS suggests the existence of 3d⁸ configuration in the ground state of Ni.

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Observation of a quasi-1D Mott-Hubbard insulator: The re-entrant Na/Si(111)-3x1 surface

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We report a case where electron-electron correlation interaction brought about by the adsorbates on a surface drives a quasi one-dimensional(1D) band insulator into a Mott-Hubbard insulator without altering the surface morphology. The system is a re-entrant Na/Si(111) surface (3x1-II) reported earlier[1]. It contains 2/3 monolayers of Na adatoms, which is formed by adding extra Na atoms on the earlier 3x1 surface at 1/3 ML (3x1-I). We have utilized several experimental tools including photoemission spectroscopy (PES) using synchrotron photons, high-resolution electron-energy-loss spectroscopy(HREELS), and scanning tunneling microscopy(STM).

We first show that the 3x1-I is a band insulator with a band gap of about 1.2 eV. Our STM images then show that the additional Na atoms on the 3x1-II surface form quasi 1D atomic chains on the 3x1-I surface. The 3x1-II surface with well ordered 1D Na chains is found to be semiconducting characterized by a unique loss peak of 0.8 eV in our HREELS data. The appearance of a surface state centered at 0.45 eV below Fermi energy turns out to form a flat surface band (band width $W < 0.25$ eV), which is another feature unique only to the 3x1-II surface.

All these data can be understood consistently when a Mott-Hubbard insulator is invoked for the 3x1-II surface. We thus estimate the effective intrasite Coulomb repulsion $U^* = 0.8$ eV for the surface. The obtained value of $U^*/W = 3.6$ satisfies a Hubbard criterion ($U/W > 1.2$) indicating that the surface is more likely a Mott-Hubbard insulator. The results from our electronic-structure, total energy, and U^* based on density functional theory further support our conclusion for the 3x1-II surface.

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Vibrational fine structure in C 1s x-ray photoemission of chemisorbed ethylene and acetylene on Ni(100)

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Using high-intensity synchrotron radiation from MAX II in Lund we studied the adsorption of ethylene and acetylene on Ni(100) by measuring C 1s photoemission spectra with high resolution. Upon molecular adsorption at 95 K the C 1s spectra exhibit a single state with vibrational fine structure, similar to the system C₂H₄/Rh(111) [1]. Using a fitting procedure we can determine the vibrational energy of the C-H stretch mode for adsorbed ethylene to be about 350 meV. This value corresponds well to results from HREELS, which convert to 375 meV for the same system [2]. Since the C-H stretch mode frequency determined by HREELS is very similar for all hydrocarbons, the relative intensities of the vibrationally excited states (called S factor) are a characteristic feature for a specific system. Comparing the results for ethylene and acetylene adsorption we can visualize a change in S factor. We also find different vibrational energies for the two systems. This could serve as a fingerprint for determining intermediate species, as for example, in the dehydrogenation reaction of ethylene on Ni(100). This work was supported by EU TMR program (ERB FMGE CT980124), BMBF (05 SF8 WEA7), and DAAD exchange program 313/S-PPP. We thank A. Nilsson for fruitful collaboration.

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Vibronic couplings in C 1s Photoabsorption Spectra of Acetylene, C₂H₂

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The angle-resolved photoion-yield spectra were measured in the inner-shell photoabsorption of a linear polyatomic molecule, C₂H₂ (acetylene). The features observed are the same as reported[1], but the energy resolution is significantly improved. Detailed discussion is possible on complicated vibronic couplings below the ionization threshold. The 0-degree and 90-degree yields indicate final states with sigma and pi symmetries, respectively. The 3p sigma-u and 3p pi-u Rydberg states are completely resolved in the same energy region. The previous experiments could not resolve them, and the previous theoretical calculations predicted the 3p sigma-u state near the 3s Rydberg state. The C1s->3p pi-u Rydberg transition shows no evidence for antisymmetric stretching vibrations. This is the first to observe that the Rydberg state keeps gerade and ungerade symmetries, without vibronic coupling related to dynamic core hole localization. On the other hand, complicated features are observed in the 3s Rydberg region. The 3sigma-u* valence state is located in the 3s sigma-g Rydberg region with no mixing between gerade and ungerade final states. The previous theoretical calculations result in a spurious Rydberg-valence mixing between 3sigma-u* valence and 3p sigma-u Rydberg states. Furthermore, the 90-degree ion yields were observed even in the 3sigma-u* and 3s sigma-g region, due to vibronic coupling through bending vibration with pi symmetry. This type of vibronic coupling is induced by the nearby C1s ->1pi-g* valence excited state with strong Renner-Teller effects.

