

INVITED TALKS

RESONANT CORE LEVEL STUDIES OF MOLECULES AND CLUSTERS: ELECTRONIC STRUCTURE AND FEMTOSECOND DYNAMICS

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Core levels have some properties which make them highly interesting for the study of atomic matter: they are atomic-like and localized even in multi-atom systems such as molecules and solids, and core holes are very short lived. The first aspect means that core level spectroscopy can give information about not only which atoms are present in the sample, but also the number and type of different sites which these occupy, and how the local electronic structure depends on the type of site. The second aspect, the short life time of core holes, enables studies of the possible dynamic development occurring during the core hole life time, i.e. a few femtoseconds or even shorter. In this talk I will give some examples of how both these properties in combination with synchrotron radiation of well defined energy and polarization can be used to study molecules and clusters:

When molecules are core-excited to a repulsive state, dissociation may occur on the same time scale as the Auger decay, i.e. a few femtoseconds. The velocity of the core-excited fragment causes shifts in the measured kinetic energy of the Auger electrons, a phenomenon known as the Auger Doppler effect [1,2]. I will discuss what can be learnt about the dynamics of the femtosecond dissociation from the experimentally observed Doppler splitting, using simple models.

Clusters consist of a small number of atoms or molecules, bridging the gap between the isolated atom and the infinite solid. A large and size-dependent fraction of the atoms in a cluster is located at the surface, which results in size-dependent physical and chemical properties. Connected to this are changes in the electronic and geometric structures. I will present new resonant Auger and photoemission measurements of free clusters, which demonstrate some possibilities offered by site-selective core excitation in these systems.

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CONTINUUM STRUCTURES IN MOLECULAR PHOTOIONIZATION

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I will present two examples of our work on molecular core level photoionization, which both show the influence of the molecular symmetry on the photoionization continuum.

In the N 1s photoionization of nitrogen, we have resolved the splitting between the singly charged N_2^+ ($1s^{-1}$) states of g and u molecular symmetry. By following the ratio of the two symmetry components with photon energy we were able to demonstrate that the continuum wavefunction in the N 1s shape resonance region of N_2 is dominated by a σ_u^* symmetry contribution.

Chiral molecules exist in two different conformations called enantiomers, which are mirror images of each other. A lot of biomolecules are chiral, with a natural preference for one or the other enantiomer. From symmetry considerations, in dipole photoionization of chiral molecules with circularly polarized light a forward/backward asymmetry of the angularly resolved intensity is possible even if the molecules are not oriented. We have observed this asymmetry in the C 1s photoionization of the C=O carbon in camphor. Asymmetry values of up to 0.05 are observed, which change sign when the enantiomer of opposite handedness is probed. Since the strength of the effect is photon energy dependent, and since similar effects have been found in the valence photoionization of bromocamphor and camphor at similar kinetic energies [1], we suggest that this is an interference effect imposed by the surroundings on the continuum wavefunction.

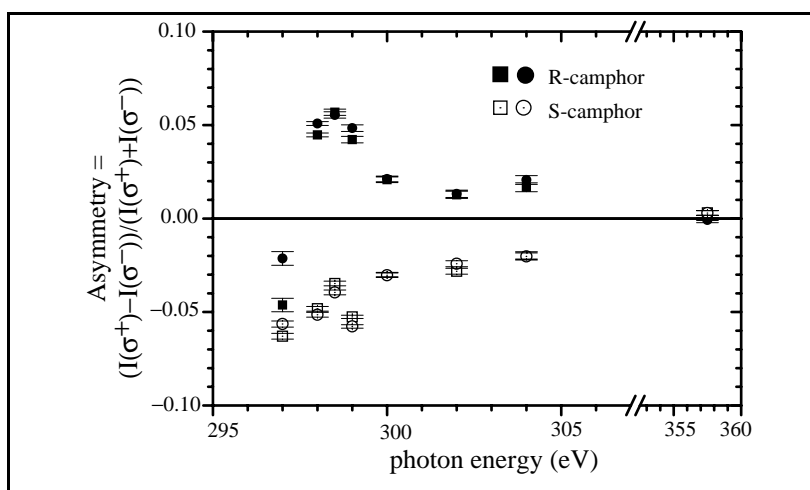


Figure 1: Asymmetry of the carbonyl C 1s photoelectron intensity of both camphor enantiomers, measured in a forward scattering geometry under an angle of 54.7° with respect to the beam propagation direction.

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NUCLEAR MOTION, SYMMETRY BREAKING, AND DISSOCIATION DYNAMICS OF CORE-EXCITED POLYATOMIC MOLECULES

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Lifetimes of the core-excited states in light, small molecules are ~ 10 fs and thus nuclear motions in the molecular core-excited states proceed before the Auger decay. Asymmetric nuclear motions in the core-excited states cause structural changes and often play a key role in dynamics of ionic fragmentation after the Auger decay. In the present paper, I will report current status of our research program on nuclear dynamics in the core-excited polyatomic molecules.

Carbon dioxide (CO_2) is a linear molecule in the ground state. When the C $1s$ core electron is excited to the lowest unoccupied molecular orbital $2\pi_u$, the doubly degenerate $1s^{-1} 2\pi_u$ states split into Renner-Teller pair states. The lower-energy state (A_1 in C_{2v}) has a bent stable geometry while the other (B_1 in C_{2v}) has a linear stable geometry. By means of the triple-ion coincidence momentum imaging technique we could probe these different geometries of the Renner-Teller pair states and determine the ratios of the excitation cross sections to the A_1 and B_1 states. Using the ratios thus obtained, we could reconstruct symmetry-resolved absorption spectra for the A_1 and B_1 excitations from the angle-resolved energetic ion yield spectra recorded at very high resolution ($E/\Delta E > 12,000$). Progressions of symmetric stretching vibrations are observed for both excitations, whereas contributions from the unresolved bending vibrations are significant only in the A_1 excitation spectrum.

The O $1s$ excitation in oxygen-contained molecules, such as CO_2 and H_2O , often exhibits broad peak structures that consist of overlap of the vibrational components which are not resolved owing to the lifetime width (~ 150 meV) broader than the vibrational spacing. We have investigated nuclear motions in the O $1s$ excited states in CO_2 and H_2O using resonant Auger spectroscopy. The measurements were carried out under the sub-natural-width conditions where the overall linewidths were much smaller than the lifetime linewidths of the core-excited states. It turned out that both stretching and bending vibrations are caused in the O $1s^{-1} 2\pi_u$ state in CO_2 as well as in the O $1s^{-1} 2b_2$ state in H_2O .

The F $1s$ excitation of highly-symmetric molecules CF_4 and SiF_4 exhibits anisotropic fragmentation. Symmetry breaking induced by asymmetric vibrations in the core-excited states and its effect in the following anisotropic fragmentation will be discussed.

The experiments reported here were carried out on beamline 27SU at SPring-8 in Japan with the approval of the SPring-8 program advisory committee, in collaboration with many colleagues whom I cannot list up all here. I thank to my colleagues for fruitful collaborations and staff at SPring-8 for invaluable help.

Comparative very-high-resolution VUV spectroscopy: laser spectroscopy of O₂

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Despite their importance in the photochemistry of the terrestrial atmosphere [1], and many experimental studies, previous knowledge of the Schumann-Runge (SR) bands of O₂, $B^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ (1750–2050 Å) has been limited by poor experimental resolution. In addition, our understanding of the SR spectrum is incomplete, many rovibrational transitions in the perturbed region of the spectrum [$B(v > 15)$] remaining unassigned.

We present new very-high-resolution measurements of the O₂ photoabsorption cross section in the SR bands. Tunable, narrow-bandwidth background VUV radiation for the measurements ($\sim 10^6$ resolving power) was generated by the two-photon-resonant difference-frequency four-wave mixing in Xe of excimer-pumped dye-laser radiation [2]. With the aid of these measurements, new rovibrational analyses of the heavily-perturbed spectral region have led to new insight into the molecular structure of O₂.

These VUV laser-spectroscopic (VUVLS) measurements are shown to compare favourably with results from two other very-high-resolution experimental techniques [3], namely laser-induced fluorescence spectroscopy (LIFS), and Fourier-transform spectroscopy (FTS), the latter performed using a synchrotron source.

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Spectroscopy and dynamics in the photoionization of neon

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A series of experiments devoted to the study of the dynamics and spectroscopy of photoexcitation and photoionization of the neon atom has been performed at the Gas Phase Photoemission beam-line of Elettra (Trieste) by the research team of the beam line and in collaboration with external users.

These experiments, which extend over a broad energy range from the region of the Ne 2s excitations/ionisation (≈ 40 eV) [1] up to and above the Ne 1s ionisation threshold (> 900 eV) [2,3] have addressed fundamental topics in atomic physics :

- i) the competition between radiative/non radiative decay of the Ne $2s^{-1}nl$ excited states [1];
- ii) the interference phenomena observed in resonant photo-double ionisation due to coherence and correlation effects[4,5];
- iii) the possibility to achieve a “complete” experiment in the study of the cascade Auger decay of inner shell excited states[6];
- iv) the spectroscopy and decay of inner shell doubly excited states[3].

On the other hand, the same experiments have allowed to exploit the resolving power, the broad energy range and the flux of the beam-line and the high efficiency of the multicoincidence end-station[7].

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SIMPLE METALS \Leftrightarrow SIMPLE CORE LEVELS ?

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Core level photoemission from simple metals is treated with the intention of firstly demonstrating what effects may be experimentally observed given the high resolution of today and secondly discussing our current understanding of the observed effects.

A number of examples of core level binding energy shifts are given. These include shifts of the surface and the near surface layers in Al and Be as well as shifts induced by alloying Al with other metals. It is demonstrated that such shifts may be calculated with very high precision by Density Functional Theory (DFT). The importance of such accurate calculations of binding energies for following e.g. the fine details of alloy formation is stressed. It is also demonstrated that inclusion of more subtle effects is necessary in order to give a full description of all the experimentally observed binding energy shifts.

The second part of the talk will concentrate on the core level lineshapes. Effects caused by excitations of vibrations in the core level photoemission process are illustrated by a number of examples. It is demonstrated that these effects may result in the occurrence of strong resolvable structure also in the case of bulk emission from a metal. E.g. for the case of Be, strong phonon replicas are produced in the 1s photoemission spectra [1] by this effect, as demonstrated in Figure 1. A much weaker coupling to phonons is found for 2p photoemission from Al, however, structure in the core level spectra is still produced. The necessity of a full understanding of these effects for the analysis of core level lineshapes of metals is stressed. Finally, the experimentally determined core hole lifetimes for Be and Al are shown to be in excellent agreement with the calculations by Almladh and Morales [2] if the core hole induced relaxation of the valence orbitals is included.

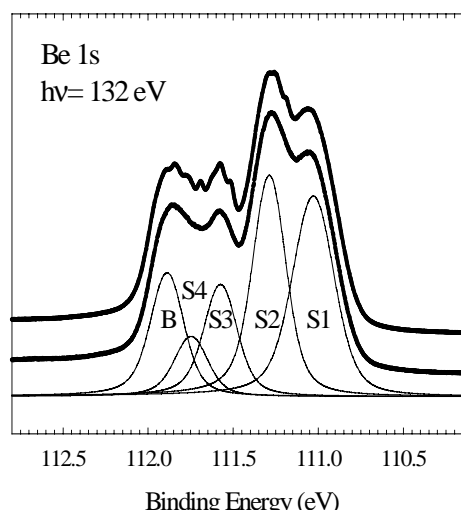


Figure 1: Be 1s core level spectra from Be(0001) measured with resolutions of ~ 70 meV (upper curve) and ~ 20 meV (lower curve).

