

**NEXAFS Microscopy of Polymers**

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Carbonaceous materials, such as synthetic and natural polymers, exhibit a rich carbon, nitrogen and oxygen K-edge Near Edge X-ray Absorption Fine Structure (NEXAFS). This is primarily due to the essentially covalent nature of the chemical bonds in these materials and the numerous possible combinations of single and multiple bonds between carbon atoms as well as hetero-atoms (oxygen, nitrogen, chlorine, fluorine, sulphur, etc.). Simple building blocks can react to result in complex macromolecules with millions of atoms. Furthermore, many polymeric systems, such as engineered polymers, latexes, multilayers, organic geochemical, and meteoritic materials, etc., are naturally, accidentally or intentionally in-homogeneous or structured. The combination of the chemical complexity of constituent polymers and the microheterogeneity found in many materials results in a multitude of systems that can benefit from micro/nano NEXAFS analysis.

We will first exemplify the basic underlying power of NEXAFS microscopy by discussing the NEXAFS spectra from a wide variety of polymers. We will subsequently review some NEXAFS microscopy applications of polymeric systems to date, spanning disciplines ranging from Polymer Science to Organic Geochemistry.

**Ground State and Low-Energy Excitations in  $\gamma$ -Ce from Correlated Band Theory\***

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The correlated electronic behaviour of the fcc-Ce is investigated using our full-potential linearized augmented plane wave implementation of correlated band theory ("LDA+U"). It is shown that the LDA+U calculations produce the correct for equilibrium lattice constant of localized  $\gamma$  phase of Ce. For the first time the binding energy for the 4f-state is calculated in agreement with the photoemission experiments. In addition to the ground state, multiple energy minima of the LDA+U energy functional are obtained for  $\gamma$ -Ce. These higher energy local minima (additional self-consistent solutions) are shown to be strongly indicative of crystal electric field and multiplet excitations.

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Momentum dependence of  $\pi$ - $\pi^*$  excitation of benzene rings in condensed phases

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The most fundamental property of a matter in relation to radiation is the so-called loss function (LF). At the low/high limit of the momentum transfer ( $q$ ) in the excitation, the LF gives optical-absorption/Compton-scattering profiles, which have been already reviewed in several references [1,2]. On the other hand, the LF for  $q \sim 1$  region has been little explored, especially for molecules in condensed phases. In this work, we investigated the LF around  $q \sim 1$  for discrete transitions in condensed molecules. In particular, the  $\pi$ - $\pi^*$  excitation of benzene rings ( $\sim 7\text{eV}$ ) was studied because it is a well-defined peak in the LF spectra. Inelastic x-ray scattering spectra of liquid benzene, benzene-hexane solutions, liquid toluene, and solid polystyrene were measured for  $0.35 < q < 1.50 \text{ \AA}$  at the wiggler line X21 of the NSLS. The benzene spectra were normalized by the f-sum rule and analyzed by Kramers-Kronig transformation (KKT) to deduce the LF as well as the complex dielectric function. The  $\pi$ - $\pi^*$  peak in the imaginary part of the dielectric function ( $\epsilon_2$ ) decreases with increasing  $q$ , and shows no marked dispersion with  $q$ , indicating that the excitation is well localized like gaseous benzene. The corresponding peak in the LF, however, exhibits a negative dispersion of  $0.5\text{eV}$  for  $0.6 < q < 1 \text{ \AA}$ , which is not observed in molecular gases [3]. The negative dispersions were found also for liquid toluene and polystyrene, but not for diluted (25mol%) benzene solution. These results can be interpreted by simple Lorentz oscillator model. The negative dispersion can be attributed to decrease of Lorentz's local field effect due to the decrease in the  $\epsilon_2$  peak intensity. Since this effect is automatically introduced in the KKT, the present results suggest that the LF ( $q \sim 1$ ) for discrete transitions in condensed molecules can be estimated by using the gas data as  $\epsilon_2$  in the KKT. This is a helpful clue to various fields where the LF in condensed phases is required (e.g. radiation chemistry), because it is generally less available than the LF in gas phase.

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**Assistance of Valence Excitations in Formation of Shape Resonances in X-Ray Absorption of Free Molecules**

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Spectral dependence of photo-excitation in CO and CO<sub>2</sub> above the C 1s edge and in SF<sub>6</sub> above the S 2p edges is examined in respect to correlated motion of the photoelectron with valence electrons. Inelastic channel in photoelectron emission couples with intramolecular interference of elastic scattered photoelectron waves provoking its changes which are enhanced at the shape resonances. The quasiatomic and optical potential concepts [1] are applied to compute spectral dependence of these cross sections. The imaginary part of the potential is defined to reproduce electron impact excitations cross section for the molecules. Our calculations have demonstrated that X-ray absorption  $Q^a$  and single hole photoelectron main line  $Q^+$  cross sections of CO, CO<sub>2</sub> and SF<sub>6</sub> are essentially deformed and the shape resonances acquire collective character allowing to consider them as 'giant' resonances. Assistance of valence excitations in their formation is found to lead to 1) decreasing of the  $Q^+$  relative to the  $Q^a$ , 2) blueshift of the resonances in comparison with the 'one-particle' position (the shift is found to be equal 2.3 eV in CO, 3.1 eV in CO<sub>2</sub> and 0.4 eV in SF<sub>6</sub>), 3) irregular behavior of the both cross sections at inelastic photoelectron thresholds and 4) resonant behavior of the  $Q^a - Q^+$  differential signal. This signal is decomposed on two parts responsible for non-adiabatic shake excitations due to core-hole creation and nearly adiabatic photoelectron impact excitations of valence shells. The 'adiabatic' part is related with deviations of the core-electron removal  $Q^r$  cross section from the  $Q^+$  due to energy transferring from the photoelectron flux to the molecular cation and dynamic polarization of valence shells in the photoelectron field. It is shown that resonant behavior of the  $Q^a - Q^+$  signal is originated by the 'adiabatic' part which is proportional to the  $Q^r$  cross section. The experimental [2,3] and theoretical cross sections of the molecules are compared. Application of one-particle descriptions to simulate collective properties of shape resonances in X-ray absorption and ionization is discussed.

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**Quantum Well Photoemission Spectroscopy of Atomically Uniform Films**

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Angle-resolved photoemission is a powerful tool for the study of valence electronic states in solids. For bulk states the technique is limited by its reliance on direct interband transitions for the determination of the  $k$  vector. The interpretation of data from a traditional band-mapping experiment requires knowledge of the photoemission final state, and direct-transition peaks are subjected to substantial final-state broadening. In principle, these problems can be bypassed by the use of a thin-film sample, where advantage is taken of the boundary conditions to define the perpendicular component of  $k$ . In a typical overlayer/substrate system, the quantum-well peaks are broadened mainly by variations in the film thickness, and a precise determination of the coverage may be difficult. Using a low-temperature growth technique and an Fe whisker sample, atomically-uniform films of Ag on Fe(100) can be prepared. In these films, peak broadening from thickness fluctuation is eliminated, and extremely sharp quantum-well peaks are obtained. A film of arbitrary thickness may display multiple sets of peaks corresponding to areas of the sample of different thicknesses, but these sets are easily resolved and so the thickness can be precisely calibrated. The quality of the spectra allow the observation of quantum-well peaks in films over 100 monolayers thick. Quantum-well peaks from both the  $sp$  and  $d$  states have been observed and used to map the associated bands. The elimination of broadening from thickness variation allows for the interpretation of the peak linewidths in terms of the quasiparticle lifetime and interfacial reflectivity, and the phonon contribution can be deduced from the temperature dependence of the spectra.

**Electronic Structure of Ge-Nanocluster Films Probed with Synchrotron Radiation**

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Clusters and nanocrystals show a wide variety of novel electronic, magnetic and catalytic properties. Germanium clusters are of particular interest since, as recent publications suggest, they display a strong blue luminescence. However, it is not clear, if this luminescence is due to surface species, oxide layers or quantum confinement. X-ray absorption spectroscopy (XAS) and Photoemission (PES) was performed on thin films of Germanium (Ge) clusters. The clusters were synthesized in situ by thermal vaporization of Ge in an Ar buffer gas and subsequently deposited on a hydrogen passivated Si-substrate. The average diameter of the clusters could be varied between 2nm and 9nm. Characterization of the nanoclusters in size and shape was done by non-contact atomic force microscopy. X-ray absorption spectroscopy at the Ge L-edge was used to measure the shift of the conduction band of the Ge-clusters as a function of particle size. We find, that the conduction band of the clusters is blueshifted compared to bulk-Ge, in agreement with the quantum confinement theory. The blueshift ranges from 0.2eV to 0.4eV for clusters between 4nm and 2nm. Preliminary photoemission data shows a very small shift of around 0.1eV of the valence band in clusters of around 3nm in size and a dependence of the valence band edge structure and the cluster film thickness. Measurements of the Ge3d plasmons show a strong increase of the surface plasmon compared to the bulk plasmon in clusters. Both measurements, XAS and PES, do not show any features of oxygen or other contaminations.

Comparison of this work to previous work done on Si-clusters of the same size and prepared in the same manner show, that the conduction band shift in Ge-clusters is much larger for clusters of the same size. Effective mass calculations of Si and Ge clusters confirm this effect.

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**Li-K Absorption Spectra of Various Lithium Compounds**

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It is well known that spectroscopy in the soft x-ray region provides a powerful technique for obtaining information about valence band structure of materials. X-ray absorption spectra give a very useful information about the band structure or chemical bond state. Recently light elements such as lithium and boron compounds and high molecular compounds included C, N and O were investigated by means of X-ray Absorption Near-Edge Structure (XANES) for various field of material science. In the meantime, lithium compounds, for example lithium battery, lithium glass and others, are interesting materials and also are used in general. However, there are no experimental data regarding the Li-K emission spectrum. Also there are few reports about Li-K absorption spectra [1-4], which was first observed in 1937 by Skinner et. al [1].

In this work, Li-K absorption spectra of various lithium compounds are measured using the beamline 2 (BL2) [5] of the compact synchrotron radiation at Ritsumeikan University in Japan. All previous absorption spectra were obtained by transmission method, but in this time Li K-edge spectra of various lithium compounds were measured by means of total electron yield method (TEY). The sample is set at nearly parallel position to entrance of the detector, and distance of between the sample and entrance of the detector is about  $100\text{ }\mu\text{m}$ . Herewith, photoelectron discharged from the sample is taken in the detector. The sample is mounted on the surface of indium metal plate. The spectra of lithium halides in this experiment agree well with previous reported data. Sonntag [2] pointed out that the weak absorption by excitation from 1s to the band of 2p of Li begins from about 54eV in LiF and the absorption has a maximum at 61.9eV. And Kunz et. al. [6] suggested that the absorption at high energy side is due to the electronic polaron. In this work also, Li-K absorption spectra of lithium halides are discussed with the theoretical spectrum calculated by DV-X molecular orbital calculation method and the origin of each peak is clarified. Some differences are observed to the theoretical and experimental spectrum, but the overall agreement is well. Using absorption spectra of lithium halides, the relation between peak positions and electronegativity is discussed.

**Linear Dichroism in NEXAFS Spectroscopy for Surface Structure Analysis of Polymer Coatings**

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Perfluoroalkyl substituted PolyMethacrylate (PFPM) polymers are today widely used as low surface-energy coatings playing an essential role in microelectronics, anti-fogging, and anti-fouling applications, and even have promising medical applications. It is generally believed that the anti-wetting properties -solely determined by the structures present in the surface region- of these and related polymers arise from the segregation of CF<sub>3</sub> groups to the surface. However, proof of a direct correlation between surface structure and surface energy, and the importance of order in the underlying bulk, is still lacking as most experimental techniques do not have the required surface sensitivity.

For preferentially oriented polymers the asymmetry in chain orientation translates to an asymmetry in the electron charge density as the electron orbitals are oriented along the molecular bonds. Such a charge asymmetry can give rise to a dependence of the Near Edge X-ray Absorption Fine Structure (NEXAFS) on the orientation of the electric field vector of the linearly polarized x-rays relative to the sample. Consequently, such a linear dichroism can be used to study orientation phenomena quantitatively. The required surface sensitivity is obtained by recording simultaneously the more bulk sensitive total (TEY) and the more surface sensitive Auger (AEY) electron yield.

Our studies of three PFPM's with different bulk order phases reveal a greater order at the surface than in the bulk, and the surface order parameter is found to correlate with the surface energy. Most importantly, temperature dependent NEXAFS measurements covering several bulk phase transitions show that the achievable surface order, and hence the surface properties, is ultimately limited by the bulk order (phase).

**Angle-resolved and High-energy Resolution Photoemission Systems at Siam Photon Laboratory**

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An angle-resolved photoemission system and a high-energy resolution photoemission system for surface and interface researches have been designed to be installed at the first beamline of the Siam Photon Source, the first synchrotron light source in Thailand. The beamline provides photon energy between 20 - 240 eV with theoretical resolving power up to 5000. Both photoemission systems are similar in design, consisting of two main chambers, i.e. an analysis chamber and a sample preparation chamber. The analysis chambers equipped with an electron energy analyzer are made of mu-metal. A SCIENTA SES-2002 electron energy analyzer will be used in the high-energy resolution system, while a VG ARUPS10 will be used in the angle-resolved system. The sample preparation chamber is mounted on top of the analysis chamber. A UHV gate valve inserted between the preparation chamber and the analysis chamber can cut the vacuum off from each other. The sample manipulator is mounted on top of the preparation chamber. Sample is treated in the preparation chamber, which is equipped with AES, LEED, evaporators and an ion gun. A RHEED system is installed only in the preparation chamber of the angle-resolved system. After the sample is processed in the preparation chamber, it is transferred to the analysis chamber by the linear motion mechanism of the manipulator. Thus, a complicated sample transfer mechanism is not required. Details of the systems will be described in this report.