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Chemical State Information from the Near-Peak region of the X-Ray Photo-Electron Spectrum

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Following the work of Tougaard [1] it is now generally accepted that the contribution to the energy loss background of a photoelectron peak arising from transport of electrons through the solid is very small at the position of the peak. Nevertheless, the sharp rise in background at the peak, as originally defined by Shirley [2] is very real and

is probably the most easily recognised characteristic of the X-ray photoelectron spectrum. To undertake quantification in XPS analysis it is normal to remove a background which is based on the original Shirley algorithm, i.e. an integration of the peak lying above background using an integration constant which allows the background to merge

with the experimental data at some point beyond the peak. The merge point is usually chosen to be one or two peak widths beyond the peak centre on the low kinetic energy side of the peak. At this point in the spectrum the extrinsic loss, defined by Tougaard has become significant and varies with the thickness of any overlayer which might be

present, including any surface contamination. Thus the Shirley scattering parameter, as the constant of integration has been called, contains a contribution from extrinsic losses and a contribution from the rise in background at the peak, which for clarity we have referred to as the intrinsic loss [3]. Because the initial part of the Tougaard background

is approximately linear it is possible to construct a synthetic background containing both contributions by adding a tail of linear slope to a Shirley type background, represented as the integral of a Gaussian/Lorentzian peak. By this means the experimental data can be matched with a set of Gaussian/Lorentzian peaks and their associated, synthetic

backgrounds without any need for prior background subtraction. This is the basis of a curve fitting program developed by Proctor and known as GOOGLY [4]. We have used GOOGLY to fit peaks of many elements and hence obtained a value for the intrinsic part of the background defining it by a parameter, kappa. Kappa varies systematically from one element to another and in particular increases to a maximum at the midpoint of the 3d transition series. This maximum corresponds to a maximum in the number of close spaced final state configurations available following

photoexcitation. The chemical state information arises from situations in which the number of final state configurations depends on the compounds formed. E.g. when aluminium reacts with a transition element to form an aluminide, then the Al 2s peak gains an intrinsic loss background which is similar to that of the transition metal [5]. In this and other cases, photoexcitation of one element in a compound has resulted losses arising from shake

Auger decay at the $1s^{-1}np$ ($n=3-5$) resonances of Ne

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The relocation of the beamline 51 as the undulator beamline I411 at the third-generation MAX II storage ring has greatly extended the usable photon energy range for gas-phase studies. We have thus been able to measure the resonant Auger spectra of neon following the excitations of 1s electrons to unoccupied 3p, 4p and 5p orbitals (photon energy ca. 870 eV). Combined with a rotatable high-resolution SES-200 electron analyzer, total line widths comparable to the lifetime widths of the core-excited states (250 meV [1]) were achieved in resonant Auger lines. Such a high resolution reveals many details in the resonant Auger spectra that were not observed in previous studies [2,3]. For example, fine structure due to the excited electron is partly resolved in the transitions to the $2p^43p$ final states. In addition to the usual spectator or shake-up resonant Auger transitions, the $1s-3p$ de-excitation spectrum shows features that cannot be explained in terms of such basic processes. A possible explanation to the effect is discussed. Experimental results are also compared with the results of calculations performed in the multiconfiguration Dirac-Fock (MCDF) approach.

Apart from measurements on the maxima of the resonances, decay spectra were also taken at both sides of the $1s^{-1}3p$ resonance with an 0.1-eV step. These measurements show that the intensity ratio between the spectator to $3p-4p$ shake-up transitions changes considerably as a function of excitation energy, in agreement with the results of ref. [3]. This effect is due to electronic state-lifetime interference.

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A Partial Reassignment of Valence Photoelectron Satellite Lines of Kr and Xe

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The electronic states of rare gases in different electronic configurations are of special interest in atomic and molecular physics since they are relatively simple and thus serve as tests for theoretical approaches. In addition to optical spectroscopies, photoelectron spectroscopy is one of the most important methods when studying singly ionized atoms. In the present report, photoelectron spectra of Kr and Xe, previously reported in [1,2], have been remeasured with high resolution in the region of $ns2np4n'l$ ($n=4$ for Kr, $n=5$ for Xe) states.

For a theoretical interpretation of Kr correlation satellite lines, a CI calculation including the LSJ states from the $4s^14p^6$ and $4s^24p^4(4d\text{-}md,5s\text{-}m's)$ configurations was carried out using the Cowan's code.

The experiments were performed on the new undulator beamline I411 at the MAX-II storage ring at Lund, Sweden. Measurements were made with very high photon energy resolution and ejected electrons were recorded with a rotatable SES-200 hemispherical analyzer. The satellite lines in photoelectron spectra were identified by comparing the Kr and Xe results to each other, to the designations given by Minnhagen *et al.* [3], Hansen *et al.* [4] and Kikas *et al.* [2], and to the results of CI calculations for Kr. Many discrepancies in the previous assignments of the photoelectron satellite lines especially of Kr were found. A reassignment of these lines is given.

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Electron correlation effects in Auger cascade of argon following $2p^{-1}4s$ excitations

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Effects of intermediate coupling and configuration interaction on the partial transition rates, total decay widths and the angular distribution parameters of the Ar resonant Auger transitions $2p^{-1}4s$ to $2p^63s^{-1}3p^{-1}4s$ and the second-step Auger transitions $2p^63s^{-1}3p^{-1}4s$, $^2P_{1/2,3/2}$ to $2p^63s^23p^4$ have been studied both theoretically and experimentally. This work is an extension to a recent study of Ueda et al [1,2].