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RECENT DEVELOPMENT IN SOFT X-RAY SPECTROSCOPY OF CORRELATED MATERIALS: HIGH RESOLUTION ABSORPTION AND BULK SENSITIVE PHOTOEMISSION

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Extremely high quality soft X-ray is supplied with high photon flux($>10^{11}$ photons/s) , high energy resolution($\hbar / \hbar >10^4$), high circular polarization($>98\%$) and low($<10^{-2}$) higher order light at the twin-helical undulator beam line BL25SU of SPring-8.¹⁾ A varied line spacing plane grating monochromator(VLSPGM) equipped with gratings of 600 and 1000/mm central groove density can cover the region from 0.22 to 2 keV by use of the fundamental radiation from the undulator. The total resolution of photoemission is better than 100 meV near 1 keV.

It is demonstrated that the mean free path of photoelectrons in correlated materials is much deviated from the so-called universal curve at low kinetic energies below few tens eV. Bulk sensitive photoemission spectra measured above a few hundreds eV are much different from the surface sensitive spectra measured slightly above or below 100 eV. The difference between the bulk and surface sensitive spectra in various Ce, Sm, Yb, as well as transition metal compounds are demonstrated.^{2,3,4)} The applicability of bulk sensitive angle resolved photoemission spectroscopy to correlated materials and its limitation will also be discussed.

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Observation of low dimensional behaviour of electronic structures in one-dimensional In-rows of clean InAs(001)4x2-c(8x2) surface.

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The breakdown of the independent-electron approximation is a fingerprint of a new class of materials: layered high- T_c superconductors and one- two- dimensional (1D, 2D) systems, where the quantum confinement constricts the electrons to deviate from *quasiparticle* behaviour. In strongly correlated fermions, in addition to the *interactions* between the electrons, which are very strong in 3D metals, we have also *correlations* between the electrons in 1D and 2D systems. In these systems, the dimension of the electron gas plays an important role in order to explain the behaviour of electronic structures and the Fermi surface. Photoemission spectra of 1D, 2D systems, actually constitute one of the most interesting issues of solid-state physics.

We report the investigation of clean In-terminated InAs(001)(4x2)-c(8x2) surface by high-resolution valence band (VB) spectroscopy. The measurements were performed in ultra high vacuum conditions (base pressure 8×10^{-11} mbar) using the synchrotron radiation on the VUV beamline of ELETTRA (Trieste). Very-ordered clean In-terminated InAs(001) 4x2-c(8x2) surface was recently examined by LEED, STM, High-resolution core-levels, and VB Angular resolved photoemission spectroscopies (ARUPS) [1]. Thanks to a rigorous conservation law of the photoelectron's momentum parallel to the surface during the emission, ARUPS is a particularly powerful probe of 2D and 1D electronic structures.

First of all, the determination of 1D and 2D, as well as the emission at the Fermi level requires the best possible samples and highest energy resolution. As demonstrated in ref. [2], by LEED and STM analysis, a good quality of untwinned In-rich InAs(001) 4x2-c8x2 reconstructed surface where the long-order range, indispensable to study low-dimensional electronic structures, is obtained after Ion Bombardment Annealing (IBA) procedure. The brightness and sharpness of the LEED pattern spots, and the low background intensity indicate that the surface is highly ordered and smooth with a very large coherence length, while the filled-state ($U=-1.2$ V, $I=0.6$ nA) STM images collected at high resolution over an area of $100 \text{ \AA} \times 100 \text{ \AA}$, show very uniform and bright rows (In rows) along the [011] direction, of impressive coherence and narrow inter-row distance.

k-dispersion ARUPS measurements of parallel and perpendicular to the chain orientations, exploiting the polarisation plane of the Electric field of synchrotron radiation, were collected on highly ordered In-rich InAs(001) surface.

1D and 2D sharp electronic structures, probably, related to one-dimension nature of the In-rows, and to geometrical characteristic of the stripes allocated on the InAs substrate, have been discovered as a function of the surface reconstruction. Strong light polarisation and photon energies dependence on these electronic structures were observed.

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FLUORESCENCE FROM DOUBLY EXCITED STATES OF HELIUM

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Fluorescence yield measurements demonstrate that the radiative decay channel dominates over autoionization for most of the doubly excited states of helium below the $N=2$ threshold [1]. In the immediate vicinity of the threshold, pronounced relativistic effects are found: the data can be understood only if LS-coupling is abandoned. Using JK-coupling, the predictions of R-matrix multichannel quantum defect theory (MQDT) are in excellent agreement with the experimental results [2].

Pronounced static Stark effects are seen in the fluorescence yield spectrum already at field strengths of a few V/cm. An electric field dependence is seen not only for the higher Rydberg states, but through the whole spectrum below the $N=2$ threshold. Especially, we find a redistribution of intensity between the radiative and autoionization decay channels when singlet and triplet states are Stark shifted to anti-crossings, where the symmetry mixing is anomalously high. These data are discussed in terms of new R-matrix MQDT results [3].

Further opportunities to study electron correlation in this prototype two-electron system are suggested by these findings. We will briefly discuss what may be learned from analyzing the influence of external electric and magnetic fields in general. The relatively long lifetime of these states, set by the radiative decay channel, makes pump-probe experiments feasible. We will also discuss the potential of examining the angular distribution, and consider high-resolution spectroscopic studies of the fluorescence from selectively excited states.

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X-ray Raman scattering from low Z materials

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X-ray Raman scattering (XRS) from core electrons of low Z materials is analogous to soft x-ray absorption spectroscopy (XAS), as long as the momentum transfer Q is small compared with the radial extent of the wave function of the core electron, involved in the inelastic scattering process. While in XAS the incident photon energy has to be tuned to the absorption edge energy under consideration, in XRS this role is taken by the energy transfer, thus leaving a certain freedom in the choice of the incident photon energy. Consequently, XRS allows to perform soft x-ray absorption studies in the hard x-ray regime, with the advantage to probe bulk properties and study systems which are not compatible with an ultra-high vacuum environment, necessary in the soft x-ray regime. Moreover, by varying the momentum transfer Q , the electric dipole selection rule, defining the final state symmetry which can be reached in an absorption process, is relaxed and, for example, electric monopolar transitions become possible.

The present status, the limitations and future perspectives of the technique shall be illustrated by presenting several experiments, performed on the inelastic x-ray scattering beamlines at the ESRF. 1) A momentum transfer dependent study of the lithium K-edge in lithium metal, recorded with an energy resolution of 80 meV at 10 keV, which allowed to extract the threshold exponents α_0 and α_1 of the Mahan-Nozières-De Dominicis many body theory [1]. 2) A study around and above the oxygen 1s absorption edge in liquid water and ice I. Significant differences in the near-edge part of the edge could be revealed and the partial radial distribution function of oxygen in liquid water could be extracted [2]. 3) A study of the near-edge region of the carbon 1s edge in pure, 1D- and 2D polymerized C60 molecules which showed significant changes due to the breaking of the C double bonds and the 2+2 cycloaddition process [3].

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Core-Level Spectroscopy, Diffraction, and Holography: Recent Developments and Future Prospect

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Several emerging aspects of vuv/soft x-ray photoelectron spectroscopy, diffraction, and holography and related x-ray emission and scattering experiments making use of third-generation synchrotron radiation will be discussed:

- photoemission or x-ray emission excited by x-ray standing waves from synthetic multilayer substrates, which permits probing species at surfaces and at buried interfaces;
- measurements with electron spin resolution and/or variable light polarization for studying magnetic systems;
- multi-atom resonant photoemission, which holds promise of directly determining near-neighbor atomic identities and other bonding and magnetic properties in nanostructures or molecules [1];
- new approaches to photoelectron and x-ray fluorescence holography providing improved resolution and/or element sensitivity;
- extension of photoemission measurements into the multi-torr pressure regime [2].

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Nanocluster Properties Characterized using Soft X-ray Spectroscopies

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The scientific world is embracing all types of nanoscience and technology through the rapidly advancing work seen in the scientific community. Central to this work is the control of properties for novel nanostructured materials, and how to incorporate them into useful devices. At LLNL, we have used third generation synchrotron radiation from the Advanced Light Source, Berkeley to perform X-ray Absorption Spectroscopy (XAS), Photoelectron Spectroscopy (PES), and Soft X-ray Fluorescence (SXF) experiments on a variety of nanostructured materials in order to better understand the properties of these novel compounds. The reduced dimensional materials characterized include diamond, Si,⁽¹⁾ and Ge nanoclusters ranging in size from 1 – 12 nm. In each case we have exploited the element selectivity of the soft x-ray methods to probe the electronic structure, bonding, and morphology of these materials as a function of particle size. In particular, we use soft x-ray probes to determine band-shift and surface effects in our nanocluster samples. For many of these material systems, knowledge of band gap widening with quantum confinement, band alignment, and surface effects is critical to rational design and utilization of these novel materials in diverse applications.

This work was supported by the Division of Materials Sciences, Office of Basic Energy Science, and performed under the auspices of the U. S. DOE by LLNL under contract No. W-7405-ENG-48, and at the ALS, LBNL under Contract No. DE-AC03-76SF00098. N.Franco is supported by the Spanish Education and Culture Office under contract PF-98-33501134. C. Bostedt is supported by the German Academic Exchange Service DAAD.

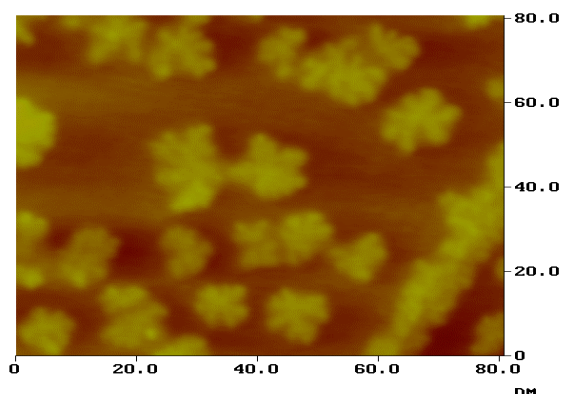


Figure 1: AFM image of Si nanoclusters on graphite surface

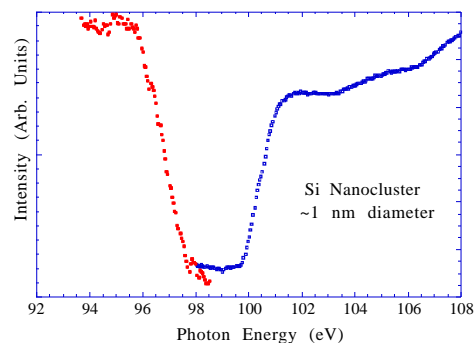


Figure 2: Band gap opening for 1 nm Si clusters as measured by Soft X-Ray spectroscopies

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ANGLE-SCANNED PHOTOEMISSION ON SWITCHABLE MIRRORS

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Yttrium can be loaded with hydrogen causing dramatic structural and electronic changes to the host lattice. In particular, shiny, metallic dihydride films become transparent semiconductors in the trihydride phase. [1] We report on the *in situ* preparation and characterisation (Fig. 1) of clean, single-crystalline YH_x films ($0 \leq x \leq 2.9$). [2] Angle-scanned ultraviolet and soft x-ray photoemission data will be presented. Direct Y dihydride growth, i.e., Y evaporation under H_2 partial pressure on W(110), is the most convenient starting point for the preparation of clean single-crystalline Y hydride films with H concentrations from the “clean metal” ($x \sim 0$) up to the lower boundary of the pure trihydride phase ($x \sim 2.9$). Upon annealing Y dihydride films the desired x can be adjusted within the α -phase or the $(\alpha + \beta)$ two-phase regime. On the other hand, the Y dihydride can be transformed into the trihydride with an ultra-high vacuum compatible hydrogenation cell within a few minutes. Direct Y dihydride growth on W(110) results in two equally populated fcc(111) domains rotated by 180° with respect to each other. Pure Y and the trihydride form an hcp(0001) oriented lattice. A detailed analysis of forward focusing maxima (Fig. 1) allows for *in situ* H concentration estimation. Ultraviolet photoemission data reveal a gap at normal emission upon the phase transformation from Y dihydride to Y trihydride.