FRAGMENTATION OF CH<sub>4</sub> DICATIONS STUDIED BY AUGER ELECTRON-ION COINCIDENCE

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The use of the tunable VUV light and soft X-ray radiation of synchrotron radiation sources has triggered a revival of interest in the spectroscopy of doubly and, more recently, multiply charged systems. Complementary information on dications and their fragmentation patterns can be obtained also via electron-impact experiments. To the purpose we have built an apparatus to study the fragmentation of dications via Auger electron-ion coincidence experiments [1,2]. In this technique an Auger electron, ejected in the decay of an inner-hole produced by the primary beam, is detected in coincidence with either the dication or the ions produced in its dissociation.

The main components of the apparatus are a Wiley-McLaren time-of-flight, TOF, mass spectrometer and a cylindrical mirror analyzer, CMA. The dications and/or their fragments, produced either by direct double ionization or via the Auger decay of a primary inner-hole, are accelerated by an electric field towards the TOF spectrometer and finally detected by two microchannel plates mounted in a chevron configuration. The Auger electron-ion coincidence spectra were obtained by using standard coincidence counting electronics based on a multi-hit TDC unit.

In this work we have studied the fragmentation of CH<sub>4</sub><sup>2+</sup>. Several coincidence measurements have been performed at different kinetic energies of the C Auger electrons, which correspond to select dication states with binding energies between 38.6 and 59.7 eV. Despite the density of dication states prevents a complete state-to-state investigation, some qualitative observation can be made. CH<sub>4</sub><sup>2+</sup> ions have been detected in none of the measured coincidence spectra. This indicates that metastable CH<sub>4</sub><sup>2+</sup> ions, if any, leave less than 4.6 μsec, the time-of-flight of these ions in our spectrometer. Then, all the possible singly charged fragments have been observed in the coincidence spectrum at the lowest binding energy of the dication, i.e. when both holes are in the outer valence bands. At higher binding energies, when one hole is in the outer valence band and the other in the inner valence, the coincidence spectra are dominated by C<sup>+</sup> and H<sup>+</sup> atomic fragments. These observations are consistent with the progressive atomization of the molecule, when the excitation energy increases, observed in SF<sub>6</sub> and CCl<sub>4</sub> [3].

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**Electron Spectroscopic Studies of 4-Mercaptohydrocinnamic Acid Self-Assembled Film on Au(111)**

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Self-assembled monolayers (SAMs) of organic molecules have been received increasing attention due to their potential applications in molecular electronics, nonlinear optics, and biological sensors [1]. The evaluation of the surface electronic structure and molecular orientation of such organic films is very important to understand surface properties and also to develop technologically useful organic systems. In this work, Penning ionization electron spectroscopy (PIES), ultraviolet photoelectron spectroscopy (UPS), and X-ray photoelectron spectroscopy (XPS) were used to characterize the 4-mercaptohydrocinnamic acid self-assembled film on Au(111). The outer most surface layer of the film was selectively detected by PIES. The analyses of PIES and UPS indicated that the surface consists of the mercaptophenyl group and the molecules form double layer by hydrogen-bonding interaction of carboxyl groups[2]. The presence of hydrogen bond in this organic film is confirmed by IR spectroscopy. In XPS for the S 2p core level, three peaks at binding energy of 161.4 eV, 162.8 eV, and 164.2 eV were observed. These peaks are originated from a bound thiolate in the under layer and an unbound thiolate on the upper layer with some contribution of thiolates physisorbed on the gold substrate. Namely, the peak at 161.4 eV corresponds to S2p3/2 of the bound sulfur, and the peak at 162.8 eV is attributed to S2p1/2 of the bound sulfur and S2p3/2 of the unbound sulfur. The third peak at 164.2 eV corresponds to S2p1/2 of the unbound sulfur. From the relative intensities of these peaks, it was found that the number of unbound sulfur is larger than the bound sulfur, and these results support the double layer formation of 4-mercaptohydrocinnamic acid on Au(111). The relation between the electronic states and film structures will be discussed at the conference.

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A Near-Threshold Study on Xe 3d Photoionization

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Photoionization from the 3d inner shell of Xe has been studied much less extensively than that from the more shallow 4d level or the outer shells. The only photoelectron cross section studies known to us [1] consisted of a few, widely spaced data points only. These data showed a rising tendency towards threshold, in disagreement with Hartree-Fock calculations and with high-resolution measurements of the photoabsorption cross section [2]. In the present work we have studied the Xe 3d photoionization with high resolution, particularly in the threshold region, in order to further investigate this behaviour. We will report results for the partial photoionization cross sections of both fine structure components in absolute units. The main feature to be noted here is the strong coupling of the  $3d_{5/2}$  line to the maximum in the cross section of the  $3d_{3/2}$  component, so far unobserved. The angular distribution parameter beta has been obtained in a backward scattering geometry, and, for the  $3d_{5/2}$  line, from measurements made within the dipole plane perpendicular to the light beam. Relativistic single-channel calculations are able to reproduce the shape of the cross section and beta-curves surprisingly well, except for the coupling of the  $3d_{5/2}$  to the  $3d_{3/2}$  line.

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**Soft X-ray Spectroscopy Via Hard X-ray Inelastic Scattering**

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Inelastic X-ray Scattering (IXS) from electronic excitations is a growing field in condensed matter research which largely profited from dedicated experimental high resolution setups at second- and third generation synchrotron radiation sources.

IXS gives access to excited state electronic configurations - either reached directly via a non-resonant inelastic process or via an intermediate resonant state - which can otherwise only be reached by soft x-ray or VUV spectroscopies or electron energy loss spectroscopy.

Compared to the above mentioned techniques, IXS provides several interesting possibilities. Due to the large x-ray penetration depth the method is bulk sensitive. Moreover, the sample environment needs not to be UHV compatible, and therefore studies under extreme conditions such as very high temperature and pressure are feasible. The aim of the present presentation is to review some of such IXS experiments carried out on the inelastic x-ray scattering beamline ID16 at the ESRF.

Specific topics that I will discuss are:

- 1) Evolution of the iron magnetic moment as a function of pressure in iron metal and iron-based invar alloys,
- 2) Near-edge and EXAFS spectroscopy at the oxygen K-edge in water, Ice I and Ice III and at the carbon K edge in C60
- 3) Q-dependence of excitonic states in LiF, and
- 4) Determination of the stretching modes in nitrogen.

High-Resolution UV-Photoemission of Solids: Success, Limitations and the Future

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Numerous studies have demonstrated that a gratifying agreement is found between UV-photoemission data and single-particle band calculations. However, many-body mechanisms can markedly modify this simple analysis and require an interpretation in terms of quasi-particles. This aspect will be illustrated for two different types of interaction: i) The very strong electron correlation in heavy fermions systems has been intensively studied by photoemission and interpreted within the framework of the single impurity model. The validity of this approach for photoemission is a permanent subject of controversy [1]. However, recent data confirm that this model predicts correctly the essential features of the spectral functions [2] and that discrepancies must be attributed to the surface sensitivity of low-energy photoemission [3]. ii) The strong electron-phonon interaction acting on the surface state of Be(0001) deeply modify its dispersion and line shape close to the Fermi energy. The analysis of this anomalous behaviour offers an remarkable illustration of a many-body effect clearly observed with photoemission [4].

A complete breakdown of the quasi-particle concept occurs in one-dimensional (1D) metals where the spectral functions are calculated with the Luttinger liquid formalism. The numerous photoemission spectra of highly anisotropic (quasi-1D) solids confirm the predicted absence of Fermi step but they systematically fail to reveal the two distinct structures accounting for the fundamental theoretical issue of collective spin and charge excitations (spinons and holons). This strange situation is not understood but might be attributed to peculiar surface effects. In order to avoid such difficulties, a periodic array of metallic chains has been created on an insulating surface. By Au deposition on a vicinal surface of Si(111) we have prepared single-atom metallic chains approaching ideal conditions of one-dimensionality. Their photoemission spectra display for the first time an explicit hint of separated spin and charge excitations with different dispersions.

These three examples illustrate the fact that the photoemission process is not setting any limit in the observation of excitations of very low energy. The crucial problem in their interpretation is that they originate from the surface region which may have properties different from those of the bulk. In addition, surface structures are by far less stable than bulk structures and any excitation spectrum accounting for extended states is blurred even by a moderate surface disorder which become very critical when the dimensionality is lowered. At low temperature, a too high flux density of the radiation used to excite the spectra can already be sufficiently destructive to hinder relevant measurements [6].

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**Surface Sensitivity and Depth Resolution of Electron-Excited Soft X-Ray Emission Spectroscopy\***

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It is well recognized now that variation of primary electron beam energy ( $E_0$ ) gives very good opportunity for organization of the non-destructive depth-resolved study of electronic structure and chemical phase composition in the surface region of solids by means of characteristic soft X-ray emission (SXE) band spectroscopy [1]. To transfer

this effective experimental method from qualitative to quantitative physical level is very important problem. To solve it one have to use fist of all a detailed description of electron ensemble (number, energy and angle distributions) at any distance from the surface. In spite of a great number of publications devoted to the depth distribution of X-

ray excitation efficiency and intensity dependence on  $E_0$  in the field of X-ray microanalysis, we find only a few works with proper analytical description of the electron distributions. We choose [2] to modify its expressions for the cases of one layer on the surface of the bulk solid and for the multi-layer sample. This allowed us to calculate a ratio of SXE intensity from very thin top layer to the intensity of the rest (bulk) emission (surface sensitivity) in dependence on  $E_0$ . Calculation of total SXE intensities from two different layers in multi-layer system and their ratios gives possibility to estimate depth resolution by varying  $E_0$  and layers thickness. Calculated data are compared with experimental measurements of SXE intensities ratios for 1 and 2 nm silicon oxide layers on c-Si and for multi-layer Mo-B<sub>4</sub>C sample with the layer thickness about 5 nm. It was found that the surface SXE contribution becomes noticeable unexpectedly far from the corresponding core shell ionization threshold (up to hundred eV). SXE signals from layers (and their ratios) have step-like dependence on  $E_0$  connected with the relative thickness of layers but in not too simple way. The best depth resolution and conditions of measurements (signal to background or signal to signal ratios) are realized in study of thin layers (from about 1 to some tens nm), located on the depths compared with their thickness.

\*Work supported by the Center of Basic Natural Sciences

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**Investigation of the BCS Density of States on a Conventional Superconductor by High-Resolution Photoemission Spectroscopy\***

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The superconducting phase transition of the conventional A15 superconductor  $V_3Si$  occurs at a transition temperature of  $T_c = 17.1$  K. According to the BCS theory [1], the zero-temperature gap width in the electronic density of states (DOS) is given by  $1.75k_B T_c = 2.5$  meV, a value which is by a factor of the order of ten smaller than for High Temperature Superconductors (HTSC). We have investigated the DOS on polycrystalline  $V_3Si$  surfaces by photoemission spectroscopy (PES) with an instrumental energy resolution of 3 meV (monochromatized He I, SCIENTA SES200). For the first time in photoemission spectra on a conventional superconductor, we could clearly show the opening of a gap around the Fermi level and the signatures of the BCS DOS on this energy scale.

A quantitative analysis of the data - based on a least-squares modelation by the theoretical BCS DOS - is in excellent agreement with the results of other experimental methods.

\*Work supported by the Deutsche Forschungsgemeinschaft

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**Threshold Photoelectron Spectroscopy using Synchrotron Radiation**

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Threshold photoelectron spectroscopy involves the photoionisation of an atom or molecule just above the excitation energy of an ionic state. It involves the detection of the photoelectrons produced in this process and since it occurs just above threshold the energies of these electrons are very small, typically  $\sim$  meV. A threshold photoelectron spectrum is obtained by tuning the electron spectrometer to detect threshold (zero energy) electrons and scanning the energy of the incident photon beam. As the photon energy passes through the excitation thresholds of the ionic states a spectrum of threshold peaks is observed which maps out the states of the ion. An important aspect of the technique is to approach as close to threshold as possible, i.e. to detect electrons of vanishingly small kinetic energy.

Threshold photoelectron studies are important for a number of reasons, both for the nature of the information they provide and because of their experimental advantages. Close to threshold, different ionisation processes become important. For example the low energy electrons move only slowly away from the ion core allowing ample time for electron correlation processes to become dominant. Close to threshold, indirect processes often occur where a highly excited neutral state lies close to the ionic state and decays to it with the emission of a low energy autoionisation electron. These indirect processes compete with the direct one and indeed can become dominant. In the case of molecules this can lead to the observation of vibrational excitation well outside the Frank-Condon region with the observation of vibrational levels up to 20 or 30. This all means that threshold photoelectron spectra are invariably very different from the conventional photoelectron spectrum and so provide much additional, new information. On the experimental side, the threshold technique offers the advantages of very high resolution ( $\sim$  meV) and simultaneously very high detection efficiency. This means that they give state of the art resolution to provide, for example, photoionisation studies at the level of individual rotational levels. This very high resolution is also well matched to the high photon resolution provided by current synchrotron radiation sources. The very high detection efficiency means that the optical monochromator slits may be reduced to get the narrowest possible spectral resolution. It also means that the technique is suitable for the study of species of very low target density, e.g. free radicals.