Partial and total transition rates and the angular distribution parameters for the resonant Auger and second-step Auger transitions have been calculated using LS- and intermediate coupling (IC) schemes for the states involved in the decay processes. The effect due to the mixing of the $2p^63s^3p^54s$ and $2p^63s^23p^34s3d$ configurations (CI) has also been investigated using the multiconfiguration Dirac-Fock method. The energy splitting between the resonant Auger final states $2p^63s3p^5(1P1)4s$, $^2P_{1/2,3/2}$ is much smaller than the natural widths of these states and thus the lifetime interference effect has to be taken into account in the calculations of the angular distribution parameters for the second-step Auger transitions.

The resonant and the second-step Auger spectra of Ar were measured at the I411 undulator beamline at Max-laboratory in Lund, Sweden. In order to determine the angular anisotropies of resonant Auger transitions a rotatable SES-200 electron analyser was set at angles 0° , 54.7° and 90° with respect to the electric vector of the incident light. High photon and electron energy resolution was achieved, which enables us to test the roles of IC and CI in the resonant Auger step. Effects of interference on the angular anisotropy have also been tested by comparing the results of two-step and one-step calculations with the experimental findings for the second-step Auger electron spectrum.

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Chemical Effects in the Resonant Inelastic X-Ray Scattering excited at the M₅ edge of Lanthanum in different environments

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The interaction of 4f electrons with the delocalized conduction band is at the basis of many crucial phenomena in rare earths and their compounds, and systems including Lanthanum are particularly interesting because the 4f⁰ occupancy of La makes the interpretation of the spectra more straightforward.

We performed resonant inelastic scattering experiments on La at beamline 12B at the ESRF (Grenoble) using the AXES grating spectrometer [1]. The x-ray beam is produced by a helical undulator and monochromatized by a dedicated monochromator [2]. Lanthanum was studied in three different environments: as simple metal, in the oxide La₂CuO₄ and in ionic LaF₃. X-ray emission was excited at several energies across the M₅ edge of La (around 834 eV). The spectra present three main features: (i) an elastic peak, (ii) a peak due to the filling of the 3d_{5/2} core-hole by a 5p electron, (iii) a peak which we attribute to transition towards an excited final state |4f¹ \underline{L} >, where \underline{L} denotes a ligand hole (for LaF₃ and La₂CuO₄) or a local charge transfer state 4f⁰-4f¹ (for the metal). This is in agreement with what has been seen³ in the case of LaAlO₃.

The outgoing photon energy $h\nu_{\text{out}}$ of the three peaks increases with incoming photon energy $h\nu_{\text{in}}$. Thus the energy transferred to the system ($h\nu_{\text{transf}} = h\nu_{\text{in}} - h\nu_{\text{out}}$) is constant at the exploited excitation energies. The peak due to 5p-3d deexcitation is found at $h\nu_{\text{transf}}$ around 19 eV for the three compounds, in agreement with previous literature⁴.

The ligand hole charge transfer final state behaves differently in the three systems, both in terms of $h\nu_{\text{transf}}$ and of intensity vs. $h\nu_{\text{in}}$. The peak is found at a $h\nu_{\text{transf}} = 5.5$ eV for La metal, 10.5 eV for La₂CuO₄ and 12 eV for LaF₃. We relate this difference to the chemical environment of La: the separation between ground state and excited final state is larger in the ionic compound than in the metal due to larger electronegativity. Accordingly there is an increase of $h\nu_{\text{in}}$ at which the loss resonates in La₂CuO₄ and LaF₃ with respect to La metal: the energy required to reach an intermediate state with a ligand hole is smallest in the metal, so that the resonance of the ligand-hole state occurs when $h\nu_{\text{in}}$ is 2.5 eV above M₅ threshold for metal and 5 eV above threshold for La₂CuO₄. LaF₃ behaves similarly to the cuprate up to $h\nu_{\text{in}} = 1.7$ eV above M₅ threshold, which is the highest exploited energy at present. We stress that the described differences are not seen in XAS spectra, that are almost identical for the 3 compounds

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A theoretical investigation of photoemission spectra from (GaAs)_m(AlAs)_n superlattices*

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Superlattices, formed by ultrathin layers of different semiconductor materials, are widely recognized for their unique electronic and optical properties. These superlattices cannot be treated as being composed of layers with their individual band structures. On the contrary, the electronic properties are determined by the superlattice as a whole. The larger periodicity perpendicular to the surface changes the symmetry of the Brillouin zone. This results in a back folding of the valence bands of the bulk material, which opens additional gaps at the edges of the Brillouin zone. We present first theoretical photoemission spectra for (GaAs)_m(AlAs)_n superlattices in the (001) orientation. The spectra are calculated in the one-step model, explicitly including the sequence of semiconductors in the initial states as well as in the final states and in the matrix elements. The initial states are represented by the half-space Green's function, given in a layer-resolved combination of atomic orbitals. The final state of photoemission which is a time reversed LEED state is determined in two ways, by calculation of scattering states including a realistic surface potential and by matching. The transition-matrix elements are numerically integrated in real space. The theoretical spectra in normal emission for an unreconstructed (GaAs)₂(AlAs)₂ surface show dispersing structures which can be traced back to direct transitions. For excitation energies around 33 eV, these emissions indicate a gap caused by back folding of the valence bulk bands. Besides direct transitions, the spectra are analysed in the sense of layer and orbital resolved density of states and matrix elements. Particularly, the layer resolved photocurrent permits to distinguish between contributions from the GaAs and the AlAs layers. The analysis is completed by a comparison with spectra calculated for the constituent homogenous GaAs and AlAs crystals. In addition to (GaAs)₂(AlAs)₂, theoretical spectra with more than two layers of both semiconductors are examined.