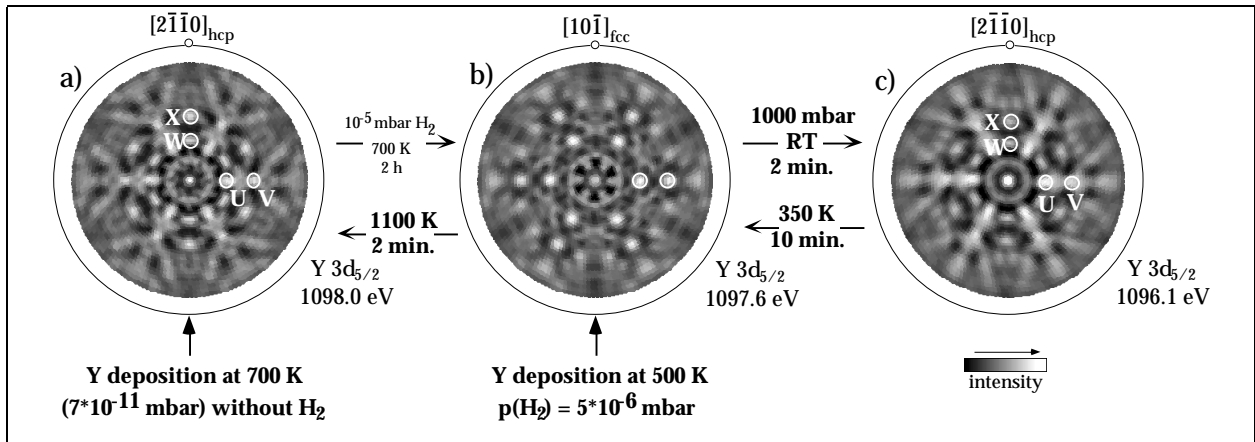


Figure 1: Photoelectron diffraction experiments on differently prepared thin YH_x films. The characteristic differences in the images allow to distinguish between the fcc and the hcp phase, to judge lattice expansion and to estimate the concentration x .

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Novel Zone Plate Doublet for Differential Interference Contrast Microscopy Fabricated by means of Electron Beam Lithography

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Electron beam lithography was used to fabricate for the first time a novel X-ray optical element to perform X-ray imaging in differential interferential contrast (DIC) with sub-mm optical resolution. With a proper fabrication process it was possible to generate a doublet of zone plates, on both faces of a 2 mm thick silicon nitrate membrane which were displaced by 100 nm within their optical resolution. The use of ZP doublets for visible light interferometry ¹, metrology and optical sensing dates back to a few decades ago. The principle of using ZP doublets for interferometry with multi-keV X-rays was described only recently ². We demonstrate similar to differential imaging in visible light microscopy a drastically increase in image contrast for low absorbing specimen using both a full-field imaging x-ray microscope and a scanning X-ray microscope at a photon energy of 4 keV.

This contribution demonstrates the feasibility of X-ray DIC generated by a doublet of two zone plates fabricated by electron beam lithography.

The ZPs are, transversely to the optical axis, displaced of 100 nm, that is, within their optical resolution that is about 200 nm. This means that also the Airy disks of their focal spots are displaced within the optical resolution. Thus, the wavefront division by the ZP doublet can be used for differential imaging with X-rays intrinsically taking advantage of the high optical resolution reachable with ZPs.

The fabrication process consists of several exposures/deposition of the alignment system and the double side fabricated (doublet) zone plates. The good reproducibility of the fabrication indicates the possibility of fabricating zone plate doublet with resolution around 50 nm. Our efforts are already pointed to that direction. The doublet was optically tested at the microscope ID21 at European synchrotron radiation facility (ESRF) in Grenoble.

We can anticipate the following advantages of using a ZP doublet for X-ray DIC imaging: (1) The alignment of the ZP doublet is comparable uncomplicated and similar to that of a single ZP. (2) This DIC technique is usable for both complementary X-ray imaging techniques, i. e. the full-field imaging and the scanning type. (3) The image acquisition does not require data processing and images are on-line visible. 4) The doublet can be fabricate for a wide energy range: from soft to hard X-rays.

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Dynamical effects at the order-disorder reversible phase transitions of Sn and Pb on the Ge and Si(111) surfaces

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Tin and lead adsorbed at one third of a monolayer coverage on the (111) surfaces of germanium and silicon display a reversible two-dimensional phase transition from a metallic $\sqrt{3}\times\sqrt{3}$ reconstruction at room temperature, to a 3×3 one at low temperatures which presents either a metallic or a semiconducting character.

The nature of this transition, which is very unusual in the general context of the initial formation of metal/semiconductor interfaces, has been strongly debated and has remained a puzzle until recently. All kinds of surface science experiments, especially variable temperature Scanning Tunneling Microscopy and state-of-the-art Synchrotron Radiation investigations, as well as the most advanced ab-initio theoretical calculations and molecular dynamics simulations have been used by several teams to explore the atomic and electronic structures of each phase and to elucidate the origin of their mutual transformations.

Different driving mechanisms have been proposed as potential candidates at the origin of these reversible, low temperature, phase transitions, namely, genuine surface charge density waves, bond density waves, Peierls-like transitions, dynamical fluctuations in the adatom vertical positions and the softening of a surface phonon. The role played by intrinsic defects and the effect of phase mixture have been also emphasized.

These various mechanisms will be reviewed and discussed in the light of novel structural results obtained by synchrotron radiation surface x-ray diffraction for both phases that demonstrate the dynamical origin of the $\sqrt{3}\times\sqrt{3}$ phase and the order-disorder nature of the phase transition [1].

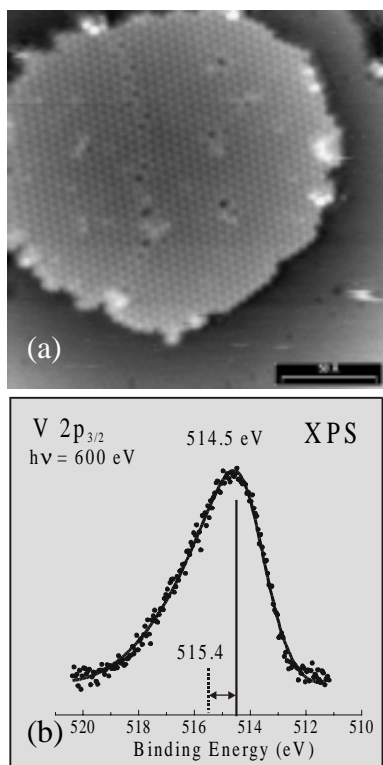
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High-resolution core level spectroscopy of „inverse catalyst“ surfaces: Probing the metal-oxide interface

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Metal single crystal surfaces decorated with nanometer size oxide island structures provide interesting model systems to study the physical and chemical properties of the metal-oxide interface. In view of their complementary nature with respect to real supported catalyst systems, namely metal particles on an oxide support, these systems may be regarded as „inverse or inverted catalysts“. Here we discuss the physico-chemical properties of two „inverse catalyst“ model systems: vanadium oxides on a Pd(111) surface and cerium oxides on Rh(111), prepared in-situ by reactive evaporation of the respective metals. The oxidation states and stoichiometries of the oxide layers have been established by X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure spectroscopy (NEXAFS), whereas the structure and morphology of the oxide particles have been characterised by scanning tunneling microscopy (STM). Figure 1(a) shows a topographic STM image of a typical vanadium oxide/Pd(111) inverse catalyst surface. The surface at 0.25 monolayer (ML) oxide coverage displays island structures of a well-ordered (2x2) oxide phase, which has been identified as a particular interface-stabilised V_2O_3 layer [1]. Its V 2p core level signature is shifted by ~ 1 eV with respect to bulk-type V_2O_3 due to the proximity of the Pd interface (Fig. 1b). The growth of V-oxides on Pd(111) is distinguished by a complex, coverage-dependent structural pattern with varying oxide stoichiometries. In contrast, Ce-oxides on Rh(111) grow as a mixture of Ce^{3+}/Ce^{4+} oxides at low coverages (<1 ML) and form CeO_2 in thicker layers.



The chemical reactivity of the „inverse catalyst“ surfaces has been gauged by studying the adsorption of probe molecules such as CO and ethylene. In the search for catalytically active sites at the metal-oxide phase boundary high-resolution XPS of adsorbate and metal surface core levels has been used to determine possible differences of adsorption sites of molecules on the oxide-decorated surfaces as compared to the clean metal surfaces. A change of the site distribution of adsorbed CO [2,3] on V-oxide/Pd(111) surfaces and different C_2H_4 species will be discussed.

Fig.1: (a) STM image of 0.25 ML V-oxide island structures on Pd(111); (b) XPS spectrum of (a)

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Electrocatalysis at Pt/YSZ Interfaces

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Large electrocatalytic effects have been observed with porous Pt electrodes deposited on solid electrolytes. To investigate the mechanistic basis of this so-called NEMCA effect (= Non-Faradaic Electrochemical Modification of Catalytic Activity) we constructed planar model systems for use in UHV. Scanning photoelectron microscopy (SPEM) has been employed to study the processes at the interface between the oxygen ion conducting solid electrolyte YSZ (= yttrium stabilized zirconia) and a microstructured 500 Å thick Pt film on top of the YSZ when electrical potentials are applied. An electrochemically induced oxygen spillover onto the Pt surface has been observed upon electrochemical pumping with a positive potential applied to the Pt film. With negative potentials the spreading of a reduction front is seen which reduces the surface zirconia to metallic Zr. It is shown that spectromicroscopy is crucial for identifying the surface changes in such complex systems.

SINGLE PASS FREE ELECTRON LASERS FOR SHORT WAVELENGTHS: FROM PROOF-OF-PRINCIPLE EXPERIMENTS TO A USER FACILITY

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Proof-of-principles experiments demonstrating high gain of single-pass free electron lasers (FELs) at wavelengths of 12 μm [1], 530 nm [2], and around 100 nm [3] have recently been reported by research teams at Los Alamos National Laboratory, Argonne National Laboratory, and Deutsches Elektronensynchrotron DESY, respectively. These novel devices are based on the concept of self-amplified spontaneous emission (SASE) proposed in the early 1980s, allowing very large gain up to saturation in a single pass through a long periodic magnetic structure. Since no optical components are required, it is believed that SASE can be used to produce intense, sub-picosecond laser pulses for a very wide, continuous range of wavelengths down to approximately 0.1 nm.

The results at DESY and the other laboratories are in agreement with theory and indicate that SASE FELs will soon become available for experiments in the VUV and soft X-ray region. The FEL at the TESLA Test Facility at DESY is currently in a test and development phase. In parallel extensive work has started on an energy upgrade of the accelerator and the FEL as well as on instrumentation for the experimental area in order to provide radiation pulses up to 200 eV photon energy for user experiments in the next development stage. This contribution will present the current status of the FEL project at DESY and the program towards a VUV/soft X-ray user facility.

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SCIENTIFIC OPPORTUNITIES WITH THE PROPOSED LCLS AT STANFORD

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Efforts are now under way to develop radiation sources that combine the unique characteristics of lasers (e.g. high peak brilliance, full coherence, femtosecond time-structure) and synchrotron radiation (e.g. high average brilliance, full tunability and variable polarization into the hard x-ray regime). The motivation is the novel scientific opportunities as will be demonstrated in this talk by the scientific case made for the proposed Linac Coherent Light Source (LCLS) at Stanford. The source is based on the SASE (self-amplified spontaneous emission) concept for the spectral region 1.5-0.15 nm. The unprecedented characteristics of this source will open up a number of new research areas. The time-structure will make it possible to study structural dynamics in the femtosecond scale, i.e. when chemical bonds are formed or broken. With the high intensity of the x-ray femtosecond pulse the structure of non-crystalline materials, including biomolecular fragments and nanostructures, can be determined and (ultimately) single biomolecules can be imaged. The LCLS radiation can be used to create and probe warm dense matter, of importance in laser plasma production, inertial fusion and astrophysics. Within atomic and molecular physics it will be possible to study multiple core-hole formation and non-linear x-ray interactions. The length/time-scales can be extended to study a broad range of phenomena in condensed and soft matter physics, e.g. nanoscale dynamics related to structural relaxation in polymers, structural phase transitions and domain switching in magnetic materials. The talk will also address future research opportunities when the LCLS characteristics have been further refined.