Recent experimental techniques to detect zero-energy photoelectrons that have been used in conjunction with synchrotron radiation will be described. These include the penetrating field technique and the pulsed field ionisation technique. The sorts of information that are obtained from threshold photoelectron studies will also be

Ultrahigh-resolution photoemission and resonant-inverse photoemission spectroscopy on CePd<sub>3</sub>

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CePd<sub>3</sub> is the most celebrated Ce-based material, which has been examined through a number of experimental and theoretical works and known to be a typical valence-fluctuating system. Bucher et al., measured the temperature- and frequency dependent optical conductivities of CePd<sub>3</sub> and CeSn<sub>3</sub> compounds.[1] Both compounds were reported to show a renormalization of the low-frequency Drude resonance. But the development of a pseudogap at low temperature was suggested only in the case of CePd<sub>3</sub> and they concluded that CePd<sub>3</sub> is a lightly doped Kondo insulator. And now, it is very meaningful to reexamine the ground state in this well-known AuCu<sub>3</sub> type cubic structure without complications of disorder.

In order to study the electronic structure of CePd<sub>3</sub> and Ce<sub>0.97</sub>La<sub>0.03</sub>Pd<sub>3</sub>, we performed temperature-dependent ultrahigh-resolution photoemission (PE) and resonant-inverse photoemission (RIPE) spectroscopy. The PE and RIPE spectra well demonstrate that there are two characteristic crossover of CePd<sub>3</sub> around T<sub>K</sub>=210 K and T<sup>\*</sup>= 40 K. As temperature decreases from room temperature, the system takes a first crossover from paramagnetic state into the local Fermi-liquid regime at T<sub>K</sub> with a change in f-peaks ratio in RIPE spectra, that is a change in 4f-occupancy. And with further decreasing temperature, a long-range coherence among the Kondo centers is developed below T<sup>\*</sup> and the DOS around E<sub>F</sub> dramatically changes. Furthermore the clear difference in PE spectra in the vicinity of E<sub>F</sub> between CePd<sub>3</sub> and Ce<sub>0.97</sub>La<sub>0.03</sub>Pd<sub>3</sub> was observed. We believe that this difference in the DOS with small amount of nonmagnetic substitution demonstrates the extremely small carrier concentration in the ground state of CePd<sub>3</sub>.

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**Application of Soft X-Ray Absorption Spectroscopy to the Study of Passive and Oxide Layers of Stainless Steels: Influence of Ion Implantation**

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X-ray absorption spectroscopy (XAS) has been used to study the influence of Si, Ce and Mo ion implantation on the properties of both passive and oxidized layers of AISI 304 stainless steel. The aim of the ion implantation process was to achieve an enhancement of the corrosion and oxidation resistance of this technological material. To investigate the effects of this process on the room temperature corrosion behavior of AISI 304 stainless steel, the passive layer formed spontaneously in contact with air for different ion implanted samples was studied. To analyse the effects of ion implantation at high temperatures, the oxide layer formed on different ion implanted samples after an isothermal oxidation at 1173 K for 32 hours was also studied. XAS was used as an appropriate technique to evaluate the chemical modifications produced by the ion implantation process. The XAS spectra at the Cr, Mn, Fe, Ni, Cu and Si 2p as well as the oxygen 1s thresholds were measured. The composition and chemical state of these species in the passive layer as well as in the oxidized layer generated by heat treatment was evaluated. The XAS spectra exhibit chemical differences between the different ion implanted samples that would give rise to different corrosion and oxidation behavior.

**XPS and TPD Study of CO Interaction with Pd-Alumina and Pd-Aluminum Systems**

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The metal-substrate and metal-metal interactions represent important effects determining the properties of supported catalysts. We investigate the CO adsorption mechanism on Pd particles supported on Al<sub>2</sub>O<sub>3</sub> and Al by the X-ray Photoelectron Spectroscopy (XPS) and Temperature Programmed Desorption (TPD).

CO-metal interaction is investigated by TPD spectroscopy of CO and by XPS of C 1s intensities that exhibit three CO-related components. The CO dissociation activity is monitored as a rise of C 1s signal at 285 eV while the molecularly adsorbed CO exhibits the intensity at 287 eV. An eventual carbidic phase formation is accompanied by the enhancement of the intensity at 282 eV. Pd-substrate interaction is determined from Pd binding energy variations.

The studies show that beside the particle size the metal-substrate and metal-metal interactions play an important role in CO-Pd adsorption process. We show that Pd initial state variations are in relation with the deposit-substrate charge transfer.

**Theoretical and experimental UPS and XAS spectra for misfit chalcogenides and related layer compounds**

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A deep understanding of the nature of chemical bonding in misfit compounds depends upon unambiguous interpretation of experimental spectroscopic data. The applicability of a one-particle theory can be judged by the quality with which complementary measurements are described. Based on the self-consistent band structure we present total and angular momentum projected density-of-states functions for occupied and unoccupied states for supercell structures  $(\text{SnS})_{1.2}\text{NbS}_2$  and  $(\text{PbS})_{1.2}\text{NbS}_2$  and their layer constituents, PbS (NaCl) and 2H-NbS<sub>2</sub> and compare them with available XPS and XAS measurements. All-electron calculations by the extended linear augmented plane wave kp method are compared with pseudopotential calculations for experimental and theoretically optimized crystal structures. To illustrate the relativistic effects due to the Pb atom we calculated optical spectra of PbS which are compared to reflectivity measurements. We present normal emission UPS spectra of the misfits  $(\text{SnS})_{1.2}\text{NbS}_2$  and  $(\text{PbS})_{1.2}\text{NbS}_2$  and explain them in terms of a model which takes into account momentum conservation and photoemission cross-section. The correspondence between electronic structure of the misfit and related layer compounds is discussed and experimentally observed intercalation effects are explained.

**Counting quantum yield of the X-ray photoeffect.**

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On the basis of generally accepted representations of the external photoelectric effect for one-dimensional case the analytical expressions for the counting quantum yield of the high-efficiency photocathodes are given for the X-ray region (1-10 keV).

These analytical expressions obey both "point" model of the X-ray photoeffect and model, in which it is necessary to take into account the terminating path-length fast true X-ray electrons. In process of the absorption of the X-ray photon it has been proposed that the slow secondary electrons have been generated uniformly along the path range of fast true X-ray electron and emitted in the elementary event of the external electron emission. The different methods of the estimation of the mean path length of fast true X-ray electrons have been analyzed. The results of calculations have been compared with our experimental measurements.

The proposed analytical expressions and obtained experimental results for the counting quantum yield allowed to explain the significant increasing (magnification in 3 times) of the complete electron emission in the X-ray region for CsI photocathodes after their special heat treatment.

**Scanning Auger microscopy - Recent progress in data analysis and instrumentation.**

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Progress in the development of instrumentation for scanning Auger microscopy has been slow, with most commercial instruments still relying on cylindrical mirror or concentric hemispherical analysers for the measurement of electron energy distributions. Because they are serial acquisition devices, the most demanding aspects of Auger microscopy, such as spectrum imaging, can be prohibitively time consuming. Moreover if the properties of the surface are changing whilst the measurements take place the results can be difficult to interpret. To lessen these problems a parallel acquisition device, the hyperbolic field analyser (HFA) [1], has been developed.

The HFA can collect an electron energy spectrum ranging from a few tens of eV to greater than 2000eV, divided into 1024 channels. The minimum acquisition time is approximately 50ms, although times of greater than 1s are generally required to obtain a satisfactory signal to noise ratio. One obstacle not shared by conventional serial acquisition analysers is the effect of the variation in efficiency of each of the 1024 channels. Although this variation in the spectrometer function is only a few percent it must be understood before small features can be identified.

Spectrum imaging brings with it problems of how to display data and how to extract useful quantitative information. Although these are not new problems, spectrum imaging with scanning Auger microscopy is not common. Some applications of the HFA will be discussed within this context.

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**Statistics of External X-ray Photoelectric Emission**

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For one-dimensional case on the basis of conventional representations for an external photoelectric effect in X-ray region, the analytical expressions for the distribution function of probabilities of appearance of electron emission events with different numbers of electrons are derived.

The introduced analytical expressions correspond to both "point" model of the X-ray photoeffect and the model, in which the path-length of fast true X-ray electrons appearing as a result of the absorption of X-ray photons by the photocathode atoms are taken into account.

The results of calculations have been compared with the experimental measurements carried out in the ultra-soft X-ray region (60-200eV).

Functions  $P(n)$  of a probability distribution of appearance of electron emission events with numbers of electrons,  $n$ , was measured with the help of the proportional counter with thin organic film used as an input window.

Thin (10nm) and thick (400nm) layers of CsI photocathodes have been investigated.

With the help of a series of the known characteristics of X-ray photoeffect the analytical expressions obtained allow receiving the distribution functions of probabilities of appearance of electron emission events with different numbers of electrons. Hence, all useful information on efficiency of different photocathodes in the X-ray region has been received.

**On Line Shape Analysis in X-ray Photoelectron Spectroscopy (XPS)**

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Any solid state x-ray photoelectron spectrum (XPS) contains contributions due to multiple inelastic scattering in the bulk, surface excitations, energy losses originating from the screening of the final state hole (intrinsic losses), and, for non-monochromatized incident radiation, ghost lines originating from the X-ray satellites. In the present paper it is shown how all these contributions can be consecutively removed from an experimental spectrum employing a single general deconvolution procedure. Application of this method is possible whenever the contributions mentioned above are uncorrelated. It is shown that this is usually true in XPS to a good approximation. The method is illustrated on experimental non-monochromatized Mg K $\alpha$  spectra of Au acquired at different detection angles but for the same angle of incidence of the x-rays. By accounting for the details of the escape process, the contributions to the spectrum mentioned above were consistently removed from the raw data ultimately giving the true intrinsic energy distribution of photoelectrons emitted at the source.

**EELS Investigation of Pd Thin Film Growth on Aluminum Oxide Substrate**

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Electron Energy Loss Spectroscopy (EELS) operated at energies from 250 to 1500 eV was used for coverage analysis of supported non-continuous layers. The alumina supported very thin Pd films were prepared by depositing small amount of Pd on thermally oxidized Al and on sapphire substrates. The film growth was investigated via variations of intensity of excited Pd plasmons and of alumina energy losses. The overlayer coverage was determined from relative contribution of deposit and substrate signal to the composite spectra taking into account the backreflecting capacity of both materials and loss event probabilities [1]. The results show high sensitivity of EELS method to the deposit thickness and continuity.

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**Measurement of the Electron Inelastic Mean Free Path of 23 Elemental Solids in  
the Energy Range 50-3400 eV**

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Electron inelastic mean free paths (IMFPs) have been measured for 23 polycrystalline or amorphous elemental solids (mainly metals) by means of elastic peak electron spectroscopy in the energy range between 50 and 3400 eV. The IMFP was determined by comparing the elastic peak intensity observed experimentally with theoretical values of the elastic reflection coefficient. The theoretical model is based on the solution of a Boltzmann type kinetic equation and neglects coherent scattering. A test of consistency of the data and the employed model revealed that the latter is valid for energies above 150 eV. The results of our analysis, which is based on electron scattering data and is entirely free of linear response theory agrees well with calculations by Tanuma, Powell and Penn [1] based on optical scattering data and linear response theory.

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**Quantitative measurement of surface excitations in quasielastic electron reflection on polycrystalline Al, Si and Au for energies between 200 and 3400 eV.**

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Angle resolved reflection electron energy loss spectra have been measured on polycrystalline Al, Si and Au samples in the energy range between 200 and 3400 eV for two different geometries (constant incidence angle and variation of the off-normal emission angle between 0 and 85 ° and vice versa). Comparison of the angular distributions for these two geometries allows to distinguish the electron surface crossing during incidence and emission. The asymmetry between the incoming and outgoing electron surface crossing that was recently predicted theoretically [1] could not be observed. The number of surface losses excited per surface crossing was measured with an accuracy of 5%. The results are compared with different models for surface excitations available in the literature [1,2,3]

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**The three step model in electron spectroscopy revisited**

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Angle resolved measurements have been performed on polycrystalline Al, Cu and Au samples. Angular distributions were obtained for a fixed angle of incidence under variation of the emission angle and vice versa. In this way, it is possible to distinguish between the penetration of the incoming radiation into the surface and the emission of the characteristic signal electrons from the surface, allowing to separately study the different processes entering the three step model for electron spectroscopy. A detailed comparison of the experimental data with the commonly accepted theories is made for the following phenomena: (1.) Intrinsic energy losses; (2.) surface excitations; (3.) excitation depth distribution in electron excited Auger electron spectroscopy; (4.) escape probability of secondary electrons; and (5.) Angular and energy distribution of Auger and photoelectrons.