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Refinement in the Analysis of Molecular Auger Electron Spectra: the $L_{2,3}VV$ Spectra of HCl and DCl

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The electronic states with two holes in the outermost valence orbital are stable in the hydrogen halides HCl, HBr and HI. Vibrational fine structure can therefore be observed in Auger transitions to such final states from the Cl 2p, Br 3d and I 4d core-hole states. The Auger spectra are further complicated by the spin-orbit and ligand-field splittings of the core-hole states. Since the ligand-field splitting of the core-hole states is of the same order of magnitude as the lifetime broadening of these states, interference effects between the excitation (photoionization) and de-excitation (Auger) process have to be taken into account.

Recently, Püttner et al. [1] performed a detailed analysis of the $M_{4,5}VV$ Auger electron spectra of HBr and DBr, where spin-orbit and ligand-field splitting as well as vibrational interference were properly taken into account for the first time, leading to a much deeper insight into the potential-energy surfaces of the states involved.

In the present study, we carried out a similar evaluation of the $L_{2,3}VV$ normal Auger spectra of HCl and DCl. For that purpose high-resolution, high-statistics Auger spectra of both HCl and DCl were measured at three photon energies using the new undulator beamline I411 at MAX II storage ring in Lund, Sweden. The Auger spectra were fitted simultaneously with the 2p photoelectron spectra, taken at the same photon energies. From the fit the vibrational energies, ω , the anharmonicities, x_{22} , and the equilibrium distances, r_e , of the potential energy curves of the final states were derived assuming Morse potentials for these states. Agreement between the experimental spectra and the fitted results for both HCl and DCl is very satisfactory.

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Modification for extending the real space range in the holographic atomic imaging experiments*

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Typically photoelectron holographic imaging (PHI) only produces atomic images for nearest and usually next-nearest-neighbor atoms to the photo-emitter [1]. A new method--the derivative transform--is presented which generally yields third and sometimes fourth nearest-neighbor atoms. As a result the assignments of atomic species to the peaks in the experimentally obtained image are facilitated. The method is exemplified by experiments for several adsorbate system SI; e.g. C₂H₄ on Si(100) [1] and As on Si(111). A theoretical model is given which shows why the method produces better results. The model uses atomic orbitals to describe the photo-emission intensities.

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Valence Excitations Observed in Resonant Soft X-Ray Emission Spectra of $\text{K}_2\text{Ni}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$ at the Ni 2p Edge

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Resonant soft X-ray emission to the valence region following the Ni 2p photoabsorption was measured for a powder sample of planar (D_{4h}) Ni²⁺ complex with low-spin 3d⁸ configuration, $\text{K}_2\text{Ni}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$. In the photoabsorption, remarkably strong satellite bands were reported in addition to the lowest Ni 2p-3d* atomic lines[1]. Two features in the satellite show different polarization dependencies, and are assigned to the metal-to-ligand charge transfer (MLCT) transitions to out-of-plane e_g pi* and in-plane b_{2g} pi* ligand orbitals, respectively, in good agreement with relaxed Hartree-Fock based static exchange approach, ab initio configuration interaction approach (CI), and density functional theory within a transition potential approach[2]. The low-lying ligand pi* orbital is essential in the metal 2p photoabsorption of 3d transition metal compounds with strong pi backbonding. The CI results indicate that the 3d electron correlation and sigma-donation effects are not important in the case of strong covalency hybridization of the ligand pi* orbitals with the occupied 3d orbitals.

These one-electron or excitonic features were discussed in the resonant Ni valence (3d) and core (3p and 3s) photoelectron spectra measured at the Ni 2p edge, where a number of satellite series become strongly observable via the resonant excitations and each satellite lowers its kinetic energy. The resonant photoelectrons are emitted between the excitons bound by the singly and doubly charged states in the intermediate and final states, respectively. Therefore, the resonant photoelectron behaviors are heavily dependent on electronic states in Ni compounds such as metallic, oxide, and molecular complex systems[4]. On the other hand, in the present work, the resonant soft X-ray emission is given between the excitons bound by the singly charged states both in the intermediate and final states. We found several singly excited valence states, not only intra-Ni excitations but also ligand excitations. Soft X-ray emission only following the lowest Ni 2p-3d* excitation indicates an evidence for intra-Ni electron correlation.