SASE FEL – toward VUV and X-ray

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Recent remarkable advances in the electron source, linac and undulator technologies lay the groundwork for a new type of radiation source – the SASE FEL. This source exceeds by many orders of magnitude all existing sources in the tunability range, inverse pulse length, and peak brilliance. Its unique properties will open opportunities for novel experiments in many scientific areas.

Several SASE FELs are operational now and several others, on a much larger scale, are planned. Results of first experiments with a SASE FEL show good agreement with the theory of these sources that has been developed over the last two decades. Also, the recent success in reaching saturation mode [1] makes it possible to move toward the very first use of the SASE FEL for application purposes.

In this paper the status of SASE FEL projects and recent experimental results will be presented. Also near-future applications experiments will be discussed.

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CONTROL OF ATOMS AND MOLECULES USING SHAPED PULSES

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During the past decade, there has been a revolution in the field of ultrafast science. Visible light pulses of only a few optical cycles in duration can now be generated from a simple laser, and their shape in time can be manipulated using new optical waveform generators.[1] Using adaptive feedback control algorithms, we can "teach" a laser to generate an optimally-shaped waveform to enhance a quantum process. This allows us for example to control the response of an atom to light by shaping the wavefunction of the radiating electron. Feedback control of quantum systems can selectively channel laser energy into a specific x-ray wavelength,[2,3] or selectively excite or suppress particular vibrations in molecules.

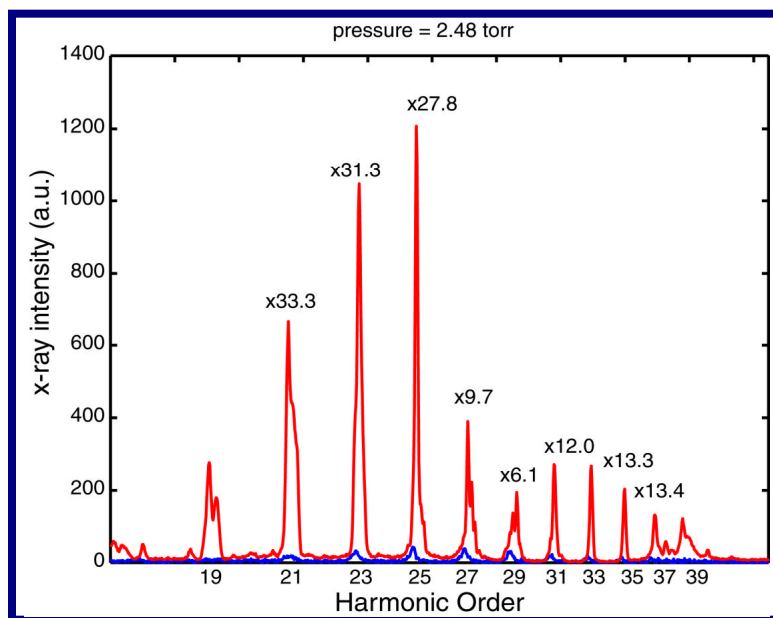


Figure 1: Optimization of a single harmonic peak in argon. Enhancements between 16 and 33 are observed for optimally shaped laser pulses, depending on the gas pressure, pulsewidth, etc.

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DIFFRACTION LIMITED FOURTH GENERATION VUV and X-RAY SOURCE BASED on a ACCELERATOR – RECUPERATOR

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Important tasks for the future generation of the VUV and X-ray sources is providing:

- full spatial coherence;
- as high as possible temporal coherence ($\Delta\lambda/\lambda < 10^{-4}$ without additional monochromatization);
- ultra short pulses of radiation (less 100 fs).

The new approach for the fourth generation synchrotron radiation (SR) source, based on using accelerator-recuperator, was proposed recently. The installation consists of the radiofrequency (RF) one-pass or multipass accelerator and long undulators. After passing through the undulators the electron beam is decelerated in the same RF accelerating structure.

The main motivation of using accelerator-recuperator was to combine the advantages of storage ring (high reactive power in beam up to 1 – 10 Gw, low radiation hazard) and linac (normalized emittance and energy spread can be conserved). The time of the acceleration in an accelerator-recuperator is small in comparison with the radiation damping time in a storage ring (factor 100 – 10 000) due to diffusion processes (quantum fluctuation of the SR in bending magnets, intra beam scattering) can not “spoil” emittance and energy spread.

In this talk diffraction limited VUV – SXR and X-ray SR source based on accelerator-recuperator with low emittance ($\epsilon_x \sim 10^{-11}$ mrad) and energy spread ($s_{E/E} \sim 10^{-4}$) on energy 3 ÷ 6 GeV with brightness $3 \cdot 10^{23}$ ph/s/mm²/mrad²/ 0.1 % Bw is presented.

The very rough cost estimations indicate, that scale of the cost is the same as for the existing third generation facilities.

UV/VUV FREE ELECTRON LASER OSCILLATORS AND APPLICATIONS IN MATERIALS SCIENCE

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The operation of storage ring Free Electron Lasers (FELs) in the UV/VUV region has recently experienced a significant progress, thus offering unprecedented research opportunities to the scientific community.

In particular, when used in combination with synchrotron radiation for pump-probe experiments, UV FELs represent an ideal light source to probe the excited states of matter. This kind of two colour spectroscopy has been pioneered on the SuperACO storage ring at LURE (Orsay), in a series of experiments on silicon interfaces. Furthermore, as demonstrated by the European FEL project at Elettra, the possibility of operating at short wavelengths with extended tunability and high power makes FELs very interesting light sources *also per se*.

An overview will be given of these kinds of experiments, together with a description of the light sources and of their main distinctive features.

X-RAY SPECTROSCOPY OF METALS IN ENZYMES – SOFT OR HARD?

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About one third of enzymes contain metal centers [1]. X-ray spectroscopy is a powerful tool for studying the molecular, electronic, and magnetic structure of these sites. Although metals in proteins are dilute, with third generation synchrotron sources, there is sufficient photon flux to ‘see’ the metal centers in EXAFS, L-edge, XMCD, fluorescence, and RIXS experiments. We have examined the Ni-Fe site in hydrogenase [2] and the oxygen-evolving Mn complex of photosystem II [3]. We will present L-edge, XMCD, and RIXS data addressing the metal electronic structure under different conditions.

Metalloproteins are frequently radiation and vacuum sensitive, and maintaining sample integrity is critical for bioinorganic x-ray spectroscopy. Our attempts to improve detection efficiency with larger solid angle crystal analyzers, higher resolution superconducting detectors, lower sample temperatures, and higher magnetic fields will be presented. In this vein, we will try to quantitatively compare the relative merits of soft (L-edge) and hard x-ray (RIXS) experiments for elucidation of electronic structure.

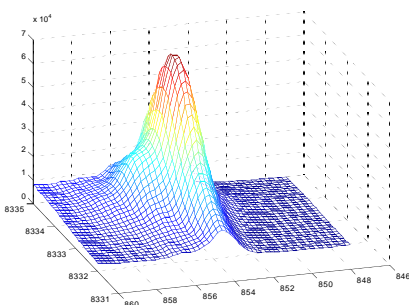


Figure 1: $2p_{3/2}3d^9$ final state structure for MnF_2 obtained by RIXS spectroscopy.

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Computed tomography of cryogenic cells

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By employing the natural absorption contrast of organic matter in water at 0.5 keV photon energy, X-ray microscopy has resolved 30 nm structures in animal cells. To protect the cells from radiation damage caused by x-rays, imaging of the samples was performed at cryogenic temperatures, which makes it possible to take multiple images of a single cell [1]. Due to the small numerical aperture of zone plates, x-ray objectives have a depth of focus on the order of several microns. By treating the X-ray microscopic images as projections of the sample absorption, computed tomography (CT) can be performed, as was previously shown using a scanning X-ray microscope [2]. Since frozen-hydrated cells are resistant to radiation damage, this approach has also been used to reconstruct frozen-hydrated algae using a full-field X-ray microscope [3]. We show here that this approach can also be used to obtain 3-D information about the location of proteins in cells.

To localize proteins in cells, immunolabeling with strongly X-ray absorbing nanoparticles was performed [4,5]. In this report, we describe the new tomography apparatus developed for the X-ray microscope XM-1 in Berkeley. Using this approach, we have combined immunolabeling techniques with tomographic imaging of frozen cells to detect protein distributions in all three dimensions inside of cells. As a first example, the distribution of the nuclear protein, male specific lethal 1 (MSL-1) in the *Drosophila melanogaster* cell was studied. Fig. 1 shows one selected X-ray micrograph projection and three slices after the reconstruction, demonstrating that the combination of CT and immunolabeling reveals protein distributions inside of whole cells.

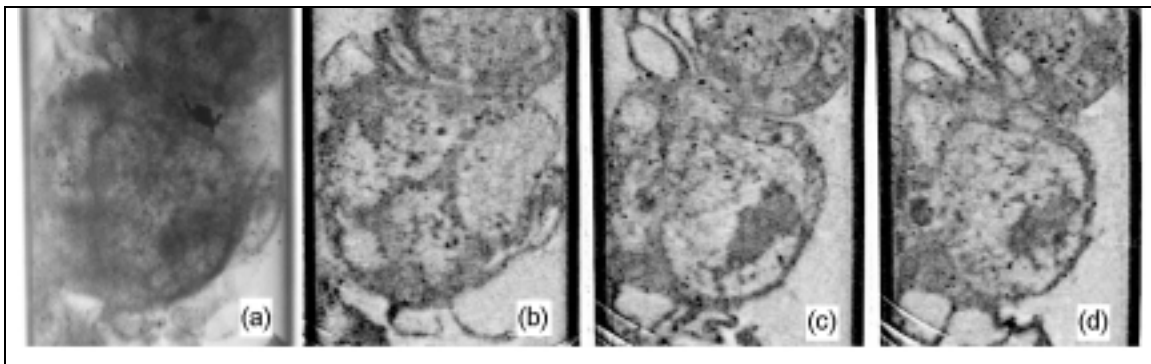


Figure 1: Panel (a) shows the first of the 48 X-ray microscope images of immunogold labeled *Drosophila melanogaster* cells constituting the tilt series, panels (b) - (d) show parallel 30 nm thick slices of the reconstructed linear absorption coefficient.

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SPECTROMICROSCOPY OF BIOLOGICAL AND ENVIRONMENTAL SYSTEMS AT STONY BROOK

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Scanning transmission x-ray microscopes can be used to investigate micrometer thick, hydrated specimens with spectroscopic sensitivity. At Stony Brook and Agere, we have developed zone plates with high spatial resolution and good working distance for these experiments. These zone plates are used in a new room temperature microscope [1] as well as in a cryo microscope [2] for studies of radiation-sensitive specimens.

One mode of spectromicroscopy involves the collection of image sequences over a variety of photon energies, allowing spectral investigations of ~50 nm regions [3]. The resulting data sets can also be analyzed using multivariate statistical analysis methods to uncover the relationship between different components of a specimen [4]. Use of these methods for studies of biological and environmental science specimens will be described.

We also briefly discuss 3D imaging methods. One approach is to use conventional tomographic methods; efforts in our group have centered on the imaging of samples cultured on flat substrates [5]. We also describe methods to go beyond the depth of focus limit of conventional tomography by using diffraction tomography, and methods to go beyond the resolution limit of lenses by using diffraction [6].