**WAVE FUNCTION COLLAPSE WITH INCREASING IONISATION; CHANGES IN BEHAVIOUR IN  
THE ELEMENTS NEAR XENON**

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Recently, changes in 4d photoabsorption with increasing ionisation along the Xe isonuclear sequence in stages up to and including  $Xe^{7+}$  have been studied in merged beam experiments using photoelectron and photoion yield spectroscopy [1, 2]. Experimental data also exist for changes along the barium [3] and iodine [4] isonuclear sequences up to the doubly ionized ion, while the 4d photoabsorption spectra of Sb [5] and Cs in stages up to four times ionized have recently been studied. In the neutrals of these species, photoabsorption spectra above the 4d threshold are dominated by a broad 4d-ef resonance, while below threshold 4d-nf transitions are absent because of the large centrifugal repulsion present in the  $l=3$  channel. In these atoms the potential has a double well character and the nf wavefunctions are essentially eigenstates of the outer well. With increasing ionization the centrifugal barrier disappears and 4f wavefunction contraction into the inner well region results in a transfer of oscillator strength from the continuum to the discrete spectrum.

Two somewhat different situations have been identified whose behavior seems to be determined essentially by the positions of the 4d-nf features in the ion relative to the location, in the neutral atom, of the 4d-ef resonance. Firstly, in the elements immediately preceding Xe in the periodic table, an increase in ionization leads to a gradual erosion of the 4d-ef resonance with its oscillator strength being shared amongst the sub-threshold 4d-nf transitions and with no 'sudden' collapse of the 4f orbital. In Sb, for example, the 4d-nf features, in stages up to  $Sb^{4+}$ , do not extend into the region of the peak of the neutral 4d-ef. Secondly, in Cs and along the Xe sequence there is an abrupt redistribution of oscillator strength from the resonance to the discrete spectrum between the second and third ionization stages where the 4d-nf features are found within the envelope of the neutral 4d-ef resonance. The situation for the Xe isonuclear sequence seems to be intermediate between these two extremes.

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**Rotationally Resolved Two-Dimensional Photoelectron Spectroscopy of Vibrational Autoionisation in Molecular Hydrogen.**

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The resonant excitation spectrum of molecular hydrogen in the region above the first ionisation threshold was measured many years ago using total cross section techniques [1, 2]. In this region ions are produced by vibrational autoionisation in which energy stored in the molecular core is transferred to the Rydberg electron. The ionisation efficiency for states that can decay with a change in vibrational quantum number,  $v$ , of minus one is high. For other states, which cannot decay by conversion of one quantum of vibration, fluorescence and predissociation compete to varying degrees. It is only relatively recently that the rotational selectivity accompanying this vibrational autoionisation has been investigated using synchrotron radiation [3]. In this work the photon energy region below the  $v = 1$  ionic threshold was investigated using two-dimensional photoelectron spectroscopy. In this technique electron yield is measured as a function of both electron and photon energy. Although the photon energy resolution was not sufficient to study the decay routes of all of the Rydberg states resolved in the earlier work, the absence of transitions in which the rotational quantum number of the ion core changed by more than one was established. This was achieved by regarding the spectra, recorded with very good electron energy resolution, as maps of electron yield as opposed to creating conventional ionic state spectra. This propensity for small changes in rotational quantum number, corresponding to an approximate conservation of the rotational angular momentum, can be understood because the rotational period of the heavy nuclei is much larger than the electron transition time [4].

Two-dimensional photoelectron spectra have since been measured over a more extensive region, covering higher vibrational levels of the ion and including electrons with kinetic energies as low as essentially zero. Additional spectra in which the proportion of para-hydrogen was significantly enhanced were recorded to aid in the identification of resonance states. The well known propensity for autoionising decays that minimise the change in vibrational quantum number was observed [5]. More interestingly, broad similarities in the rotational structure of autoionising decays populating successive vibrational levels could be discerned and hence resonance states with anomalous rotational branching ratios identified.

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**Laterally resolved determination of  $sp^2/sp^3$  ratio - investigation of carbon thin films**

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Defects on the  $\mu\text{m}$ -scale on the surface of amorphous carbon (a-C) or diamond films are critical, because they locally change the physical and chemical behaviour. For applications like the use of the films as protective hard coatings there is the need for a technique, which is capable to distinguish quantitatively between carbon phases with different hybridisations and which gives a laterally resolved determination of chemical composition. This goal can be reached by combination of X-ray Absorption Spectroscopy (XAS) with Emission Electron Microscopy (EEM). By combining the site selectivity of the XANES spectroscopy with the lateral resolution of the photoemission electron microscope, it was possible to separate the different phases of carbon, to measure the relative  $sp^2/sp^3$  content of carbon films with microscopic resolution and to detect local graphitic phases on diamond thin films by mapping of the finger- print- like  $p^*$  orbital. Spectral features observed in artificial graphite films can be explained with C-H bonds. In the future, micro- XANES becomes a very useful technique not only for the examination of carbon thin films, but also for a wide range of other coatings, some of them containing carbon. Examples are  $\text{CN}_x$ , WC, SiC, Cr, CrC,  $\text{Al}_2\text{O}_3$ ,  $\text{C}_3\text{N}_4$ . All the chemical elements in these coatings have core levels (K or L edges) in the soft X-ray energy range, which is easily accessible at most of the synchrotron radiation sources presently running.

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**Photoemission from Atoms and Molecules, Orientation and Polarization effects**

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Beyond the characteristic line structure of each photoelectron spectrum, photoemission studies of atoms and molecules can provide information on the dynamics of the photoemission process in form of photon energy dependent partial cross sections and photoelectron angular distributions.

This information is, however, in most cases not sufficient to completely describe the photoemission dynamics in terms of dipole matrix elements. Determination of these matrix elements is the key for a direct quantitative comparison with the various theoretical calculations in this field. One way to achieve this goal is the use of oriented molecules and polarized atoms as a target instead of randomly oriented gas phase targets [1,2]. The photoelectron angular distributions of prepared targets reveal many more dynamical properties of the photoemission, such as different types of dichroism. More generally, these angular distributions are expansions of spherical and bispherical harmonics which are directly related to the transition matrix elements, including their relative phases in a specific way. In atomic photoionization, for example, the magnetic and circular dichroism in the angular distribution of photoelectrons is always proportional to the sine of the phase shift between the  $l+1$  and  $l-1$  components of the outgoing photoelectron waves, whereas in molecular photoionization this quantity is related to the phase shift between the sigma and pi components of the emitted photoelectron waves. These connections will be demonstrated for photoemission from polarized open shell atoms and oriented small molecules. The status of our understanding of the photoemission process in terms of the underlying transition matrix elements is discussed.

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**Circular Dichroism in the Valence-Photoionization of Free NO Molecules**

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We have measured NO  $4\sigma^{-1}$  inner valence photoelectron angular distributions in the molecular frame. Using circularly polarized light of two different helicities we were able to derive the circular dichroism in the angular distribution (CDAD) of the photoelectrons [1]. The CDAD describes the difference between the angular distributions for the two different light helicities. While the angular distributions have to be described by a rather big number of matrix elements and phase shifts, the CDAD is a function of only a few terms containing information on the relative phase shift between the outgoing sigma and pi continuum waves.

The CDAD has previously been measured for molecules adsorbed on surfaces [2]. To our knowledge this is the first time that it has been observed on fixed-in-space molecules in the gas phase. The target molecules were not statically oriented before the photoionization took place. Applying the axial recoil approximation we derived the molecular orientations in the moment of photoionization by measuring the complete velocity vector of the molecular fragments. For this purpose, we developed a time-of-flight and position sensitive photoelectron-photoion-coincidence technique [3].

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**Measurement of X-ray absorption spectra (XAS) of insulators by a partial electron yield method using a electron flood gun**

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XAS spectra of solid samples in the soft x-ray region are obtained by monitoring electron yield or fluorescence yield. The former has an advantage of large yield particularly when the energy of x-rays is lower than 1 keV, but at the same time has a serious problem of charging. In many cases, samples are powdered and dispersed on metal plates to avoid heavy charging. In the present study, we have used a electron flood gun combined with a low-energy Ar ion gun that were recently developed for X-ray photoelectron spectroscopic measurement of insulators (1). The XAS measurements were performed in the partial electron yield mode using a micro-channel plate (MCP) and a retarding mesh to avoid the low-energy electrons from the flood gun. In addition, the whole assembly of the MCP and the retarding mesh was covered with a cylindrical tube so that the low-energy electrons could not reach the MCP. It was found that elimination of charging requires precise control of experimental conditions, such as Ar partial pressure, acceleration voltage and emission current of the Ar ion gun and the flood gun, and the retarding voltage. We demonstrate XAS spectra of several insulating samples including polymers and ceramics.

(1) US. Patent 5,432,345

Decay of Coherently Excited States Produced by Photon-Electron and  
Electron-Electron Interactions: Effects on Angular Distributions

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The angular distributions in spectator Auger decay  $\{Ne1s\}3p \rightarrow \{Ne2p\}3p$  and cascade Auger decay  $\{Ar3s\}\{3p\}4s \rightarrow \{Ar3p\}$  have been analyzed. In both processes the decaying complex is a set of energetically closely spaced atomic states. In Ne it results from the photoexcitation of Ne ground state into four  $\{Ne1s\}3p$  states, whose natural widths exceed their energy separations. In Ar the preceding resonant Auger decay of a photoexcited  $\{Ar2p\}4s$  state produces a set of ionic states, which further decays nonradiatively.

As the decaying state is a coherently excited superposition of atomic states the angular distribution depends on the different excitation probabilities of the atomic states involved, as well as their associated phase differences [1,2]. This requires modifications to the familiar two-step description of the scattering. The resulting angular distributions have been calculated using a relativistic K-matrix code implemented to the multiconfiguration Dirac-Fock package. Configuration interaction and the angular momentum coupling scheme have profound effects on the calculated spectra in both cases [3,4]. Decay of coherently excited states thus provides an excellent opportunity to investigate the electron-electron dynamics.

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**Algorithm to Determine Inelastic Electron Scattering Cross Sections from Reflection Electron Energy Loss Spectra; Applications in Quantitative XPS**

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We present a simple algorithm for separation of elastic and inelastic electrons in low energy resolution REELS and for subsequent determination of the differential inelastic electron scattering cross section. This quantity is required in the QUASES [1] procedure for quantitative XPS analysis of surface compositions with sub nano-meter depth resolution. QUASES analysis only requires the cross section to be known with a fairly low ( $\sim 2$ -5 eV) energy resolution. For fast data acquisition, it is therefore often an advantage to operate the electron spectrometers at a low energy resolution. This however gives rise to considerable overlap between elastic and inelastic electrons in the REELS spectrum. The quality of the algorithm proposed here is tested by application to series of broadened REELS spectra from Si and Fe. These two materials have very different inelastic scattering cross sections and therefore they serve as a good test of the general validity of the algorithm. The application of the determined cross sections for quantitative surface analysis of nano-structure morphologies with XPS is discussed.

[1] <http://www.quases.com>

**PES of liquid early transition metals with high vapour pressures**

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The investigation of liquid elements with PES is restricted to some 20 elements of the periodic table because of the high vapour pressures of the liquid states and the need of UHV conditions in the spectrometer. To overcome this limit we have introduced the new technique of time resolved PES during pulsed laser heating. This technique allowed us to measure several elements in the liquid state of which the early transition metals Ti, V, Zr, Nb, Mo, Hf, Ta and W are presented here. These neighbouring elements which nearly cover a square area of the periodic table were chosen to show an overall trend in the liquid state when going from 3d to 5d metals and varying the number of d-electrons. The 4d metals for which DOS-calculations in the liquid state exist, show a good agreement between theory and experiment in shape and bandwidth. The use of eight subsequent time windows also enabled us to observe the solid-liquid-solid transition as seen by the marked changes in the UPS spectra of the different phases. Furthermore a solid-solid-transition (hcp-bcc) has been observed for the elements Ti and Zr.

Study of electron structure of metal cluster fragments  $[Mo_3S_7]^{4+}$  and  $[Mo_4S_4]^{4+}$

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The experimental ( X-ray emission and XPS) and theoretical study of electronic structure of series of metal cluster compounds with trinuclear  $[Mo_3S_7]^{4+}$  core and simple ligands Cl<sup>-</sup>, Br<sup>-</sup>, dte<sup>-</sup>, (S<sub>2</sub>)<sup>2-</sup> has been carried out. It is interesting to note that in these compounds the shortened contacts between three axial S atoms and anions take place. The charge state of atoms, the density of electron states in the valence band, and partial contributions of metal and ligand atoms to the density of electron states in the valence band have been determined. This information is of interest as basic information for the study of metal cluster compounds with complex ligand surrounding, polymeric structures, and for intercluster and ligand-ligand interactions.

It was found that the charge on atoms of disulphide pair in  $[Mo_3S_7]^{4+}$  is near zero and charge state of disulphide pair atoms is equivalent. The charge on terminal sulphur atoms in the  $[Mo_3S_13]^{2-}$  cluster is negative. In cluster  $[Mo_3S_7Cl_6]^{2-}$  the charge states of Cl atoms are equivalent, but in polymeric compound  $Mo_3S_7Cl_4$  those are different (bridge and terminal atoms). The substitution Cl for ligand disulphide pair brings to the decrease of electron density on metal atoms.