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Interplay Between Orbital And Magnetic Long Range Order By Resonant X-Ray Scattering

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The influence of orbital ordering on the electric and magnetic properties of strongly correlated 3d transition metal systems has attracted significant theoretical and experimental interest since the early 1960s. But it is only in the last few years, after the discovery of colossal magnetoresistance in perovskite-type manganites, that the physical phenomena related to charge, spin and orbital degrees of freedom have been recognized as a central issue in a broad range of materials, so much as to become one of the most popular topics in hard condensed matter physics. An important step forward in this field is represented by the very recent observation that resonant X-ray scattering may provide an accurate and direct experimental method to observe the long-range order for orbital occupancy. The orbital degeneracy is commonly lifted by the crystal field and/or by Jahn-Teller distortion, however, there are systems like V_{2O_3} where one can infer the existence and structure of orbital order only by the knowledge of the magnetic structure, which depends strongly on the occupied orbitals. The experiments were carried out at the ID20-ESRF beamline on a Cr-doped V_{2O_3} single crystal. The orbital Bragg peaks appear at the Néel temperature ($T_N=180K$) at the forbidden antiferromagnetic and charge reflections, and can be observed only when tuning the incident photon energy to the pre-edge of Vanadium K-photoabsorption. This resonance involves a transition from 1s core levels to 3d electronic states via weak quadrupolar transitions. Crucial in these studies was the observation of a peculiar dependence of the diffracted intensity on the azimuthal rotation angle around the orbital scattering vector. Moreover, from the analysis of the complex angular dependence of scattered polarized photons the spatial symmetries of ordered orbitals can be calculated.

Two-Color Photoemission by Time-Correlated Laser and Synchrotron Pulses*

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Laser-based pump-probe techniques have been widely applied to study the various aspects of the dynamics of valence electrons. Comparable dynamical studies involving inner-shell electrons, however, are scarce since ultrashort photon pulses in the XUV and X-ray range are far more difficult to obtain. At such a high photon energy, particularly in combination with high-intensity laser pulses, two-color two-photon photoemission (2C-2PPE) would, for instance, allow to probe core level binding energies in the presence of some laser-induced transient modification. An example would be the transient optical isomerization and the resulting change of the dipole moment in large molecules. More generally, with this new technique the change of a given core level energy may be followed in real time as the system undergoes a structural change (dynamical ESCA). But even without a geometrical change, the effect of transiently excited valence electrons on the electronic screening dynamics and hence on the inner-core binding energies would be of great fundamental interest.

A user facility dedicated to time-resolved 2C-2PPE by combining laser and synchrotron photons is now becoming available at BESSY II. The MBI undulator beamline uses one plane mirror and three toroidal spherical gratings in order to cover the 15 to 350 eV photon energy range. Presently, laser photons near 1.6 eV and 3.2 eV are delivered from a 80 MHz Ti:sapphire laser system. Phase and frequency locking of the pulses is achieved by electronic high-frequency mixing and active control of the laser cavity. The time delay between the laser and the synchrotron pulses is adjusted either by an optical delay line or electronically. For multi bunch (500 MHz), which at present is the standard mode of operation at BESSY II, the sixth laser harmonic (precisely 83.333 MHz) is locked to the synchrotron master clock. A multi purpose surface apparatus equipped with a rotatable hemispherical electron energy analyzer and a number of standard surface analytic tools is available for users. The corresponding gas phase setup is under construction.

We present the features of the MBI user facility together with the beamline's performance characteristics. In order to demonstrate the high brilliance and the small focal size of the synchrotron light achieved at our beamline we present for the very first time photoemission spectra from a liquid salt/water jet of 6 mm diameter in the 30 eV to 120 eV photon energy range [1]. We also discuss our current laser-pump/synchrotron-probe 2C-2PPE experiments aimed to unravel the excited-state energetics and dynamics in some selected large organic molecules: Parahexaphenyl with its potential application for organic light emitting diodes [2], and a phthalocyanine-based

Surface Dynamics in Organic Films Studied by Time-Correlated Laser and Synchrotron Pulses

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We present experiments using time-correlated ultrashort laser and synchrotron pulses at BESSY II, a third generation synchrotron in Berlin. The new MBI user facility is dedicated to study photon-induced processes in adsorbate systems by time-resolved two-color two-photon photoemission (2C-2PPE). Our first experiments at BESSY II were dedicated to study films of para-sexiphenyl (6P), a material of technological significance for organic light emitting devices. The intense radiation of the undulator causes a loss of conjugation in 6P as evidenced by a decrease in intensity of delocalized pi-orbital features in the photoemission spectra. Depending on the degree of this effect surface charging was observed. We have analyzed the possibility to compensate the synchrotron-induced surface charging by laser-pumping electrons into excited states. Using time-resolved 2C-PPE, we will determine the absolute binding energies as well as the population dynamics of 6P molecules in the excited states as these are important information for understanding and optimizing the light emission process. Photoelectron spectroscopy using synchrotron radiation was also performed on films of a Cu-phtalocyanine based system (synthesized at MBI). Our main interest here is to study the electronic structure and dynamical screening effects as a function of the size of the extended pi-electron system in such complex molecules.