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SOFT X-RAY MICROSCOPY OF SOFT MATTER - HARD INFORMATION FROM TWO SOFTS

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Scanning transmission x-ray microscopy (STXM) and photoelectron emission microscopy (PEEM) provide quantitative chemical analyses at sub-100 nm spatial resolution. Contrast from near edge X-ray absorption (NEXAFS) features provides sensitive differentiation of species which have similar elemental composition but are chemically distinct [1]. The experimental techniques will be presented and the capabilities illustrated by examples from a number of recent studies: phase segregation in polyurethanes ([2] - see Fig. 1) and polymer blends [3], nano-structured polyurea capsules, water filtration membranes, and protein adsorption on polymers relating to biomaterial optimization. The presentation will emphasize the capability of adapting soft X-ray spectromicroscopy to a wide variety of samples, from wet systems, to submonolayer surface analysis, to in situ material transformations. I will describe the status of recent instrumental improvements including: improved accuracy via interferometric control of scan stages, 3 dimensional imaging, and development of new dedicated beamlines for X-ray microscopy at the Advanced Light Source and at the Canadian Light Source.

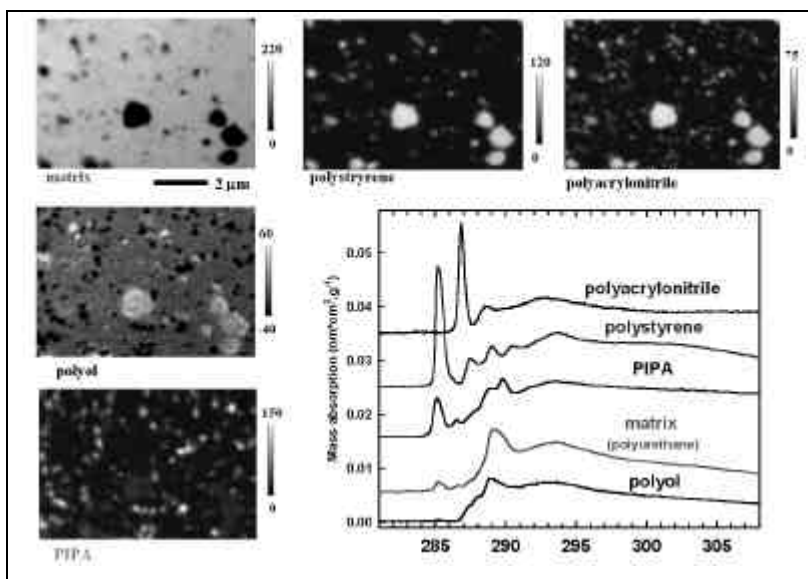


Figure 1: Quantitative component maps (nm^2/g^2) derived from fits of the indicated reference spectra to a C 1s STXM image sequence of a polyurethane containing filler-particles [2].

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Imaging Cells Using Soft X-ray Microscopy

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Understanding complex living systems requires a thorough comprehension of the function of individual cells within the organism. And to understand those cells, we must understand the functional units comprising them – the proteins and nucleic acids. Although extensive information about proteins can be obtained through the use of molecular biology, biochemistry, and crystallography, determining their function within cells requires sophisticated imaging techniques. Light microscope analyses of fluorescently tagged markers yield critical information about the location and behavior of proteins, as well as many details of protein-protein interactions, at the level of resolution of the light microscope (150-200 nm). Although better resolution can be obtained using electron microscopes, this approach requires elaborate, labor-intensive, cell processing procedures that potentially introduce artifacts. X-ray microscopy is an emerging biological imaging technique for the examination of intact, hydrated cells as well as the structural distribution of proteins in those cells. The resolution is 5-8 times better than that achieved by light microscopy and the information obtained from the image contrast is highly quantitative in nature. The ultrastructure of whole hydrated cells can be determined in rapidly frozen cells that have not been exposed to chemical fixatives, stains or contrast enhancement agents, as shown in Figure 1. In addition, the location of proteins can be determined at better than 50-nm resolution using immunocytochemistry techniques. Ultimately, the use of X-ray cryo-tomography facilitates three-dimensional reconstructions of cells as well as the precise localization of proteins in those cells. We are now in a position to conduct studies of specific proteins in living cells using light microscopy followed by determination of the ultrastructural localization of those proteins in the same cells using soft X-ray cryo-tomographic imaging techniques. Using these techniques, we are combining the power of protein-specific live cell fluorescent light microscopy with the unique high spatial resolution, whole cell imaging methods of X-ray microscopy for high-throughput analyses of protein function in cells.

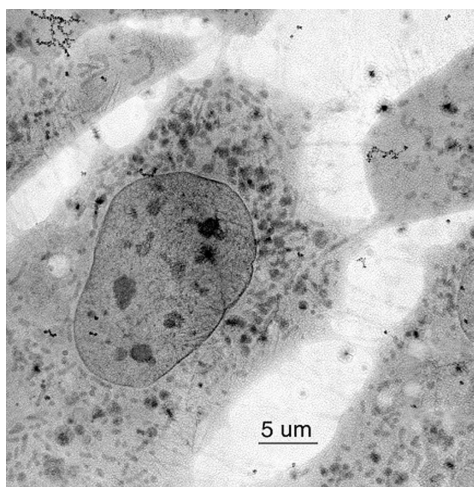


Figure 1. Cryo X-ray micrograph of whole, hydrated fibroblast (NIH-3T3) cell that was rapidly frozen using a blast of liquid nitrogen-cooled helium gas then examined in the soft x-ray microscope at the Advanced Light Source at Lawrence Berkeley National Laboratory. No chemical fixatives or contrast enhancement agents were used. The image was obtained using a photon energy of 517 eV ($\lambda = 2.4$ nm). X-ray magnification of 2400 x, 0.034 NA, 20 nm pixel size.

SPIN-RESOLVED SPECTRO-MICROSCOPY AT THE ATOMIC LEVEL

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Spin-split electronic states at surfaces of ferro- and antiferro-magnetic materials were studied by spin-resolved scanning tunneling spectroscopy combining extremely high spatial and energy resolution [1-3]. By using ferromagnetically or antiferromagnetically coated probe tips the spatial distribution of a particular spin component could be mapped, thereby allowing the direct real-space observation of magnetic domains and domain walls with subnanometer spatial resolution [4-6]. For antiferromagnetic samples, the different orientation of magnetic moments could even be made visible at the atomic level [7].

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Recent achievements in multi-keV X-ray microscopy

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X-ray microscopy techniques are emerging as powerful and complementary tools for sub-micron investigations. Soft X-ray microscopy traditionally offers the possibility to form direct images of thick hydrated biological material in near-native environment, at a spatial resolution well beyond that achievable with visible light microscopy. Natural contrast is available in the soft X-ray region, in the so-called “water-window”, due to the presence of absorption edges of the major constituents (C, N, O). Recent advances in manufacturing techniques have enlarged the accessible energy range of micro-focussing optics and offer new applications in a broad range of disciplines. For example, X-ray microscopy in the 1-10keV energy range is better suited to map trace elements in fluorescence yield, for 3D tomographic imaging and micro-diffraction.

This presentation will be biased towards sub-micron microscopy developed on the ID21 beamline at the ESRF. The main technical developments, involving new focussing lenses or novel phase contrast geometry, will be presented. Strengths and weaknesses of X-ray microscopy and spectro-microscopy techniques will be discussed and illustrated by examples in Biology, Materials Sciences and Geology.

Zone-plate-based Scanning Photoemission Microscopy at SRRC: Performance and Applications

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Adapting classical spectroscopic methods to the new challenge of studying nanomaterials, imaging techniques are the trendsetter in recent years. Among them is scanning photoemission microscopy (SPEM), where the sample surface is raster-scanned by a focused soft x-ray beam, collecting photoelectrons at each point with an electron energy analyzer. We developed such a station at SRRC in Taiwan [1,2], which is now fully in operation. The spatial resolution is close to the ultimate resolution of the zone plate of about 0.15 μm . A set of 16 photoelectron images at different kinetic energies can be simultaneously acquired in one single scan, which typically takes several minutes. Photonenergies between 250 eV and 800 eV can be fully utilized with easy alignment procedure for zone plate and OSA. Both, sample and zone plate can be transferred *in-situ* to attached chambers. The microanalysis capability of the SPEM station is demonstrated in Fig. 1, showing images of an area from a field effect transistor. In collaboration with different user groups, various experiments have been performed. We will present results on SiO_x patterns on Si_3N_4 substrate, carbon nanotubes, structured self-assembled monolayers and others. Strength and weakness of this microscope will be discussed.

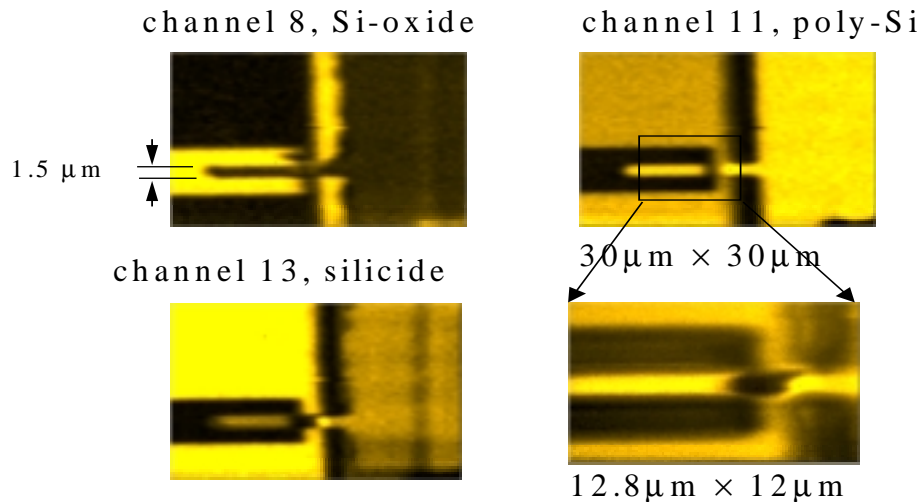


Fig 1: Si₂p SPEM image of a section between drain, gate and source of a FET transistor, illustrating the capability of spatial resolution and chemical state selection using the 16-channels of the analyzer for different kinetic energies. Enhanced intensities show areas of SiO₂, poly-Si and TiSi₂, respectively.

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Nanospectroscopy using aberration correction: the SMART project

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The ongoing miniaturization in technological devices and the progress in surface science demands instrumental methods for characterization on a length scale of only a few atomic distances. Up to now, the state-of-the-art instruments for that purpose are scanning tunneling (STM) and atomic force microscopes (AFM) which can investigate the surface, the film morphology, and the geometric structure even on an atomic scale. However, the disadvantages of scanning probe microscopes are (a) the relatively slow data acquisition due to serial detection and especially (b) the fact that they do not allow a sufficient spectroscopic, electronic, and chemical analysis.

Alternative techniques are the PEEM (photo electron emission microscope) or - even better - the LEEM (low energy electron microscope) combined with an imaging analyzer and a tunable high brilliance synchrotron radiation source. Besides the fast imaging (a few 10 ms time scale due to parallel detection) which allows the in situ and real time study of processes like growth, surface reaction, annealing, phase transitions, etc. these spectromicroscopes enable a comprehensive spectroscopic, electronic, and chemical analysis on a length scale corresponding to their lateral resolution. This lateral resolution has been pushed in the last decades, but is limited to 5 nm in LEEM and to about 10 to 20 nm in spectroscopic PEEM by the unavoidable spherical and chromatic aberrations.

The SMART project will overcome this limit by introducing an electrostatic mirror together with a highly symmetric magnetic beam splitter in an optimized optical design. This corrector compensates for the spherical and chromatic aberrations as recently demonstrated and will improve the lateral resolution by a factor of 10 and, at the same time, will increase the transmission by two to three orders of magnitude. When completed this instrument with a theoretical lateral resolution of 0.3 nm at an energy resolution of 100 meV is surely going to open new possibilities in surface science and investigations of nanoscaled technological devices.

The SMART project, involving 5 different research institutions in Germany, is funded by BMBF under contract 05 SL8 WW1 8.