The electronic structure of compounds with cubane cluster  $[Mo_4S_4]^{4+}$  core with simple (Cl, Br, S, Te) ligands has been studied. Structural analysis of polymeric compounds with  $[Mo_4S_4]^{4+}$  cubane cluster with bridge ligands Cl, Br, I shows that the ligands form tetrahedra with shortening interligand distance. The energies, composition and symmetry of occupied and free orbitals have been determined. It is shown that the HOMO correspond to the M-M bonds, but contain the considerable S 3p contribution.

**Investigation of the  $\sqrt{3}\times\sqrt{3}R30^\circ$  Sb/Si(111) structure by X-ray photoelectron diffraction\***

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In the past the structure of thin Sb-films on Si(111) was investigated by several methods [1,2]. Sb is considered as a surfactant for the homo- and heteroepitaxial growth on Si. Therefore Sb intercalation at the surface was investigated for various conditions. For a coverage between 0.9-1.0 ML a  $\sqrt{3}\times\sqrt{3}R30^\circ$  Sb/Si(111) structure was found with Sb-trimers on the surface [1]. We investigated this structure by angle-resolved X-ray photoelectron diffraction. The diffraction pattern of the Sb 3d signal ( $E_{kin}=720$  eV) is dominated by forward scattering. We compare experimental with calculated patterns [3] as a function of coverage for Sb at and below the surface.

In the energy-scanned modus of photoelectron diffraction, the intensity modulation function was calculated for Sb at and below the surface varying the stoichiometry. In this modus only weak modulations from subsurface Sb were simulated. In angle-scanned mode, the calculated  $2\text{-}\pi$  photoelectron diffraction patterns vary significantly if additional Sb is located below the surface. We found preparation conditions where the assumed subsurface Sb-layer concentration was around 0.1 ML. The main features in the experimentally recorded patterns agree well with the calculated results for Sb below the surface. In a first model the amount of subsurface Sb decreases rapidly from the highest concentration at the surface.

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Electronic structure of the quasi-one-dimensional organic conductor TTF-TCNQ\*

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The charge transfer salt TTF-TCNQ is an organic quasi-one-dimensional conductor which at 54 K undergoes a Peierls phase transition into a charge density wave (CDW) phase. Here we present a study of its electronic structure by angular resolved photoelectron spectroscopy (ARPES) and density-functional band structure calculations in the local density approximation (LDA). Our ARPES spectra show two sets of  $k$ -dispersive spectral features in agreement with the results of a previous study [1]. By a comparison to the LDA band structure they can be attributed to TCNQ- and TTF-derived conduction bands, respectively. The position of the Fermi vector accounts well for the observed CDW periodicity. Spectra measured above the Peierls temperature did not recover a metallic Fermi-Dirac edge, but can be characterized by a pseudogap-like spectral onset, possibly caused by CDW fluctuations. Whereas the ARPES data confirm the qualitative behavior of the conduction bands and a splitting of the TCNQ-bands predicted by the LDA calculation, the experimental bandwidths and splittings exceed those of the band theory by more than a factor of two. In the range of the TCNQ-bands we observe an additional spectral feature which is not accounted for by the LDA results. Its behavior is reminiscent of the "shadow band" resulting from  $2k_F$ -fluctuations in the one-dimensional Hubbard model [2], but the observed energy scale is much larger than expected from estimates of the hopping integral  $t$  and the exchange energy  $J$ . We also show examples of rapid surface decomposition induced by the exciting UV radiation, which severely limits the surface lifetime for photoemission studies of the intrinsic electronic structure.

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Vibrational Excitation of CO<sub>2</sub> at the O1s-1  $\sigma_g^*$  Shape Resonance

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X-ray absorption of CO<sub>2</sub> in the immediate O 1s threshold region is characterized by the shape resonant behavior at 542 eV assigned conventionally with a transition into the  $5\sigma_g^*$  molecular orbital. However, in contrast to the O 1s photoabsorption cross section the spectral dependence of the O 1s single hole photoelectron main line does not indicate any corresponding resonance [1]. Post-collision interaction (PCI) occurring in the cation field is the main candidate to rationalize the divergence between these cross sections in the low energy regime, but since the molecular ion assists in transferring energy from the photoelectron to other degrees of freedom, molecular vibrational excitations cannot be neglected. To investigate this channel in photoelectron - photoion interaction the experimental [1,2] and theoretical O 1s threshold behavior of the partial absorption and single-hole ionization cross sections for CO<sub>2</sub> is examined with respect to variations in the vibrational fine structure of the photoelectron main line. To compute the spectral dependence of the absorption and main line cross sections the quasiautomatic and optical potential concepts are applied [3]. The essential energy dependence of the vibrational structure of the photoelectron line at low kinetic energies is attributed to molecular excitations induced by impact of outgoing photoelectron. This inelastic channel in the photoelectron emission of CO<sub>2</sub> couples with intramolecular interference of scattered photoelectron waves to disturb the shape resonance behavior of both the absorption and main line cross sections. To take this interchannel coupling into account the imaginary part of the molecular optical potential is determined based on the electron impact vibrational excitation cross sections for CO<sub>2</sub>. This semi-empirical approach to photoexcitation dynamics gives a clear perspective to bridge shape resonance phenomena in X-ray absorption, photoionization and electron-molecular scattering.

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**High-resolution Core-level Photoelectron Spectroscopy at BESSY II\***

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The high resolution and high flux of the third generation synchrotron radiation source BESSY II has been employed to yield new insights into the structure of the electronic continuum and the nuclear dynamics in molecular core level photoionisation.

The  $3\sigma_u$  resonance of the  $1s$  photoionization channel in  $N_2$  has been one of the key examples in research on shape resonances and just recently has attracted new interest due to the possibility of doing photoionization experiments on aligned molecules [1]. By presenting results in which the gerade/ungerade splitting of approx. 95 meV in the N  $1s$  photoelectron line is resolved, we can show the first observation of the selective amplification in the  $1\sigma_g$  component by the shape resonance. In accordance with theory even at high kinetic energies the intensity ratio of the two components is not unity.

In two aromatic molecules, benzene ( $C_6H_6$ ) and furan ( $C_4H_4O$ ), the vibrational structure of the C  $1s$  photoelectron line has been resolved. In both cases, the excitation of a low energetic (~100-130 meV) mode dominates and has a coupling constant unusually high for inner shell photoionisation. Comparison of the spectra of benzene and deuterated benzene shows no significant change in frequency, which leads us to assign these low energy vibrations to deformations of the carbon ring structure.

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**Dynamical Localisation in the C 1s Photoionisation of Hydrocarbons\***

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Interaction of the electronic and vibrational structure of photoionic states, so-called vibronic coupling, has been recognized in the last few years as an important effect in core level photoionisation. A prerequisite for this mechanism to occur is the existence of closely spaced electronic states of different symmetry, which can be coupled by

a non-totally symmetric vibration. In the showcase example, O 1s photoionisation of CO<sub>2</sub>, the gerade and ungerade vacancy states are coupled by an antisymmetric vibration [1]. While in CO<sub>2</sub> the totally symmetric and antisymmetric vibrations are clearly separated energetically, this is not the case in other molecules, e.g. typical hydrocarbons. In the C 1s photoelectron spectra of ethene (C<sub>2</sub>H<sub>4</sub>) and ethane (C<sub>2</sub>H<sub>6</sub>) for example, the major vibrational feature is the excitation of a C-H stretch mode, which by its energy alone could be assigned as symmetric or anti-symmetric, that is caused by vibronic coupling. These results can be compared with the spectra of the asymmetrically deuterated isotopomers, (1,1 C<sub>2</sub>D<sub>2</sub>H<sub>2</sub>) and (1,1,1 C<sub>2</sub>D<sub>3</sub>H<sub>3</sub>). In both cases an analysis in terms of two localized C-H and C-D modes is favoured rather than a delocalized mode involving H and D movements. This result is not trivial, since the electronic symmetry of the molecule is not broken by the deuteration. In a matrix formalism for the vibronic Hamiltonian [2] it is possible to relate the vibrational spectra of non-deuterated and asymmetrically deuterated molecules and thus to derive results even for the cases where the two modes in question cannot be separated spectroscopically.

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**Angle Resolved Photoemission: today's applications and future perspectives using VUV FEL-Radiation**

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Angle resolved photoemission in the VUV regime is today's most powerful tool for the determination of the electronic structure of a variety of materials. Band mapping has developed as routine application of the technique. More sophisticated modes taking angular distributions of photoelectrons at varying photon energies provide full k-space access of the electronic structure and gain insight into the topology of Fermi surfaces. Photoemission line shape studies enable to study properties of the ground state such as spectral functions. With modern synchrotron radiation sources high energy- and angle- resolved experiments can routinely be performed. They generally suffer, however, from spatial integration due to the limited size of the light spots.

Choosing the quasi two dimensional layered material 1T-TiTe<sub>2</sub> as model system we give examples for today's applications of photoemission regarding band structure and Fermi surface determinations in first and higher Brillouin zones. We show the reliability of Fermi surface determinations using standard approaches like maximum intensity or -gradient methods and develop an accurate procedure for the determination of Fermi vectors. Line shape studies of the Ti3d band performed to obtain details of electron-electron and electron-phonon interactions elucidate the limits of today's photoemission.

To push the limits either sample qualities or spatial resolution need to be increased for high energy- and angle resolving experiments. We present perspectives for an angle resolved photoemission nanoscope aiming at combined resolutions up to 1 meV, 0.1° and 10 nm using VUV radiation of the Free Electron Laser currently developed at HASYLAB / DESY.

**Interaction of the Metastable Molecular Oxygen with the Dangling Bonds of a Si(111)-(7x7) surface**

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We have measured the valence band spectra of oxygen adsorbed Si(111)-(7x7) surface by ultraviolet photoemission spectroscopy (UPS) for understanding the interaction between the metastable molecular oxygen and the Si dangling bonds. In order to observe the Si surface states and the states originated by the adsorbed oxygen clearly, we adopted three different measurement geometries using the linearly polarized synchrotron radiation light. Using these three geometries, we see that three metastable states grow up simultaneously at 2.1, 3.8 and 5.1 eV following the decrease of the back-bond state as the dosage increases. The growth of the metastable states saturate at a dosage of approximately 1 L. After annealing the sample at 600 K, the three metastable states disappear and an unusual state attributed to the dangling bond is observed at 0.5 eV. When we dose oxygen to the surface, which atomic oxygen is already adsorbed into the back-bond, the growth of the metastable states becomes fast and saturates at a dosage lower than 1 L though their intensities do not decrease. These results lead to a conclusion that the metastable molecular species does not interact with a dangling bond of the Si(111)-(7x7) clean surface, but with a dangling bond modified by an atomic oxygen adsorbed into the back-bond. We will also present the STM/STS results to show the difference in the binding energy and density of states between the dangling bonds of the Si(111)-(7x7) surface and those of the dangling bonds modified by atomic oxygen adsorbed into the back-bond.

Band structure of the misfit compounds  $\text{NbS}_2\text{PbS}$  and  $\text{NbS}_2\text{SnS}$ : Experiment and Theory

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Because of the attractive features of the van der Waals epitaxy and because of the general two-dimensional properties of the layered dichalcogenides, new heterostructure compounds intermixing these materials of hexagonal symmetry with layers of the cubic chalcogenides are highly interesting. The resulting structures of alternating hexagonal and cubic symmetry exhibit a misfit with respect to one of the layer parallel crystal axes which suggests new binding types to occur. The misfit layer compounds  $\text{NbS}_2\text{PbS}$  and  $\text{NbS}_2\text{SnS}$  may be viewed as PbS or SnS double layers inserted into each van der Waals gap of the transition metal dichalcogenide  $\text{NbS}_2$ . Contrary to the very weak bonding between the layers of simple transition metal dichalcogenides the misfit compounds reveal a rather strong coupling. Consequently, the electronic structure of misfit compounds is expected to differ particularly for those orbitals responsible for the inter layer coupling.

Employing angle resolved photoemission spectroscopy using synchrotron radiation in combination with band structure calculations we determine experimental and theoretical momentum resolved band structures for the misfit compounds  $\text{NbS}_2\text{PbS}$  and  $\text{NbS}_2\text{SnS}$  which were grown by chemical vapor transport. The high quality of the crystals was confirmed by x-ray diffraction. Structural parameters entering the calculation of the electronic structure were obtained from wide angle reflectivity data. On the basis of an high accuracy extension of the linear augmented plane wave method (LAPW) the densities of states resolved with respect to atom and orbital contributions and the band structure have been calculated for the misfit compounds as well as for their constituents  $\text{NbS}_2$ , PbS and SnS. The comparison between experiment and theory lays special emphasis on the deviations from a simple superposition of the electronic structures due to the strong bonding between the layers of the misfit compounds.

**New Approaches to the Determination of Fermi Vectors by ARPES**

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Angle resolved photoelectron spectroscopy (ARPES) in combination with synchrotron radiation is a well-established tool for directly probing the k-space information of the electronic structure of solids. With the recent improvements in resolution and in collecting photoemission data from the full hemisphere ARPES has particularly emerged as a powerful approach to the determination of Fermi surfaces of high temperature superconductors and other correlated electron systems. The accuracy of Fermi surface mapping by ARPES, however, has rarely been questioned and it turns out that even for the extensively studied BiSrCaCuO it seems to be not at all clear whether the topology of the normal state Fermi surface shows hole-like pockets around the corners or electron-pockets around the center of the Brillouin zone [1].