Investigation of the SiO₂/Si(111) interface by means of photoelectron diffraction

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The interface of silicon oxide to silicon plays a crucial role in modern semiconductor technology. Due to the advancing miniaturization of semiconductor devices (e.g. MOSFETs) the atomic structure at the interface becomes increasingly important. From the scientific point of view, this interface stands as an example for a transition from a well ordered crystalline structure to an amorphous overlayer. Photoelectron diffraction measurements of the silicon 2p core level were performed to investigate the interface structure of the various oxidation states of silicon. Ultrathin SiO₂ films were thermally grown on Si(111). The Si 2p spectra were recorded with a photon energy of 155 eV and with high resolution (70meV) at the U-49/1-SGM beamline at BESSY II. The photoemission data show the Si 2p signal and its four chemically shifted components, Si¹⁺, Si²⁺, Si³⁺, and Si⁴⁺ [1].

In the present work we combine chemical state specificity of high-resolution photoemission with structure sensitivity of photoelectron diffraction. Structural information is obtained by comparison of the experimental photoelectron diffraction patterns with simulated multiple-scattering calculations [2] for model clusters of Si^{x+}. We present experimental 2- π photoelectron diffraction patterns for the various oxidation states of Si. The patterns differ in their symmetry as well as in their intensity distribution as a function of emission angle. This directly shows the different atomic environment of different chemical shifted emitters. A chemical abrupt interface consisting of silicon suboxides between silicon and SiO₂ was proposed in previous investigations [3]. The simplest model for the interface structure is obtained by joining a bulk-truncated Si lattice to pure SiO₂, with all of the dangling bonds from both sides stitched together. Since thermal oxidation is a local and random process, the distribution of possible local bonding configurations is explained by a statistical cross-linked model [3]. Each oxidation state occurs in various bonding configurations. Thus the experimental data are compared with superpositions of simulated patterns for possible model clusters. This allows us to explain main features of the experimental patterns .

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Single and Double Ionization Studies of SiF₄ by Using Synchrotron Radiation and Photoelectron-Photoion-Photoion Coincidence Spectroscopy (PEPIPICO)*

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The SiF₄ molecule has received much attention because of its potential role as etching agent in chemical plasmas [1]. It has been shown by photoelectron and mass spectroscopy [2],[3], that resonances observed in core level photoabsorption spectra of gaseous silicon molecules, are associated with a complex and rich pattern of electronic relaxation processes that competes with direct dissociation into neutral fragments. In addition, Si 2p core excitation in the SiF₄ molecule favours multivalence excitation and ionization stressing the importance of spectator transitions [4]. In this work, the total ion yield, photoelectron-photoion (PEPICO) and photoelectron-photoion-photoion (PEPIPICO) spectra of SiF₄ have been measured, using synchrotron radiation in the 21.21 to 120 eV photon energy range. The measurements were performed at Brazilian National Synchrotron Radiation Facility

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Angle-Resolved Photoemission Spectroscopy of Highly Overdoped Bi2212

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Experimental results on highly overdoped Bi2212 single crystals ($T_c \sim 55K$) using a high resolution angle-resolved photoemission spectroscopy (ARPES) are presented. This study focuses on two aspects of the data; the changes with k in the overdoped sample alone and the changes at a given k between samples with different doping. In the overdoped compounds the dispersion in the Gamma-Y direction shows little change above and below T_c , which is different than what is seen in optimally and underdoped Bi2212. Near the M point, a relatively flat dispersion is observed in the overdoped samples. The lineshapes for EDC's near M have some similarity with the lesser-doped compounds, with a sharp peak at low binding energy and a broader, low intensity "hump" at a higher energy. However, unlike the optimally-doped compound, it will be shown that sharp peak persists at temperatures above the T_c of the overdoped crystal. We summarize the spectral differences between the overdoped samples versus the more studied optimally and underdoped compounds and discuss the implications for overall understanding of the cuprate materials.

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**Determination of the Phase Composition of Surface Layers in Porous Silicon by XPS and USXES
Technique**

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Porous silicon (PS) is a new prospective material for micro- and optoelectronics since it reveals an intensive photoluminescence (PL) in the visible spectral range. However, the applications of this material are restrained due to the time instability of this luminescence. It can be connected with the change of composition for surface layers as a result of interaction with air as well as with a possible outlet of hydrogen from the pores. Most of the authors consider this effect as related to PS oxidation resulting in a shift of PS band and the change of its intensity.

X-ray photoelectron spectroscopy (XPS) and ultrasoft X-ray emission spectroscopy techniques have been applied in this work for analysis of PS surface layer composition just after obtaining, exposure in the air and low-temperature oxidation. Using decomposition of XPS spectra in the range of Si 2p-level different binding energies have been obtained that correspond to different chemical states of silicon atoms in the surface layers of PS.

Basing on USXES technique with the use of specially elaborated program the presence of different chemical of silicon was determined by the energy spectra of valence electrons of PS represented by Si L_{2,3}-band. The program compiled spectrum from Si L_{2,3} spectra of different chemical standard samples and compared it with the experimentally obtained spectrum of PS. Both methods of analysis allowed to detect the formation of very low-oxidized silicon on the surface of PS which is never observed on the surface of single-crystalline Si.