Surface antiferromagnetic order of transition metal oxides studied by photoemission microscopy

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Antiferromagnetic oxides play an important role for exchange biasing of coupled magnetic multilayers. We present studies of AF oxide surfaces and magnetic films deposited on such surfaces by spatially resolved soft x-ray photoabsorption. Spatial resolution is achieved by measuring the total electron yield, which is a measure for the absorption, in an emission electron microscope. Contrast between antiferromagnetic domains occurs because of linear magnetic dichroism in the core level absorption edges. For cleaved NiO surfaces we find a bulklike termination of the magnetic structure at the surface [1,2]. The domain pattern shows stripes running along (100) directions in the surface, with typical widths on the scale of 10 μm . The width of antiferromagnetic walls between so-called T domains is found to be about 100 to 200 nm, depending on the type of wall [3]. A new type of S-like domain wall is observed within T domains, which can be described as a 180° rotation of the AF vector. Such walls are not fully compensated. For sputtered surfaces, the same domain pattern is observed as for cleaved ones, however, the magnetic structure is partially relaxed. For CoO films of more than 8 monolayers thickness, the films show antiferromagnetic order at room temperature. This shows a significant enhancement of the CoO Néel temperature. The domain pattern of ferromagnetic Co films deposited on NiO is governed by the underlying AF domain pattern, and shows collinear exchange coupling with the substrate.

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Magnetic X-Ray Absorption and Scattering

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The inner-shell absorption coefficient of circularly polarized x-rays depends in general on the projection of the local magnetic moment of the absorbing atom onto the photon propagation direction. A comparison of the dichroic effects (or XMCD = X-Ray Circular Magnetic Dichroism) for two spin-split initial states provides in addition an unique possibility to get insights into spin and orbital contributions separately by applying sum rules. Especially for the $L_{2,3}$ -absorption in (3,4,5)d transition elements and the $M_{4,5}$ -absorption in Rare Earths the magnetic contribution to the absorption can reach values of more than 20%. This results in a sensitivity to the average moments of less than 0.005 Bohr magnetons, a possibility to study magnetism of highly dilute systems and submonolayers with a coverage of only a few percent.

The dichroic absorption effects are closely related to the magnetic scattering amplitude via Cramers-Kronig relations. Thus a variety of methods, which use the strong magnetic part in resonant scattering, could be developed in the last years.

Nearly every spectroscopic, crystallographic and imaging technique, which can or has to use x-rays in the energy ranges, where the large dichroic effects occur, can be in principle be extended to its “magnetic counterpart” providing special and lateral resolution of magnetic structures.

In this contribution the physical origin of XMCD is outlined briefly in a simple picture and the physical origin of the sum rules and their limits are discussed. To demonstrate to complementarity of soft and hard x-ray studies in the magnetic absorption an scattering mode we present recent results on Pt-Co bi- and multilayers, which give unique insights into the modified Co and induced Pt magnetization profile, the role of the orbital momentum and the influence of the interface roughness on the magnetism of these systems.

We report on new developments in the field of magnetic imaging with circularly polarized x-rays as the magnetic transmission and photoemission microscopes. Recent results on modern magneto-optic storage media and artificial nanostructures are shown, where the magnetic domain pattern and their development in external magnetic fields have been quantitatively displayed in an element-specific manner with a lateral resolution of better than 30 nm.

Magnetic coupling in thin layers and superlattices investigated by resonant scattering of polarized soft x-rays

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Magnetism of surfaces and thin layers is a field of research that has taken full advantage of the possibilities offered by the polarized light delivered by new synchrotron radiation sources. The term *x-ray magnetic dichroism* was introduced by analogy with magneto-optical effects in the visible region. Magnetic scattering of x-rays was first demonstrated by de Bergevin and Brunel using a conventional x-ray source working on NiO. The availability, in the late eighties, of tunable wide band sources in this field has made *resonant* x-ray magnetic scattering (XRMS) experiments possible. Here one selects photon energies that correspond to the onset of core electron excitations. The first experiments were performed over the 4 - 10 keV energy range, in order to match Bragg diffraction conditions for typical lattice spacings. Soon after, the presence of large magnetic effects at core resonances located in the soft x-ray range (50-2000 eV) was demonstrated, especially in 3d transition metals and rare-earths. In particular, magneto-optics effects are stronger when the photon energy is tuned across an absorption edge that directly involves the *magnetic* orbitals. Experiments in the soft x-ray region are particularly suited to studying 3p or 2p → 3d resonances in transition metals and 4d or 3d → 4f resonances in rare-earths, as large magnetic signals are thus combined with the element selectivity of core excitations. Soft x-ray experiments have since been performed not only in the specular reflectivity mode but also under the angular conditions of Bragg diffraction from ordered multilayers of appropriate chemical modulation period.

Soft x-ray resonant magnetic scattering is characterized by some specific properties that make it an indispensable tool among the techniques that use spectroscopy to investigate magnetism. XRMS is naturally sensitive to structural properties. Relying on core resonant processes, it is also a spectroscopic tool, therefore element selective and sensitive to electronic properties. Using polarized x-rays, the scattered intensity contains information on the sample magnetic ordering, just as in any other dichroism technique. The interplay between incoming and outgoing photon polarization gives more flexibility in the choice of experimental geometries: both ferro- and antiferro-magnetic ordering, for instance, can be studied using either circularly or linearly polarized radiation. Finally, the photon-in / photon-out character of the XRMS process is very useful when working in presence of strong and/or time dependent fields.

Examples will be given of recent applications of resonant scattering of polarized x-rays to the study of the magnetic properties of thin layers and superlattices, including quantitative determination of element specific magnetic moments.

EXPLORING THE FERROMAGNETIC – ANTIFERROMAGNETIC INTERFACE USING PEEM

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The investigation of magnetic multilayers is an active research area which is driven by the interesting physics as well as by their application in the magnetic storage industry. The magnetic properties of these multilayers are often influenced by the arrangement of the spins near the interfaces. One example is the so-called exchange bias effect, which is the alignment of a ferromagnet (FM) by coupling it to an antiferromagnet (AFM). This effect is routinely used in the manufacturing of advanced magnetic recording heads and will be used in tomorrow's nonvolatile magnetic memory devices. Though the phenomenon of exchange bias was discovered in 1956 the origin of this technological important effect is still poorly understood. In particular information about the microscopic arrangement of the magnetic structure at the FM/AFM interface is missing which is largely due to the lack of techniques capable of determining the magnetic structure of thin antiferromagnetic films. Here we present results obtained with photoelectron emission microscopy (PEEM), showing for the first time the domain pattern on both sides of a FM/AFM interface [1,2]. In particular the systems LaFeO₃/Co and NiO/Co [3] were investigated using the photoelectron emission microscope at the Advanced Light Source in Berkeley (the so-called PEEM2 [4]).

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Quantum well states and interlayer coupling in magnetic nanostructures

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It is well recognized that the existence of spin-polarized quantum well states (QWS) in magnetic multilayers plays an important role in understanding the phenomena of oscillatory magnetic coupling and giant magnetoresistance. Photoemission provides the most direct observation of QWS in k-space. The unique capabilities now available at the Advanced Light Source (ALS) at Berkeley make it possible to *image* QW states on the atomic scale. Scanning photoemission experiments are performed across wedged samples using a small photon spot size (50-100 μ m) with high brightness ($>10^{12}$ photons/sec at a resolving power of 10^4). Recent photoemission results from ALS on the Cu/Co(100) QW system are presented using single- and double-wedge samples. Firstly, using a Ni monolayer to probe the Cu QWS at different positions, it is shown that the QWS in metallic thin films can be described by the envelope function of the Bloch wave. Secondly, quantum interference between two QWS is discussed, as are its implications with respect to the magnetic coupling. Finally, by measuring the magnetic coupling by means of the magnetic linear dichroism, the relationship is demonstrated between the oscillatory magnetic coupling and the oscillations of the density of states at the Fermi level.

LACK OF ATOMIC CHARGE LOCALIZATION IN TRANSITION METAL MIXED VALENCE OXIDES.

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The knowledge of the electronic state of the metal atom in mixed valence oxides is a point of fundamental interest in order to understand their different and unusual macroscopic properties. Generally, transition metal oxides has been described in terms of the ionic model which implies a transfer of d electrons to the neighboring oxygen atoms where the remaining electrons are fixed to the transition metal d-orbitals. It has been suggested that spatial atomic charge localization gives rise to the charge ordered phases. An archetypical example of this description is the Verwey phase in magnetite. Recently some phases in mixed valence manganites have been explained as charge ordering states. We will show here, that X-ray absorption spectroscopy and resonant scattering experiments demonstrate the lack of atomic charge localization, either spatial or temporal in these two important systems.

Magnetite was studied by means of resonant X-ray scattering at the iron K-edge. The evolution of the intensity of the (002) and (006) forbidden reflections as a function of the incoming x-ray beam energy, the azimuthal angle and the polarization dependence of the scattering process was studied. The experimental results were correctly explained in terms of the anisotropic character of the octahedral iron atomic scattering factor. These reflections were studied above and below the Verwey transition temperature. Identical behavior was observed at high and low temperatures showing the same kind of anisotropy in the two phases. Accordingly, this experiment demonstrates the lack of charge fluctuation between octahedral atoms in the high temperature phase and the absence of real charge ordering in the insulating phase[1,2].

Mixed valence manganites were studied by high resolution X-ray absorption spectroscopy recording the intensity at the maximum of the Mn K_β emission line. Our analysis showed that the electronic state in intermediate compounds could not be considered as a mixture of Mn³⁺ and Mn⁴⁺ pure states[3]. We have also reanalyzed the recent published X-ray resonant scattering experiments on the so-called charge ordered manganites showing that although these experiments demonstrated the existence of two different kinds of Mn atoms, they can not be identified as Mn³⁺ and Mn⁴⁺ ions. Moreover, the resonant scattering experiments can be well explained by the anisotropy of the anomalous scattering factor due to small distortions of the local geometrical structure[4].

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TRANSPORT OF K ON RH(110) DURING THE CATALYTIC REACTION OF H₂ + O₂

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We report on the lateral transport of potassium deposited on a Rh(110) single crystal surface during the catalytic H₂ + O₂ reaction. It is known that under certain conditions of the catalytic H₂ + O₂ reaction the Rh surface switches between oxidized and reduced state. The transition takes place via a sharp front travelling over the surface. These so called chemical wave-fronts were followed on a Rh(110) surface modified by preadsorbing a submonolayer coverage of potassium. It is shown that the chemical waves initiate transportation of potassium with the fronts while the potassium atoms themselves effect the chemical waves. This process is leading to a type of selforganization that produces a lateral inhomogeneous surface on a macroscopic length scale (several hundred μm up to 1 mm). The working principle of this new type of catalytic behavior could be understood with the help of the experimental data obtained at the ESCAMICROSCOPE at ELETTRA [1].

Microstructuring of the Rh surface by evaporating Pt patches of ~100 μm diameter leads to a modified behavior of the system. During the H₂ + O₂ reaction potassium atoms move inside the Pt-patches producing a stationary pattern. The formation and the chemical status of these patterns could again be characterized making use of the capabilities of the ESCAMICROSCOPE.

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CORE EXCITATION INDUCED BOND BREAKING OF CHEMISORBED MOLECULES PROBED BY EMISSION OF IONS, NEUTRALS AND ELECTRONS

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Photodesorption and photofragmentation of adsorbed molecules by core electron excitation has attracted constant interest since the advent of tunable soft X-ray sources. Reasons are i) that the allocation of the primary excitation to a distinct atom allows us to start the reaction at a definite site, at least for heteronuclear molecules; ii) that by their electronic decay primary core excitations serve as a source for strongly antibonding and well localized valence states which can cause bond breaking even if substrate or co-adsorbate induced electronic quenching is fast; and iii) that the distinct lifetime of the core hole can be used as an internal clock for investigations of the dynamics of the photochemical process. Furthermore, the decay electrons are ideal probes for monitoring the electronic evolution. As a result, studies of core induced bond breaking of isolated molecules are commonly based on data of emitted electrons and photoions created upon core decay. For chemisorbates particularly on metal surfaces, however, substrate-adsorbate charge transfer is very fast and neutral products are important as well.