It is generally assumed that ARPES measures the spectral function of the one-particle system times the Fermi function which leads to simple criteria for extracting the Fermi vector from photoemission data like (i) maximum intensity at the Fermi level, (ii) maximum gradient of the energy integrated photoemission intensity or (iii) fitting ARPES peak positions over several emission angles and extrapolating the dispersion to the Fermi level. However, none of these techniques explicitly considers the detailed mechanism of the photoemission process. In particular, matrix element effects are totally neglected and make these simple criteria highly questionable.

Employing high resolution photoemission spectroscopy on the Fermi liquid reference compound 1T-TiTe<sub>2</sub> we show here that the simple methods (i), (ii) and (iii) suffer from systematic errors of up to 15% with respect to typical Brillouin zone dimensions and demonstrate how the Fermi vector component parallel to the surface can be determined with high accuracy when matrix element effects are explicitly eliminated either by subtracting ARPES spectra taken at different temperatures or by correcting the maximum gradient method for the matrix element factor. In addition, we show that the Fermi vector component perpendicular to the surface can be extracted from photoemission measurements with various photon energies by comparing the photoemission intensity map with state of the art band structure calculations.

[1]Y. Chuang et al., Phys. Rev. Lett. 83, 3717 (1999)

Molecular-Field Splitting of  $2p_{3/2}$  Levels in Second-Row Atoms

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Technological improvements have recently allowed spectroscopists to resolve or deconvolute into two components the  $2p_{3/2}$  peak in spectra of molecules containing phosphorous, sulfur, and chlorine. This splitting, found in molecules of less than cubic symmetry, arises because the less symmetrical molecular surrounding of the core hole removes some or all of the degeneracy of the  $2p$  orbitals. It is therefore referred to as molecular-field splitting. In particular cases, such as in  $SC_2$ , the molecular-field splitting is a major feature of the high-resolution spectrum, and it needs to be included in any reasonable model of the spectrum. However, more than adding complexity, the molecular-field splitting offers information about the asymmetry of the electric potential about a specific atom.

The present contribution is concerned with the theoretical description of molecular-field splitting, both from a conceptual and a computational point of view. The underlying physical mechanisms are firstly discussed within the framework of an electrostatic model, which, however, fails to predict the correct magnitude of the observed splittings. Next, an accurate ab initio model is presented, capable of reproducing the molecular-field splitting to essentially experimental accuracy. A key point in these calculations turns out to be the inclusion of core-valence electron correlation. While these calculations are quite demanding with respect to computer resources, it is subsequently shown how second-order Moller-Plesset perturbation theory may be used to obtain useful estimates of the core-level splitting even for medium-sized molecules.

Based on the ab initio calculations, a qualitative model is developed for molecular-field splitting of the  $2p$  shell in second-row atoms. This model facilitates a discussion of what may be learned about the valence electron structure from

observing the splitting of a deep core level like  $S2p$ . The question of whether chemical effects may be manifested in the splittings observed in  $2p$  photoelectron spectra is examined in the case of sulfur.

**Auger Resonant Decay Following  $1s \rightarrow np$  ( $n=3,4,5$ ) Excitation in Neon**

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The decay of inner shell excited states provides relevant spectroscopic informations on atomic states as well as a deep insight on the relaxation mechanisms of the inner hole. The energy of the excited ion states are obtained from the positions of the peaks in the spectrum, whereas the relative line intensities gives informations on transition matrix elements. The predictions of the decay spectra is also a severe test for theoretical models.

Neon is the simplest closed-shell system where calculations can be performed, and it is the best candidate for this kind of study. Whereas the decay of the  $1s$  hole has been widely studied [1], less attention has been devoted to the decay of the ( $1s^{-1} np$ ) excited states. To our knowledge, only the results of the non-radiative decay of the  $1s \rightarrow np$  resonances to the  $2p^{-2}$  final ion states have been reported in the literature [2,3].

Following a previous study of the photoabsorption spectrum in the region of the  $1s \rightarrow np$  ( $n=3,4,5$ ) excitations [4], here we report on an experimental and theoretical study of the non-radiative decay spectra of those resonances.

The multi-analyser apparatus of the GasPhase Photoemission beamline at Elettra, equipped with ten individual electron spectrometers, was employed in this study. Each analyser has a resolving power and an angular acceptance that can be varied up to 5000 and from  $\pm 0.5$  to  $\pm 3$  deg, respectively, to match experimental requirements. The analysers are mounted on two frames and can be positioned at different angles with respect to the photon polarisation direction. Moreover the summed signals from the ten analysers can be used to obtain angular-integrated cross sections, with a high overall luminosity.

We have obtained Auger decay spectra in the kinetic energy range from 750 to 820 eV. All the allowed non-radiative decays to the final ion states with  $[2s^{-2} n'p]$   $[2s^{-1} 2p^{-1} n'p]$   $[2p^{-2} n'p]$  electronic configurations, where the last ones correspond to metastable states, and the others can further decay via Auger/Radiative emission, have been observed. The positions of the measured peaks are consistent with the  $Ne^{+}$  excited states measured in photoemission spectra [5,6]. A comparison with the predictions of an ab-initio calculation will be also presented.

High-Resolution Photoemission studies of the Layered Perovskite  $\text{Sr}_2\text{RuO}_4$ \*

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We present new angle-resolved photoemission (ARPES) data on the quasi-two-dimensional strongly correlated material  $\text{Sr}_2\text{RuO}_4$  and address the controversy between the Fermi surfaces derived from the de Haas van Alphen (dHvA) and earlier ARPES measurements. In contrast to the previous reports, we find that the ARPES Fermi surface is in agreement with that measured in the dHvA experiments. We demonstrate that extended Van Hove singularity detected in the early experiments and interpreted in the terms of the hole-like Fermi surface exhibits a strong temperature dependence and disappears completely at  $\sim 130\text{K}$ . In addition to the Van Hove singularity we are able to resolve two bands forming the electron-like Fermi surfaces detected in the dHvA experiments. Further we identify spectroscopic signatures of the crossover from 3-dimensional to 2-dimensional metallic behavior observed in the transport measurements. Finally, we discuss the nesting properties of the Fermi surface in view of recent neutron scattering measurements that have revealed incommensurate spin fluctuations in this material.

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**Correlation effects in Auger cascade studied by angle resolved Coincidence Electron Spectroscopy : the  $1s \rightarrow 3p$  excitation in neon.**

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The decay mechanism of a core excited atomic state is of particular interest when the ion formed by the Auger resonant emission decays further, via emission of a second-step Auger electron. It has been shown [1] that in this case, measurement of the angular correlation between the two ejected electrons can highlight the dynamic of the decay process, as well as provide spectroscopic information of the states involved.

We report on the study of the cascade decay of the  $1s \rightarrow 3p$  resonant excitation in neon, where a resonant high energy Auger electron  $e_{A1}$  (kinetic energy 787 eV) is emitted in a first step leaving the single ion in an excited state  $[2s\ 2p^5\ 3p, ^1P]$ . The ion undergoes a further decay to the double ion state  $^1D$  or  $^1P$ , with the emission of a second step Auger electron  $e_{A2}$  at lower energy (22.5 eV and 25.5 eV respectively).

The angular correlation between the two final electrons  $e_{A1}$  and  $e_{A2}$  has been measured for the first time, in a coincidence experiment performed at the Gas Phase beam line of ELETTRA [2]. This type of investigation is not far from the so called complete experiment, defined as the one capable of fully determining the quantum-mechanic quantities for a process, and neon is the simplest closed shell atom, for which an ab-initio theoretical approach to inner-shell processes can be attempted.

The present study is the extension of previous experiments, consisting of the high resolution Ne K-shell photo-excitation spectrum [3] and of the measure of the angle resolved, resonant non radiative decay. The various Auger de-excitation channels have been observed throughout the series

$[1s^{-1}\ np]$ , for  $n=3,4,5$  and for the different final configurations  $[2p^4\ mp]$ ,  $[2s2p^5\ mp]$  and  $[2s^{-2}\ 2p^6\ mp]$ . The multi-coincidence apparatus of the beamline was employed. It is equipped with ten individual electron spectrometers and is particularly suited for measuring angular distributions of coincidence signals, with count rates as low as few  $10^{-2}$  Hz per pair of detectors.

The results show an evident increase in the anisotropy of the coincident signal, whose amount changes with the state of the double ion and depends on the orientation with respect to the light polarisation. It has been amply discussed in the literature how it is possible, from these experiments, to extract information on the ratio of transition amplitudes and on phase differences.

Both results, coincidence and uncorrelated spectra of the  $e_{A1}$  and  $e_{A2}$  electrons will be presented at the conference.

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**Mechanism of Ion Desorption Reaction of PMMA Thin Film Induced by Core Excitation**

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Site-specific bond scission following core excitation has been studied for the aim of controlling chemical reactions. Recently, it became clear that PMMA (polymethylmethacrylate) thin film indicates remarkable site-specificity in the photon stimulated ion desorption (PSID)[1]. Auger electron-photoion coincidence (AEPICO) experiments have been performed in order to clarify the PSID mechanism of PMMA using Hiroshima synchrotron radiation source (HiSOR). Remarkable enhancement of  $\text{CH}_3^+$  ion coincidence signal in the higher Auger energy region was observed at the specific resonant core excitation of carbon atom in the methoxyl group.

In this work, we have reproduced Auger electron spectra of PMMA using ab initio calculation and specify the Auger final states leading to the site-specific bond scission. Methylisobutyrate was used in the calculation as a model molecule of PMMA monomer-unit, and optimized using HF/cc-pVDZ. Auger transition probability is approximated as overlap integral between the initial core orbital and the final valence orbital. Because the core orbital is localized at a specific atom, this overlap was evaluated as Mulliken population of the valence orbital on the specific atom. Auger electron energy was obtained from the difference in total energies between neutral and ionic molecules.

The result of the calculation at carbon atom in the methoxyl group indicates that Auger final states involving valence holes in the O- $\text{CH}_3$  bonding orbitals exist in the higher Auger energy region. This suggests that the Auger final states enhance the O- $\text{CH}_3$  bond scission observed in the AEPICO experiments.

\*Work supported by a Grant-in-Aid on Research for the Future "gPhotoscience" (JSPS-RFTF-98P01202) from Japan Society for the Promotion of Science.

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**First principle calculations of core-hole effects on Fe K $\beta$  spectra under high-pressure**

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It is well known that the Earth's core is essentially composed of solid iron or iron-dominated alloys. The structural and magnetic properties of these materials under high-pressure conditions are very important to understand our Earth. Structural properties have been widely studied both experimentally and theoretically. Satellite intensities of K $\beta$  spectra emitted from 3d transition metals are very sensitive to spin-state in condensed matter. Recently, K $\beta$  x-ray emission spectra of iron and iron oxides and sulfides were measured under high-pressure conditions [1], which lead to estimate magnetic moments, i.e. spin-state of 3d in iron atom, under high-pressure conditions through the line shape analysis of x-ray emission spectra.

First principle calculations are performed here in order to estimate spin-state of iron in pure-iron, and iron oxides and sulfides under high-pressure conditions. Two kinds of calculational methods, a) the Full-potential Linearized Augmented Plane Wave (FLAPW) [2] and b) the Discrete Variational X $\alpha$  (DV-X $\alpha$ ) [3] methods, are employed for ground state calculations, i.e. state without core-hole, changing a volume of crystal. The DV-X $\alpha$  methods are used for the calculations with core-hole, in which initial and final states of K $\beta$  x-ray emission are calculated. Large differences in spin states between these two states with and without core-hole are found by these calculations.

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**Soft X-ray Absorption Edge Spectroscopy of Gaseous and Solid Inorganic Species**

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Precise measurement of the X-ray absorption edge energy value and structure provides detailed chemical and physical environmental information about the particular element in its compounds. In favourable situations details of the electronic structure are also obtained. We have systematically measured absorption edges for a variety of solid and gaseous inorganic compounds which have been selected to span the widest range of valence state and molecular structure environments as possible for the elements in order to provide a basis for analyzing comparative behaviour. Our studies have focussed, in particular, on compounds containing nitrogen, phosphorus and sulfur. In cases where two elemental edges are present (e.g. K and L edges of phosphorus) both edges have been measured. The edge position variation with valence and structure provides a fingerprinting "chemical shift" and trends in chemical shift have been analyzed and compared. Examples of detailed spectroscopic analysis of simple gaseous molecular species such as  $\text{NSF}_3$ ,  $\text{OPF}_3$ ,  $\text{NF}_3$ ,  $\text{PH}_3$ ,  $\text{PF}_3$ ,  $\text{PF}_5$  etc., supported by  $X\alpha$  and Gaussian calculations, will be presented with comparisons. Edge analyses of selected solids such as binary transition metal phosphides and transition metal phosphine and sulfide complexes will also be described. Most measurements have been done on the CSRF DCM, Grasshopper and SGM monochromators with some additional measurements taken on the SRC HRMON monochromator.