Photoelectron photoion coincidence study of organometallic complexes

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Photoelectron photoion coincidence (PEPICO) spectroscopy has been used to investigate the dissociation dynamics of $\text{CpCo}(\text{CO})_2$, $\text{CpMn}(\text{CO})_3$, CpMnMnCp , and $\text{BrCo}(\text{CO})_5$ complexes, where Cp = cyclopentadienyl (C_5H_5). These studies were conducted over an energy range from the ionization energy of about 8 eV to 14 eV, the limit of the discharge light source. The molecules are important catalysts used in the synthesis of cyclic and straight chain hydrocarbons. The PEPICO technique involves photoionization with dispersed vacuum uv radiation generated by a hydrogen discharge lamp. Electrons and ions are extracted in opposite directions by an electric field of 20 V/cm. Initially zero energy electrons are passed through a filter and provide the "start" for measuring the ion time-of-flight (TOF). Asymmetric TOF distributions are used to extract the dissociation rate constants for CO or Cp loss reactions. From these rates and the fitting of the breakdown diagram, metal-carbonyl bond energies are measured. These experiments will be continued at the Chemical Dynamics Beam line of the ALS using a higher resolution and higher photon energies.

Thickness dependence of electronic structure and magnetism of Fe/Rh(001)

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The 1:1 charge-transfer organic salt DMTSA-BF₄, where DMTSA is 2,3-dimethyltetraseleno-anthracene, have attracted the interest of many researchers because of the high electrical conductivity and metallic physical properties above ~150K[1]. So far, it has been considered that the 1:1 charge-transfer salt becomes a Mott insulator due to the Coulomb interaction since the 1:1 charge-transfer salt has half-filled band. The origin of the metallic physical properties for DMTSA-BF₄ is not clear at present. In order to obtain the information on the electronic structures such as the band structure, density of states, and the orbital characters, we have performed the photoemission experiments for DMTSA-BF₄. As the size of needlelike shaped DMTSA-BF₄ synthesized by electrochemical reduction is not large enough to carry out the ordinary photoemission measurements, we used the photoelectron spectromicroscopy instrument (FISONS, ESCALAB-220i-XL)[2]. The typical sample size used here was less than 2×0.2×0.1mm³. The clean surface was obtained by scraping the sample surface using an edge of a razor.

From the wide range of the photon energy dependence of the photoionization cross-section, the atomic orbital characters of the observed spectral features in valence band region are determined. The features at ~1 eV, ~3 eV, and ~6 eV are predominantly derived from Se 4*p* states. The broad feature at ~8 eV is predominantly derived from C 2*p* and F 2*p* states. The features between 12 and 18 eV are predominantly from Se 4*s* and C 2*s* states. In the photoemission spectrum near the Fermi level the clear Fermi edge was not observed. It is suggested that DMTSA-BF₄ has a pseudo-one-dimensional band structure [1]. No clear Fermi edge may reflect one-dimensional electronic structure for DMTSA-BF₄. In addition, the Se 3*d* core-level photoemission spectrum for DMTSA-BF₄ is compared with that for DMTSA. The Se 3*d* core-level photoemission spectrum for DMTSA-BF₄ showed the tail at the higher binding energy side as compared with that for DMTSA. The difference of the Se 3*d* core-level photoemission spectra between DMTSA-BF₄ and DMTSA is probably due to another chemical component by the different charge state.

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A Combined Study of Photoelectron Spectromicroscopy and Laser Annealing For Si(111) Surface

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The photoelectron spectromicroscopy is one of the attractive methods to investigate the electronic structure for various materials because a lot of applied usages are possible as compared with the ordinary photoelectron spectroscopy [1]. One of the advantages of the photoelectron spectromicroscopy is to measure the specific small area of the sample. Making the most of the advantage, we have performed the combined study of the photoelectron spectromicroscopy and the laser annealing. A merit of the laser annealing is that it is possible to anneal the specific small area of the sample by irradiating the focused laser light to the sample with less degassing and without the heating unit in the vacuum. In addition, the effect of the electric field used to keep the sample to high temperature is not needed if we use the laser annealing. Therefore, it is considered that the electronic structure at high temperature can be easily measured. As a typical example of the laser annealing, we have investigated the electronic structure at high temperature for the Si (111) surface, which changes from 7x7 to 1x1 structure at ~830ÅC. At room temperature, three surface states were observed at ~0.2, ~0.8 and ~1.8 eV in UPS. With increasing the annealing temperature, the surface state at ~0.8 eV disappears. The temperature dependence of the spectral features obtained in our measurements is essentially identical to that previously obtained by Yokotsuka et al. [2]. The Si 2p core level photoemission spectra with high energy resolution were also observed. Using a curve fitting analysis, Si 2p core level photoemission spectra were decomposed by a bulk and five surface components. With increasing the temperature more than ~830ÅC, the surface component at the lower binding energy, which originated from the rest atoms, retains constant. This result indicates that the surface period is changed without changing the local structure. In the conference, we discuss the temperature dependence and the laser induced effect (Surface photovoltage).