We have developed sensitive devices for the detection of these neutral reaction products [1], and for the measurement of kinetic energy distributions of ions and neutrals emitted from surfaces [2]. Utilizing photodesorption and photofragmentation data from CO and N₂ chemisorbed on Ru, Ni and Cu surfaces, we demonstrate that ions and neutrals are complementary probes for different parts of the K shell excitation region. Ions are mainly emitted for primary multi electron states, whereas neutrals dominate for one electron excitations. Kinetic energy data help to disentangle the different contributions. Special emphasis is laid on atom selective bond breaking by π -resonant excitation [3] and its modification by surface effects, on possible contributions of ultrafast dissociation during the lifetime of the core hole, and on interatomic excitation transfer monitored by stimulated desorption of ions.

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SURFACE KINETICS BY FAST CORE-LEVEL PHOTOEMISSION

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The study of surface reactions is one of the oldest applications of core level photoemission [1]. The field has greatly benefitted in recent years by the combination of third generation synchrotron radiation beamlines with state of the art detection systems which has greatly reduced the data acquisition times and improved the energy resolution. Core photoemission spectra with an energy resolution resolution better than 200 meV from carbon, nitrogen and oxygen 1 s levels of chemisorbed species can now be measured in less than a second, thus enabling to study the kinetics of surface reactions. We will present real time XPS studies performed at the SuperESCA beamline at ELETTRA of the interaction of simple molecules with single crystal surfaces. Given the high resolution, complementary information on the evolution of surface species is obtained by measuring the time dependence of the surface shifted components of the substrate core spectrum. It will be shown that by following the surface concentration of each species in its adsorption states as a function of time it is possible to highlight the interplay between the adsorption rate and changes occurring at the surface during adsorption and desorption.

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THEORETICAL PREDICTIONS OF OXYGEN INDUCED SURFACE CORE-LEVEL SHIFTS: A PROBE OF THE LOCAL OVERLAYER STRUCTURE

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The knowledge of the geometrical structure of atoms and molecules adsorbed on metal surfaces is a very important step towards understanding the gas-surface interactions that are the basis of heterogeneous catalysis. It is well known that X-ray photoelectron spectroscopy (XPS) is a useful experimental technique, complementary to others such as low-energy electron diffraction (LEED) for the determination of the adsorption geometry. The core levels of chemisorbed atoms are very sensitive to the adsorption site and additionally the core-level binding energies of the substrate atoms are influenced by the adatoms. Nevertheless, this experimental information is by no means direct; actually, it is the synergy between experiment and theoretical calculations of the initial- and final-state contributions to the core-level shifts that allows for the validity of structural and electronic models and provides insight into the nature of bonding and screening at surfaces and the physics that underlies surface structure.

As an example of a *trend* and its interpretation, the oxygen adsorption on Rh(111) and Ru(0001) surfaces is studied using density-functional theory calculations of the initial- and final-state contributions to the shift in the Rh $3d$ and Ru $3d$ surface core-levels as a function of oxygen coverage, Θ ($0 \leq \Theta \leq 1.0$ monolayer). Shifts in the core-level binding energies of surface atoms induced by adsorption have often been attributed solely to charge transfer between adsorbate and substrate atoms. Adsorption of oxygen shifts the Rh $3d$ and Ru $3d$ surface core-levels to higher binding energies with the magnitude of the shift depending almost linearly on the number of directly coordinated O atoms. This correlation is robust with respect to differences between initial- and transition-state theory calculations of the surface core-level shifts. A relation is established between the detailed geometry of the O adlayers and the changes observed in the Rh $3d$ [1] and Ru $3d$ [2] XPS spectra. Surprisingly, a simple model, which attributes the O induced shifts not only to charge transfer but also to an increase effective coordination of surface atoms provides a sound basis for the interpretation of the origin of the shifts while improving our understanding of the O-metal interaction.

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The interaction of ethylene with perfect and defective Ag(001) surfaces.

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Ethylene epoxidation, catalyzed by silver, is one of the most important selective oxidation processes based on heterogeneous catalysis on a metal surface.

We present a theoretical investigation of ethylene adsorption on Ag(001), based on state-of-the-art density-functional calculations. The process was simulated at coverage 1/4 and considering several possible adsorption sites in a (2x2) surface unit cell of perfect Ag(001). After full structural optimization the largest binding energy was found to be only 90 meV, corresponding to the top site. By contrast, we predict the binding energy to be twice and three times as large when the molecule is adsorbed on a monatomic step and on adatom defects, respectively. Monatomic steps are modeled by an Ag(310)-(2x1) surface, while adatom defects are simulated by an Ag adatom in the four-fold hollow site of a (2x2) surface unit cell. Adsorption of ethylene on oxygen pre-adsorbed Ag(001) surface is currently under investigation.

Theoretical description of the magneto–optical properties of arbitrary layered systems

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The calculation of the optical properties of ordered solids can nowadays be done in a more or less routine way. Even the magneto–optical effects caused by the interplay of magnetism and spin–orbit coupling can be investigated in a quantitative way by using modern methods of band structure calculation. However the interpretation of the corresponding magneto–optical spectra is by no means straightforward. In addition there are still several important classes of materials that are not accessible to ab initio type investigations.

To allow for a detailed analysis of the magneto–optical properties of periodic magnetic multi layer systems the concept of the layer resolved optical conductivity $\sigma^{ll}(\omega)$ applied by means of a conventional band structure method is introduced. It will be shown for several transition metal multi layer systems that the layer projected optical conductivity $\sigma^l(\omega)$ of an atomic layer is influenced by only very few neighboring layers. This property can be exploited within the Baukasten principle that aims to predict the magneto–optical properties of a complex layer system from the properties calculated for a closely related but simpler one.

In addition a more general scheme will be introduced that allows to define the frequency–dependent optical conductivity tensor for arbitrary layered systems in a layer–resolved way. This opens in particular the way to deal with the magneto–optical properties of magnetic surface layer systems and to calculate the corresponding magneto–optical Kerr spectra. The formalism, based on a fully relativistic description of response theory in arbitrary order, will be described in some detail. For an implementation the very flexible spin polarized relativistic Korringa–Kohn–Rostoker (SPR–KKR) method of band structure calculation has been used. Corresponding results for the surface layer systems Au(001)/Fe/au and Cu(110)/Co will be presented and discussed.

Charge Ordering and Electronic Structure of $(\text{La}_{2-x-y}\text{Sr}_x\text{Nd}_y)\text{CuO}_4$ Stripe Phase and $(\text{La}_{2-x}\text{Sr}_x)\text{CuO}_4$ High- T_c Superconductors

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We have carried out extensive high resolution angle-resolved photoemission measurements on $(\text{La}_{1.4-x}\text{Nd}_{0.6}\text{Sr}_x)\text{CuO}_4$ (Nd-LSCO) ($x=0.10, 0.12, \text{ and } 0.15$) [1,2], a model system with static stripes, and $(\text{La}_{2-x}\text{Sr}_x)\text{CuO}_4$ (LSCO) ($x=0.0\sim 0.30$) [2,3], a system that spans the whole range from Mott insulator ($x\sim 0.0$) to spin glass ($0.03 < x < 0.05$) to high temperature superconductors ($0.05 < x < 0.30$). The LSCO system also contains possible diagonal stripes in the spin glass region and dynamic vertical stripes in its superconducting region.

We have observed that the stripe phase (both static and dynamic) exhibits dual nature in its electronic structure. On the one hand, it shows one-dimensional feature with the frequency integrated spectral weight confined inside 1D straight segments in the momentum space; the low energy excitation is confined near $(\pi, 0)$ and $(0, \pi)$ anti-nodal regions. On the other hand, it shows spectral weight near the $(\pi/2, \pi/2)$ nodal region and an associated Fermi surface, indicating a charge motion perpendicular to stripes. The observation of this dual nature in the electronic structure of the stripe phase indicates an order-disorder competition in the system.

By studying $(\text{La}_{2-x}\text{Sr}_x)\text{CuO}_4$ system over its whole doping range ($x=0.0\sim 0.30$), significant new insight can be obtained on how a Mott insulator is doped into a high temperature superconductor and how the electronic structure evolves from the underdoped, to the optimally doped to the overdoped in the superconducting range. We have also identified an energy scale in the quasiparticle dispersion of LSCO over its entire doping range and its implications to high temperature superconductivity will be discussed.

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Photoemission Studies of Self-Energy Effects in High Tc Superconductors and other Materials

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Recent instrumentation developments in photoemission are providing new insights into the physics of complex materials. With increased energy and momentum resolution, it has become possible to examine in detail different contributions to the self-energy or inverse lifetime of the photohole created in the photoexcitation process. This information may be extracted either from momentum distribution curves, the photoemitted intensity as a function of momentum at constant binding energy, or from the more traditional energy distribution curves, the intensity as a function of binding energy at constant angle or momentum. In studies of metallic systems, such as Mo, it is possible to isolate and identify the different contributions to the quasi-particle lifetime including electron-electron, electron-phonon and electron-impurity scattering.[1] In studies of 2H-TaSe₂ a new decay channel reflecting the presence of the CDW gap is identified.[2] In contrast to these systems, studies of the high Tc superconductor, Bi₂Sr₂CaCu₂O_{8+x}, show that the material behaves like a non-Fermi liquid rather a Fermi liquid.[3] Further, detailed studies of the latter material reveal that interactions with magnetic excitations in the system lead to renormalization effects at the superconducting transition.[4]

This work has been carried out in different collaborations with Tonia Valla, Alexei Fedorov, Barry Wells, Zikri Yusof, Jinue Xue, Kevin Smith, Qiang Li, Genda Gu, N. Koshizuka, and Frank DiSalvo. The work at BNL is supported by the Department of Energy under contract number DE-AC02-98CH10886

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FERMI SURFACE TOPOLOGY AND ANGLE-RESOLVED PHOTOEMISSION RESULTS OF Bi2212 SINGLE CRYSTALS

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Angle-resolved photoemission (ARPES) has been a useful tool to study single particle properties of high- T_c superconducting materials [1]. There are two main approaches of ARPES that are used to study the Fermi surface features of the high- T_c superconductors. The traditional method is based on the measurement of energy distribution curves (EDC) in all high-symmetry directions of the Brillouin zone (BZ) in order to determine the reciprocal space localization of the Fermi level crossing of the quasi-particle bands. The second approach is based on measuring the photointensity within a narrow energy window at the Fermi level (E_f) defined by the spectrometer and photon source resolution to get the distribution of spectral weight near the Fermi level in the k space. This second approach has the advantage that it provides a global view of the topology of the Fermi surface throughout the whole BZ. However, the photointensity images are influenced by strong matrix elements which depend on the angle between the polarization vector of the photon beam and the wave vectors of the initial and final state involved in the photoemission process [2].

In this communication, we report on recent photoemission data of the normal state of Bi2212 compounds ($T_c = 91$ K) recorded using high-resolution synchrotron radiation ARPES at LURE. As a function of the incident photon energy, we have performed complete scans of the BZ in two different polarization geometry detections. Particular attention has been paid to the current controversy on whether or not the Fermi surface is electron- or hole-like in the vicinity of the $M(\mathbf{p}, 0)$ high symmetry point. By mapping the spectral weight in the momentum space, we have found substantial additional information concerning the symmetry of those initial states that define the Fermi surface contours. The completeness of our results provides a clear identification of the key features associated to the Fermi surface of the Bi-based high T_c superconductors.

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Correlation Effects on the Electronic Structure of Half-Metallic Transition Metal Oxide Thin Films*

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Transition metal oxides have recently attracted renewed attention due to their important magnetic and electrical properties. Half-metallic oxides such as Fe_3O_4 and CrO_2 have been attracted much attention and been considered as important potential materials for spintronics. These two systems have been considered as spin injection sources due to their possible half-metallic behavior.