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Orientation of unsaturated hydrocarbons on Pd(110) studied with NEXAFS and STM

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On almost all of transition metal surfaces, the rehybridization of the ethylene molecular orbital occurs upon adsorption to give di-sigma arrangement and results in the loss of the C--C double bond character. However, few of the exception is ethylene adsorption on Pd surfaces where pi-bonding at low temperatures is found like that at noble metal surfaces [1,2]. On noble metal surfaces, it desorbs without decomposition upon raising the sample temperature. In contrast to this, on Pd(110), the adsorbed ethylene is dehydrogenized into the adsorbed ethynyl.

In this study, the adsorption structure of ethylene and ethynyl is studied by near-edge x-ray absorption spectroscopy (NEXAFS) and scanning tunneling microscope (STM). The adsorption site of these molecules are determined on the basis of the STM image analysis. A top adsorption site is found for the adsorbed ethylene, and a short bridge site is found for the adsorbed ethynyl. From the azimuth dependence of shape resonance in NEXAFS spectra, the orientations of these adsorbed molecules are determined. The alignment of the C--C bond is different between these molecules. The C--C bond aligns along  $\langle 1-10 \rangle$  for the adsorbed ethylene and that aligns along  $\langle 001 \rangle$  for the adsorbed ethynyl.

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**Optical Spectral Weight and the Physics of Correlated Electron Systems**

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Abstract: The essence of the 'strong correlation' problem is that interactions reduce the ability of electrons to move in a solid. Optical conductivity probes, over a wide range of time scales, the ability of electrons to move, and is therefore a key probe of correlated electron physics. A simple and robust feature of the conductivity is the 'spectral weight'; the integral of the conductivity over a frequency range. I will present theoretical results for spectral weights of correlated electron systems and, by comparing these to data, show how they elucidate the physics of manganites, high temperature superconductors and other materials.

The dominant interaction in the manganites will be shown to be the electron-phonon coupling while the interaction in the cuprates will be shown to be of electron-electron origin. Optical evidence for non-fermi-liquid behavior will be presented.

Desirable extensions of our measurement capabilities will be mentioned.

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**Understanding Electronic Structure of Bi(Pb)-Sr-Ca-Cu-O Compounds**

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Transition metal oxides exhibit a wide range of behavior ranging from high temperature superconductivity to insulators as well as wide and narrow band gap semiconductors. In high  $T_c$  cuprates, the  $\text{Cu}_2\text{O}$  plane is the basic structural ingredient for the electronic properties and hence one of the main objects of many theoretical models. The Cu K-edge X-ray absorption spectroscopy on high  $T_c$  cuprate systems provides information on electronic and atomic structure around the central photo absorbing Cu atom. We present the experimental results of Cu K edge X-ray absorption near edge structure (XANES) of  $\text{Bi(Pb)}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  (Bi2212) and  $\text{Bi(Pb)Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$  (Bi2223) superconducting compounds measured at Synchrotron Radiation Research Center, Taiwan. These spectra are compared with Cu K edge of CuO and  $\text{Cu}_2\text{O}$  to derive the electronic structure of these novel superconductors.

**Resonant and non resonant photoelectron emission and Auger emission from molecules\***

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A review will be given of recent research on free molecules using undulator radiation from a third generation synchrotron radiation source in combination with high-resolution electron spectroscopy in order to study resonant and non resonant emission of electrons from free molecules. The work has been performed at beam line I411 at the MAX II laboratory[1,2]. This new facility makes it possible to study photoelectron and deexcitation spectra, excited around the C1s, N1s, O1s and F1s edges, under full vibrational resolution. By examples from several molecules it will be shown that this spectroscopy has a very large potential for information. The simplest form of the Lifetime Vibrational Interference (LVI) theory is not adequate for describing the experiments at this level. The experimental results will therefore be compared to more advanced theoretical models, including several new types of resonance mechanisms.

\*Work supported by the Swedish Natural Science Research Council (NFR)

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[2] M. Bässler et al. to be published

**Role of the Incident Beam Diffraction in EELS of Metal Surfaces \***

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Recently we have performed the calculations [1], which show that, in contrast to the "dipole-mode" treatment of inelastic scattering at surfaces, when the incident electron penetration under the surface is neglected, much difference in the calculated spectra arises, if this electron is allowed to enter under the surface before being reflected. As an example, the intensity of the multipole plasmon grows by about two orders of magnitude. In that preliminary work, we used very simple model of the incident electron reflection from the hard-wall at some depth into the metal and RPA dynamic response of the surface. While in the dipole regime the kinematics of the incident electron does not influence the energy-loss spectra, which are determined by the energy-loss function only [2], when an electron penetrates under a surface the exact kinematics becomes of major importance. Now we present the calculations using the 'realistic' LEED wave- functions of elastic scattering and TDLDA dynamic response of the surface. The calculations are performed for (100), (111), and (110) surfaces of Cs, K, Na, and Al . A good agreement with experimental EELS in regard of relative intensities of the bulk, surface and multipole plasmons is obtained.

\* Work supported by Grant - in - Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

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**Electronic structure of water in Ih ice studied with core-level spectroscopies**

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Hydrogen has a unique property to form asymmetric bonds to neighboring atoms. Ice is a unique material that hydrogen and oxygen atoms in the crystal are connected both covalent and hydrogen bonds. Well known unusual physical properties are strongly connected to this unique bonding in ice. Does hydrogen bond have covalent or ionic bonding nature? This has been controversial since the age of Pauling [1].

Here we report electronic structure of water in Ih ice, a thin film grown on Pt(111), studied with combination of core-level spectroscopies, near edge X-ray absorption spectroscopy (NEXAFS), X-ray emission spectroscopy (XES) and resonant inelastic X-ray scattering spectroscopy (RIXS) and theoretical simulation (DFT calculation). The experiments were performed at MAX-LAB, Sweden. The details of the endstation is described elsewhere [2]. The theoretical simulation of spectra was done using the deMon program [3].

NEXAFS and XES results indicate a reconfiguration of molecular orbitals of water upon hydrogen bond network formation. In O-K edge NEXAFS,  $4a_1$  resonance is severely suppressed indicating a pseudo totally symmetric character of this orbital. This pseudo totally symmetric character is confirmed by missing of p-character in  $3a_1$  orbital in XES. From above evidences, we propose the symmetrization in the electronic structure of water in Ih ice.

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Vibrationally Resolved Resonant Auger Studies of Core-Excited NO Near N and O K-edge

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Nitricoxide is an interesting molecule because of its open-shell structure as well as an intermediate case between N<sub>2</sub> and O<sub>2</sub>. Theoretically, the resonant Auger calculations have been sited within the framework of lifetime vibrational interference (LVI)[1] which does not examine the possible interference among different electronic intermediate states. Experimentally, so far the previous core-level resonant Auger studies of NO have been limited by rather poor excitation- and electron-energy resolution of over 700 meV [2]. Consequently, those result in a large incoherent excitation of the intermediate states and vibrationally unresolved decay spectra; the later in turn smears out certain interference effects which otherwise could have been observed.

In this work, angle-resolved RA studies at both N and O K-edge are carried out systematically in conjunction with angle-resolved partial electron yields measurements. The experiments were performed at the undulator beamline I411 at the MAX II storage ring in Lund, Sweden [3]. The beamline is equipped with a modified SX700 monochromator and a rotatable hemispherical SES200 electron spectrometer. With a 5-mm-exit-slits setting, the photon-energy bandpass at N and O K-edge is around 70 meV and 105 meV, respectively. Thus we were able to achieve photon energy resolution less than or comparable to both the spacing and the lifetime width of the vibrational intermediate states involved in the core-excitation process [3], and combining with an 80-meV electron spectrometer resolution, to resolve a large number of vibrational final states. Not only the new experimental results provide opportunity to examine calculations, such as vibrational potential curves, more closely than those by absorption measurements, but also the data analysis show that the LVI framework alone is not adequate to fully describe our experimental findings.

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**Spatial Variations of the Interface Composition during Surface Chemical Reactions**

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A common phenomenon in heterogeneous catalytic processes is the development of spatiotemporal patterns, which in fact represent propagating reaction fronts resulting in regions of different composition and structure of the interface including adlayer and the catalyst surface [1]. Photoelectron spectromicroscopy developed at the third generation synchrotron sources provides essential information for the chemical identity and local concentrations of the surface species, which was the main obstacle for modeling the reaction-diffusion processes in reactions when the adlayer contains more than one adsorbate.[2, 3]. Here we will present the most recent study on the development of lateral variations in the surface composition during  $\text{H}_2 + \text{O}_2$  reaction on a K-covered Pt and Rh(110) surfaces. The experiments were performed with the scanning photoelectron microscope at Sincrotrone Trieste. The K 2p, K 3p, O 1s, Rh 3d and Pt 4f electronic levels were used as fingerprints of the interface local chemical composition. Combination of chemical specific imaging and micro-spot spectroscopy have provided direct evidence for lateral re-distribution of K occurring during the  $\text{H}_2 + \text{O}_2$  reaction. The role of the substrate was manifested comparing the local composition of the reaction patterns formed under the same reaction conditions on a Pt patch deposited on a Rh(110) surface. The effect of the coadsorbed species on the effective strength of the K-substrate bond and on the K mobility are considered as key factors for the observed self-organization processes leading to depletion of K behind the propagating reduction front and accumulation of K in the rest O-covered areas.

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**Vibrationally Resolved X-ray Photoelectron Spectra of C1s and N1s in Hydrogen Cyanide**

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The electronic structure of cyanide and nitrile compounds, featuring a carbon-nitrogen triple bond, leads to a rich chemistry and presents interesting systems for spectroscopic studies.

In particular, the simplicity of the HCN molecule allows for detailed interpretations of the spectra.

In spite of this, hydrogen cyanide is rarely studied, possibly due to its toxicity.

In this study, the carbon and nitrogen 1s levels of hydrogen cyanide were investigated using X-ray photoelectron spectroscopy. The experiments were performed at MAX II, Sweden's third-generation synchrotron radiation source, at beam-line I411. Thanks to the combination of a high-resolution SX-700 monochromator and an SES 200 electron

spectrometer, spectra of outstanding quality were obtained, including well-resolved vibrational structures.

In order to aid interpretation of the vibrational structures, high-level ab initio calculations were carried out for the neutral molecule as well as for the two core-hole states, providing accurate geometries, vibrational frequencies and normal modes for these species. The thus computed vibrational energies and Frank-Condon factors afford excellent fits to the experimental spectra.

The C1s spectrum shows a strong adiabatic transition accompanied by well-resolved transitions to three excited levels in the C--N stretching mode. It is noteworthy that the C--H mode is not excited to an appreciable extent in this case.

In the N1s spectrum, the adiabatic transition is seen together with transitions to excited states of both the C--N and C--H stretching modes, with somewhat higher intensity associated with the former of these. We find that the spectrum is well described when vibrational states of 0, 1, and 2 quanta of energy are taken into account.

**Electronic Surface States and Surface Magnetism of Fe(110) and Co(0001)**

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To investigate the surface electronic structures of Fe(110) and Co(0001) and the correlation of the electronic states with the magnetic properties of the respective surfaces, we performed spin-polarized inverse photoemission (SPIPE) and spin-polarized secondary electron emission (SPSEE) measurements on ultrathin Fe and Co films, epitaxially grown on W(110). The closed packed surfaces of Fe(110) and Co(0001) both have wide energy gaps at the center of the surface Brillouin zone, which allow the existence of electronic surface states. Using SPIPE on Fe(110), a crystal-induced sp-like surface state at the Fermi edge has been detected for the first time. Despite of being crystal induced the surface state exhibits only a small exchange splitting of about 0.1 eV, probably due to certain peculiarities of the Fe band structure close to the N point, which will be discussed in detail. In contrast, the corresponding crystal-induced surface state on Co(0001) shows a clear exchange splitting of 0.7 eV with the majority spin component just above the Fermi edge. Besides these crystal-induced states there are also image-potential surface states on Fe(110) and Co(0001). They are located at 4.4 and 4.6 eV above the Fermi level with similar exchange splittings of 77 and 73 meV for Fe and Co, respectively. The similar size of the splittings, in spite of the quite different exchange splittings of the magnetic d bands, is explained with the energetic positions of the states within the energy gaps. All results are well described within the theoretical framework of the one-step model of inverse photoemission. Additional SPSEE measurements reveal changes of the surface magnetization concerning size and direction. Adsorption studies with H<sub>2</sub> and CO on Fe(110) will be presented that give further insight into the correlation between magnetic and electronic properties. H<sub>2</sub> adsorption leads to an increase of the spin polarization of emitted secondary electrons. For CO adsorption on Fe films of about 20 monolayers thickness an in-plane spin reorientation transition is observed. This transition can be reversed by electron-stimulated desorption of CO. The observed changes in the magnetic properties are discussed along with SPIPE results on the electronic structure.

High resolution K-edge spectroscopy of oxygen transient species: excitation and ionization of the metastable O<sub>2</sub> singlet molecule and O (<sup>3</sup>P) atom.

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Abstract:

The high photon intensity and resolution available at third generation synchrotron undulator beamlines is revealing finer details in the soft x-ray spectra - particularly of small molecules. The higher sensitivity also allows the study of some elusive species, reactive intermediates and metastable molecules and atoms.

In this work the K-edge photoionization spectrum of metastable O<sub>2</sub> molecules in their first excited singlet state and O (<sup>3</sup>P) atoms has been investigated at high resolution. Both species were prepared on-line using a microwave discharge.