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Relation between Inelastic Scanning Tunneling Spectroscopy of adsorbates and their vibrational deexcitation: a theoretical study

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We present a Green Functions formalism that allows to study the excitation and deexcitation of adsorbates under STM operation, in a unified way [1,2]. With it, we have calculated the spatially resolved Inelastic Tunneling Spectroscopy image of acetylene molecules on a Cu(100) surface [2], in good agreement with experiments [3]. The same formalism allows us to obtain the vibrational lifetimes of the adsorbates when they relax via electron-hole pair mechanism. We find an approximate relation of proportionality between inelastic tunneling fraction due to a given mode in STS and its inverse lifetime in most cases, however exceptions to this occur due to the many orbital character of the tunneling process.

We have calculated both the 'IETS' and the 'vibrational lifetimes' for the concrete example of CO/Cu(100), obtaining values in agreement with experimentally measured inelastic fractions [4] in IETS, and with previous theoretical calculations of vibrational lifetimes [5]. The relation between the two phenomena is clarified.

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X-Ray Absorption Near Edge Structure Spectra at the K-Edge of Boron Atom in Sodium Borate Glasses and Crystals

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Sodium borate glasses of the system $x\text{Na}_2\text{O} - (100-x)\text{B}_2\text{O}_3$ ($x = 5-35$) have been prepared by melt quenching method and x-ray absorption near edge structure (XANES) spectra at the boron K-edge in these glasses, amorphous B_2O_3 , crystalline NaBO_2 and $\text{Na}_2\text{B}_4\text{O}_7$ have been measured using the total electron yield method over the range of 180-230 eV with a compact synchrotron radiation source at Ritsumeikan University. Boron K-edge XANES spectra have a prominent peak at 193 eV and some broad absorption bands in the range 195-210 eV. These spectral features are very similar to those of glasses in the systems $\text{Na}_2\text{O} - \text{B}_2\text{O}_3 - \text{SiO}_2$ and $\text{K}_2\text{O} - \text{B}_2\text{O}_3 - \text{SiO}_2$ [1]. The prominent peak at 193 eV is assigned to the transition of B1s to $p^*\tilde{1}^*$ in the sp^2 hybridization and the broad absorption bands are attributed to the transition of B1s to $p^*\tilde{*}$ in both sp^2 and sp^3 hybridizations. The center of the broad absorption bands shifts to lower energy side with increasing the Na_2O content, which means that the number of three-fold boron atom (B^3) coordinated by three oxygen atoms decreases, but the number of four-fold boron atom (B^4) coordinated tetrahedrally by four oxygen atoms increases. The XANES spectra are deconvoluted into the three components of B^3 , B^4 , and multiple scattering resonance to obtain the existence ratio of B^4 in the glasses. The B^4 ratio is in good agreement with the reported values using ^{11}B NMR[2] for the glasses with high Na_2O content.

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Surface Electronic Structure of Lanthanide Metals from Soft X-Ray Emission

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We report on the separate observation of $O_3(5p_{3/2})$ soft X-ray emission (SXE) from bulk and top-layer surface atoms of well-ordered La, Sm and Lu (0001) metal films - grown on W(110). Spectral intensity distribution of the O_3 SXE band reflects the s- and d-like valence density of states (sd-DOS). With the facilities of valence band photoemission (PE) such information can in principle not be derived. To achieve surface sensitivity of usually bulk-sensitive SXE we lowered the primary electron energy E_0 from about 200 eV down to close above the 5p ionization threshold of the respective lanthanide metals. With the reduction of E_0 we expected to reduce the core-hole creation depth leading to increasing relative contributions of SXE created at surface atoms, with respect to SXE from bulk atoms. A suppression of satellite emission with decreasing E_0 seems to be the most probable reasons of spectral shape change - in addition to the change of surface SXE contribution. The experiments were performed with a spectrometer providing an optical energy resolution of about 200 .. 600 meV (depending on photon energy) and a base pressure in the experimental chamber in the low 10-11 mbar range [1]. Sample preparation procedure was described in [2]. O_3 SXE bands measured under relatively high E_0 (200eV) could have been safely assigned to SXE from bulk atoms. Positive differences (in spectral intensity) between the 200eV-spectra and the other spectra, recorded under lower E_0 , were associated to surface SXE and negative difference to satellite emissions. It was found that all measured SXE spectra are precisely reproduced by a linear combination of the 3 obtained subspectra. Noticeable satellite emission was just detected in the case of Sm O_3 SXE. The positions of the spectral intensity maximum of the surface spectra are shifted relative to the bulk ones by +0.25 eV in La, -1.45 eV in Sm and +0.6 eV in Lu, in good correspondence with the 5p surface core-level shifts (SCS) determined by PE. All surface SXE spectra are much narrower than the bulk emission: by ~35% in La and Lu and by ~50% in Sm (FWHM) and they are unressembling with respect to the bulk spectra. The strong surface effect in Sm SXE was explained as a consequence of the well-known Sm metal surface valence transition. Using 5p SCS we combined surface and bulk sd-DOS into a common binding energy scale revealing that the bulk DOS completely overlaps the surface DOS.

The present results demonstrate new opportunities in the study of the surface phenomena by the means of SXE valence band spectroscopy.

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