In this talk, we present studies on the electronic structure of epitaxial CrO_2 and Fe_3O_4 thin films using advanced synchrotron spectroscopic techniques, including spin-polarized soft X-ray polarization-dependent absorption, magnetic circular dichroism (MCD) and photoemission. The issues of the electron correlation effects on the electronic structures of epitaxial CrO_2 and Fe_3O_4 thin films will be addressed. Epitaxial Fe_3O_4 thin films were in-situ grown on $\text{MgO}(100)$ substrates and RHEED and LEED measurements show that the surface of these films exhibits the characteristic $c(2 \times 2)$ reconstruction. Photoemission measurements demonstrate that the spin-polarization of the top of the valence band is not completely spin-polarized with minority-spin electrons as predicted by LDA theoretical calculations. The photoemission results will be accounted for in terms of strong electron-correlation effects that set an upper limit for the spin polarization of the first ionization state at about -67%.

Soft X-ray polarization-dependent absorption measurements of epitaxial CrO_2 thin films grown on $\text{TiO}_2(100)$ substrates show strong orbital anisotropy in the O 2p holes. In addition, our spin-resolved polarization-dependent O 1s absorption results of CrO_2 thin films provide a direct spectroscopic evidence showing the evolution of the electron-correlation effect on the electronic structure in the vicinity of the Fermi level. The spin-polarization measurements also show that the conduction electrons near the Fermi level is almost fully spin polarized, consistent with the half-metallic properties of CrO_2 as predicted by band structure calculations

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Fermi surface of Sr₂RuO₄ by ARPES: a longstanding controversy

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The electronic structure of Sr₂RuO₄ is investigated by high-resolution angle-resolved photoemission spectroscopy (ARPES). We address the controversial issue of the Fermi surface (FS) topology, showing that a $\sqrt{2} \times \sqrt{2}$ surface reconstruction (as confirmed by LEED) and, in particular, the detection of surface bands are responsible for previous conflicting interpretations. By cleaving the samples at different temperatures and varying the incident photon energy, we could separate the bulk from the surface electronic structure, concluding that the bulk FS as determined by ARPES is consistent with LDA and de Haas-van Alphen results. In addition, ARPES provides direct information on the exact shape of the FS and confirms, in particular, the nested topology of two of the three different sheets of the FS [1]. Furthermore, by comparing the surface electronic structure with band structure calculations for a reconstructed and/or ferromagnetic surface, we could test the hypothesis of surface ferromagnetism in Sr₂RuO₄, which may have significant ramifications for determining the mechanism of superconductivity in the bulk. This way, we could conclude that the ARPES data are most readily explained by the $\sqrt{2} \times \sqrt{2}$ surface reconstruction, with no evidence for surface ferromagnetism [2].

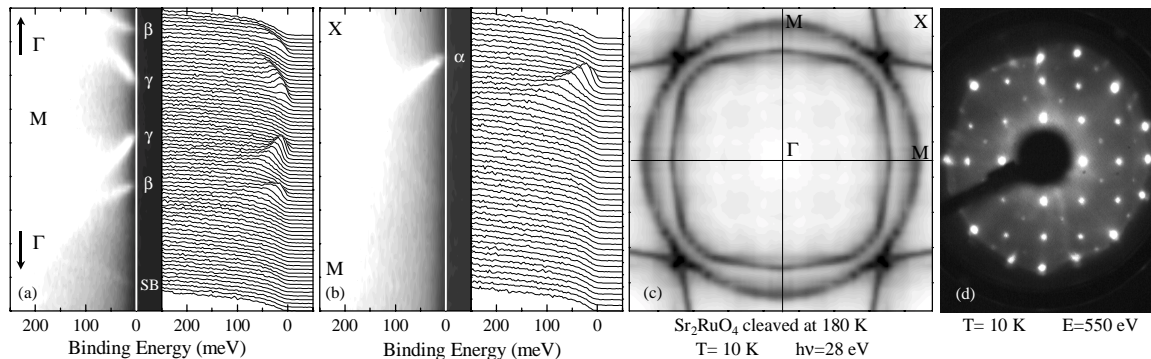


Figure 1: ARPES spectra and corresponding intensity plot along Γ -M- Γ (a), and M-X (b). Fermi surface mapping obtained by integrating the ARPES spectra over a 5 meV window at E_F (c). Low-energy electron diffraction pattern showing the fractional reflection due to the $\sqrt{2} \times \sqrt{2}$ surface reconstruction (d).

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K-RESOLVED ONE AND TWO PHOTON PHOTOEMISSION AROUND THE FERMI LEVEL.

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Angle scanned photoemission experiments of occupied *and* ‘unoccupied’ states are presented. Ni(111) and the interface of hexagonal boron nitride on Ni(111) [1] serve as model systems for an itinerant ferromagnet that is truncated with vacuum or a single layer insulator.

He I one photon photoemission reaches thermally excited electrons up to $5 k_B T$ above the Fermi level and large k_{parallel} ($< 2 \text{ \AA}^{-1}$) values. This gives insight into a magnetically active region with unoccupied minority d-bands [2]. The exchange splitting of the sp-bands and

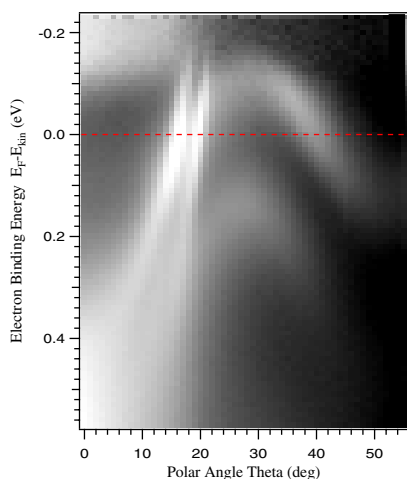


Figure 1: He I β excited electron bands of a magnetically active region in Ni. The data are normalized with a Fermi function. Clearly, exchange split d-bands (parabolas) and sp-bands (steep lines) are observed.

the d-bands is accurately determined. The spin polarization of the individual bands is inferred from band structure calculations. It is seen how the exchange splitting and the energies of the bands are affected upon the *h*-BN/Ni interface formation. *h*-BN acts as an atomic grating and induces umklapp processes.

Two photon photoemission (2PPE) ($3.01 < h\nu < 3.14$ eV) accesses the occupied and unoccupied electronic states around the L-neck in the Fermi surface of nickel. Occupied surface states and on *h*-BN/Ni(111) an image potential state, are identified. The polarization dependence of 2PPE is discussed in view of the identification of the spin polarization of these states.

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Valence band structure of quasicrystals studied by photoemission: dispersing states and quasi-Brillouin zones

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Quasicrystals possess perfect long-range structural order in spite of the fact that their rotational symmetries are incompatible with long-range periodicity [1]. The question whether the unusual physical properties of quasicrystals, such as a low electrical conductivity and electronic contribution to the specific heat, are a consequence of these exotic structural properties is largely unresolved, since an interpretation of valence electron state nature, in terms of either extended (as in periodic crystals) or localized states (as in amorphous materials), is still missing [2]. To address this question, we have measured the momentum (\mathbf{k} -) dependent distribution of the electronic states in d-AlNiCo using high-resolution, \mathbf{k} -resolved photoemission measurements at the Advanced Light Source in Berkeley. The photoemission data show that the valence electrons feel the symmetry of the quasicrystalline structure, since angular intensity maps provide clear evidence for a tenfold or twofold (AlNiCo) rotationally symmetric emission pattern. The structure of decagonal AlNiCo is interesting since it combines periodic order, along the tenfold axis, with quasiperiodic order in the planes normal to the tenfold axis. Valence band spectra show peaks that disperse continuously with wave vector, in the periodic as well as quasiperiodic directions [3]. The effective mass of some of these states approaches $m^*=1$, indicating a high degree of delocalization. Constant energy surfaces in momentum (\mathbf{k})-space show that the s-p bands have spherical energy surfaces, emanating from the locations of strong in-plane diffraction spots, supporting a picture in which the strongest Fourier components of the atomic potential define a quasi-Brillouin zone. We also find d-derived states of both localized and delocalized character which cross the Fermi level, and thus form a well-defined Fermi surface. Considering that the response function of the electrons derives from the detailed topology of the Fermi surface, these results have a bearing on many of the electronic properties of decagonal AlNiCo in particular and quasicrystals in general.

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Spectromicroscopy with the SPELEEM

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The combination of spectroscopic photo emission with low energy electron microscopy (SPELEEM) in one instrument allows a comprehensive characterization of surfaces and thin films and processes occurring on and in them. The talk describes briefly the principles of the combination, the first commercial instrument in which it is implemented and initial results obtained with it at the new nanospectroscopy beamline at ELETTRA. This initial work is concerned mainly with ultrathin Co films on W(110) and their interaction with Au and Cr films, with emphasis on the magnetic domain structure. Two aspects will be discussed: i) the influence of energy filtering of the secondary electrons on the resolution in x-ray magnetic circular dichroism photoemission electron microscopy (XMCDPEEM) and ii) the relative merits of energy-filtered XMCDPEEM compared to spin-polarized low energy electron microscopy (SPLEEM) such as fast image acquisition in SPLEEM and chemical specificity in XMCDPEEM. Depending upon the progress of the work results on Cr overlayers on Co and on the influence of Pb as surfactant will also be presented.

ADVANCES IN THE THEORY OF PHOTOELECTRON DIFFRACTION AND HOLOGRAPHY

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The theory of photoelectron diffraction and holography has developed in various directions in recent years, in order to interpret a wider range of experiments, particularly those enabled by new synchrotron radiation facilities. These include measurements that depend on photon polarization and electron spin, as well as low-final-energy data that are sensitive to the electronic structure of a surface, and different kinds of resonance. Thereby, the technique is moving toward the detailed interpretation of magnetic and bonding effects, among other applications.

The extension to low final energies will be illustrated with the modeling of recent photoemission experiments from fixed-in-space CO molecules, in and out of resonance [1]. Non-muffin-tin corrections and the effect of the electron hole will be discussed. This example serves as a severe test case before application of our new methods to surfaces.

A very efficient scheme for the convergent calculation of multiple scattering in large atomic clusters will also be presented: the new code, called EDAC, includes spin- and polarization dependence [2]. It can be run interactively in limited form on the web at <http://electron.lbl.gov/~edac/> and will be downloadable in the near future.

Regarding photoelectron holography, an improved approach has been developed, called differential holography, which reduces the negative effect of the forward scattering peaks [3]. It thus cleans up artifacts in the resulting image, a much needed improvement.

Finally, the recently created Synchrotron Radiation Research Theory Network (SRRTNet) will be described: it serves to bring together theorists and experimentalists involved in synchrotron-based and related research. See <http://www.cse.clrc.ac.uk/Activity/SRRTnet>.

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Progress of High-Resolution Photoemission Spectroscopy in Strongly Correlated Electron Systems

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Recent remarkable progress in the energy and momentum resolutions in photoemission spectroscopy (PES) opens an opportunity to challenge the long-standing fundamental problems in strongly correlated electron systems, where the detailed electronic structure very close to the Fermi level plays an essential role in characterizing the material and phenomena. The energy and momentum resolutions have been progressively improved in these ten years, reaching 1 meV and 0.01\AA^{-1} , respectively. This means that we are able to investigate the electronic structure of crystal by slicing the Brillouin zone into 10^6 pieces with an accuracy of 1 meV. High-resolution ARPES is now routinely used to map out the state-of-art band dispersions and the Fermi surface with a great accuracy. A “dressed” electron, quasiparticle, near E_F has been directly observed by high-resolution ARPES.

In this talk, I review the history, present status, and future of high-resolution PES with a stress on the importance in the strongly correlated electron systems such as high-temperature superconductors and heavy f-electron materials.