For the molecule the transition to the  $\pi^{*1}\Pi$  state has been identified below the ionization threshold, using total-ion-yield spectroscopy. Above the edge the previously unobserved <sup>2</sup> $\Delta$  state of the O<sub>2+</sub> core-hole ion has been located by photoelectron spectroscopy. The results provide a link between the singlet and triplet manifolds of the core excited states of the oxygen molecule.

The 1s excited states of the oxygen atom were also studied. The high resolution allowed the characterization of higher members of the Rydberg series and first lifetime measurements of those states.

**Needs and Applications of Electron Spectroscopy Within The Wafer Semiconductor Processing Industry**

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The future health of the semiconductor processing industry depends on its ability to continuously shrink critical dimensions (CD), such as gate lengths and thickness, interconnect line widths and via sizes, and barrier layer thickness. This, plus the explosion of new material sets in use ( eg. Cu, SiON, low k and high k ), directly leads to an increased need for both analytical laboratory instrumentation and for production level metrology (the differences are discussed) with combinations of, (a) better spatial resolution, (b) surface and ultra thin film sensitivity, and (c) chemical state sensitivity.

Electron Spectroscopies are obvious key candidates here, and there are now full wafer Scanning Auger Microscopes in the industry joining the SEM/EDS equivalents that have been there for over a decade. In some respects, however, electron spectroscopy is too surface sensitive and it is not obvious that an old technique, EDS, which has undergone spectacular advances in spectral resolution using microcalorimetry detection schemes, will not win the day. These advances have led to the possibility of EDS at low voltages, greatly improving the small volume probing depth and reducing damage of buried circuitry, and also providing chemical state information. The issue is whether the liquid He cooled detector schemes can be made reliable and simple enough for industry.

After laying out the general needs, likely scenarios for meeting them, and gaps left, I will give some specific examples of current state-of-art use of electron and electronic spectroscopy ( Auger, XPS, and EDS ) in the area of full wafer small particle detection and characterization. This is a critical area in the National Semiconductor Road Map. At the 100nm node ( 2 to 3 years from now ) “killer” defects are at the 30-50nm size, and so particles of this size violate spec. The particle root cause analysis requirements caused by such particle specs are the equivalent to having to find and analyze a grain of salt on a football field.

**Theoretical Photoemission and X-Ray Emission Spectra of Nickel and Cobalt Disilicide Films**

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The results of the calculation of photoemission and x-ray emission spectra of some transition metals (TM) silicides ( $\text{NiSi}_2$  and  $\text{CoSi}_2$ ) are performed. Calculation of these films spectral characteristics was carried out in terms of the film linearized augmented plane wave method. The comparison of the calculated densities of electronic states of all nonequivalent atoms of the films and obtained theoretical x-ray emission and photoemission spectra of these compounds with known experimental spectra of the bulk and film samples has allowed to make the following sentences: 1. The valence band of films is shaped on the main by TM d-states, localized close 3.2 and 2.3 eV below  $E_F$  for  $\text{NiSi}_2$  and  $\text{CoSi}_2$  accordingly, with an impurity of s- and p-states, distributed along all band; and also by Si s- and p-states, concentrated in two energy regions (6 - 12 and 0 - 2 eV lower  $E_F$  for  $\text{NiSi}_2$ , 5 - 11 and 0 - 1 eV lower  $E_F$  for  $\text{CoSi}_2$ ) with an impurity of Si d-states. 2. The structure of photoemission spectra of films is stipulated by TM d-states and Si s-states at small excitation energies (12 - 50 eV). At higher quantum energies the shape of spectra is determined only by TM d-states. 3. The characteristic double-peak structure of K and  $L_{1s}$  x-ray emission spectra of Si is explained by the development of d-s,p-resonance. 4. The shape of  $\text{Si-L}_{2,3}$  spectra is mainly determined by s-states; d-states are exhibited as a small maximum in the region of 2 - 3 eV below Fermi level. The drop of near to  $E_F$  peak intensity in  $\text{Si-L}_{2,3}$  spectrum of  $\text{CoSi}_2$  film in comparison with  $\text{NiSi}_2$  is bound with electronic density redistribution owing to the decrease of valence electrons number at the transition from nickel to cobalt.

**Reactions on Model Emission Control Catalysts Studied by Soft X-ray Photoemission\***

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Automotive emission control catalysts are complex systems consisting of active noble metal particles (Pt, Rh), a reducible rare earth oxide ( $\text{CeO}_2$ ) and an inert oxide support ( $\text{Al}_2\text{O}_3$ ). We have fabricated well defined model catalysts by evaporating Ce onto single crystal Ru(0001) in an  $\text{O}_2$  ambient.  $\text{CeO}_x$  grows as a thin, single crystal film with a (111) orientation. The typical film thickness is  $\sim 5$  nm which eliminates sample charging during photoemission. Controlling the  $\text{O}_2$  partial pressure during evaporation can alter the Ce oxidation state. The Ce oxidation state is ascertained by Ce 3d, Ce 4d or Ce 4f photoemission. Rh or Pt is then evaporated onto the  $\text{CeO}_x$  surface. The noble metal particles have a surface area of  $\sim 0.1$  ML. This model catalyst surface is then exposed to gases typically found in an automotive exhaust stream. NO, CO,  $\text{H}_2\text{O}$ ,  $\text{SO}_2$  and  $\text{C}_2\text{H}_4$  have been studied so far.

Surface species are identified by soft x-ray photoemission as a function of Ce oxidation state, noble metal coverage, adsorbate coverage and temperature. Photoemission is also used to monitor changes in the oxide and the noble metal during the reactions. NO and  $\text{SO}_2$  interact strongly with the  $\text{CeO}_x$  substrate. Adsorption of NO on highly reduced  $\text{CeO}_x$  can produce up to six different N 1s states. These have been identified as  $\text{N}_2\text{O}$ ,  $\text{NO}^-$ ,  $\text{N}^{3-}$  and two essentially neutral N species.  $\text{SO}_2$  adsorbs strongly on both oxidized and reduced  $\text{CeO}_x$  forming  $\text{SO}_3^{2-}$ . CO and  $\text{C}_2\text{H}_4$  do not interact strongly with  $\text{CeO}_x$  but adsorb on the Rh particles.  $\text{C}_2\text{H}_4$  can abstract O from the ceria after decomposition on the Rh and desorb as CO. The oxidation state of the Ce affects the reactivity of the Rh particles. NO and CO dissociate more readily on Rh on reduced  $\text{CeO}_x$  than on Rh on oxidized  $\text{CeO}_2$ . The degree of dissociation can be followed in the N 1s and C 1s spectra.

Recent investigations have focused on the interaction between two different gases co-adsorbed on the model catalyst surface. CO and NO on Rh on reduced  $\text{CeO}_x$  form OCN rather than  $\text{CO}_2$  as is seen on Rh single crystals. As the surface temperature is increased,  $\text{C}_x\text{N}_y$  species are formed.  $\text{C}_x\text{N}_y$  species are also seen when NO and  $\text{C}_2\text{H}_4$  are co-adsorbed. The occurrence of these unique reaction pathways has been explained by considering the effect of the removal O from the Rh surface by reaction with the  $\text{CeO}_x$ .

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Mn-concentration dependence of Fermi-level pinning in Ga<sub>1-x</sub>Mn<sub>x</sub>As

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The possibility to add magnetic impurities at relatively high concentrations into GaAs has opened new exciting prospects of combining magnetic phenomena with high-speed electronics and optoelectronics. The numerous investigations of Ga<sub>1-x</sub>Mn<sub>x</sub>As alloys that have been carried out so far have revealed interesting material properties, the most notable being ferromagnetic ordering. Although there is strong evidence showing that the ferromagnetic ordering is hole mediated, the detailed understanding of the coupling mechanism remains a subject of debate. Using photoemission, we have investigated the development of the electronic structure in Ga<sub>1-x</sub>Mn<sub>x</sub>As systems with up to 7% Mn.

In the present report we focus on the dependence of the Fermi level ( $E_F$ ) pinning upon Mn concentration. The experiments were carried out at beamline 41 at the Swedish national synchrotron radiation facility MAX-lab. The samples were prepared in a dedicated MBE system, attached to the electron spectrometer to allow sample transfer in ultrahigh vacuum. The GaMnAs layers were grown on Si-doped substrates at a temperature of approximately 200 °C. The growth rates, as well as the Mn concentrations, were determined in situ by RHEED oscillations, and were checked ex situ by Auger electron spectroscopy and high resolution X-ray diffraction. All photoemission data were recorded at room temperature. For Mn concentrations around 1% we found that the Fermi level is located approximately 0.3 eV above the VBM. In the range 1.5-2.5% it drops to a position very close to the VBM, where it remains up to about 3% Mn content. According to conductivity measurements the alloy should become metallic in a range approximately 3.5-4.3%. Indeed, we found that the Fermi level drops almost 0.2 eV below the VBM in this range. At even higher concentrations an unexpected effect was observed: the Fermi level shifts back towards VBM, and above 5.5% it is pinned near VBM. Our experimental resolution was not sufficient to decide whether it actually shifts back into the band gap, but it is clear that the hole density must be strongly reduced. The reported metal-insulator transition above 4.3% Mn is, therefore, not necessarily due to localization of holes, but reflects rather a strong reduction in hole density. We also note that the Curie temperature exhibits a maximum at the Mn concentrations where we found the lowest  $E_F$ . This is consistent with the idea that the ferromagnetic coupling is hole mediated. Our results indicate a varying character of the Mn impurities with concentration. Such variations are also observed directly via changes in the Mn3d-derived emission.

Photoelectron spectroscopic studies of thin PTCDA layers on TiSe<sub>2</sub>\*

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The growth and electronic structure of the organic semiconductor 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) deposited on TiSe<sub>2</sub> has been studied by means of angle resolved photoelectron spectroscopy. Different film thicknesses ranging from 2 to 6 monolayers (ML) were investigated. For increasing PTCDA film thickness the spectrum is shifted towards higher binding energies, the shift being 0.5 eV for the HOMO when the film thickness is increased from 2 to 6 ML of PTCDA. We believe that this difference in energy is a result of final state relaxation effects with a reduced screening from the semi-metallic substrate in thicker films. The two peaks with highest kinetic energy are associated with molecular orbitals located on the perylene core of the PTCDA molecule and the lower lying peaks are connected to orbitals concentrated on the anhydride groups [1]. The latter peaks have a reduced energy shift compared to the mentioned perylene associated peaks. Assuming that the relaxation effect should result in a rigid shift of the whole spectrum, we draw the conclusion that the anhydride groups interact with the substrate, leading to a broadening of the spectrum. The minor difference in the shape of the 2 and 6 ML spectra, indicate that the PTCDA is only weakly interacting with the substrate. The ARPES spectra show an angular dependence in the intensity of the PTCDA peaks due to directional characteristics of the molecular orbitals. This indicates that the molecules are preferentially oriented parallel to the substrate. Small energy shifts of the HOMO peak are systematically observed for different emission angles. The shift is approximately 60 meV when the emission angle is increased from 0 to 45 degrees. This angular dependence is ascribed to an increased screening with probing depth.

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Sudden interchannel coupling in the Tl 6p ionization above the 5d threshold

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Strong photoionization channels may significantly affect the behavior of weaker channels due to the coupling by electron correlation. The showcase example for such a situation is the Xe 5p photoionization in the vicinity of the 4d shape resonance. This effect can be understood as the polarization of the atom, induced by the strong photoionization channel, giving rise to enhanced electron emission in the weaker channel. This intensity enhancement has a pronounced impact on the phase shift between the two outgoing photoelectron waves  $\epsilon_{l+1}$  and  $\epsilon_{l-1}$ . This phase effect occurs, however, in the few cases studied so far, not suddenly at the threshold of the new photoionization channel, rather it evolves along with the intensity variation of the strong channel. In the Xe case, for example, it basically develops with the appearance of the shape resonance in the 4d channel inducing a similar but less pronounced change in the phase shift of the 5p channel. This smooth variation of all photoionization parameters makes the whole process behave like a resonance in the sense of broad band autoionization between two continuum channels.

The question arises if there exist cases where the coupling between two channels appears suddenly above threshold and not mediated by a resonance feature in the continuum of the stronger channel. In order to reveal such a behavior only two channels should be involved. In particular no onset suppression for the stronger channel as in Xe 4d should be present, because such channel suppression tends to weaken the coupling between the two original photoionization channels. Such a case is the Tl 6p photoionization in the vicinity of the 5d threshold.

In order to perform a partial wave analysis, the linear magnetic dichroism in the angular distribution (LMDAD) of thallium 5d and 6p photoelectrons has been measured between  $h\nu = 30$  eV and 50 eV [1]. In contrast to the behavior of the Xe 5p photoionization at the 4d threshold, our results show that above the Tl 5d threshold strong interchannel coupling effects induce a sudden increase in the asymptotic phase difference of the s- and d- wave for the Tl 6p ionization. This additional phase difference determines the photoionization behavior in a wide range of kinetic energy from 20 to 100 eV. H.K. acknowledges the support of the European Union and the Leverhulme Trust Company (London). N.A.C. acknowledges the Max-Planck-Society for financial support. This work was supported by the Deutsche Forschungsgemeinschaft.

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