

PHOTOEMISSION SPECTROSCOPY OF HALF-METALLIC PEROVSKITE MANGANITES $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$

J. -S. KANG[a], T. W. NOH[b], C.G. OLSON[c], and B. I. MIN[d]

[a] Department of Physics, The Catholic University of Korea, Puchon, 422-743, Korea

[b] Department of Physics, Seoul National University, Seoul 151-742, Korea

[c] Ames Laboratory, Iowa State University, Ames, Iowa 50011, U.S.A.

[d] Department of Physics, Pohang University of Science and Technology, Pohang 790-784, Korea

By using photoemission spectroscopy, the electronic structures of the colossal magneto-resistive (CMR) perovskite compounds of $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ (PSMO; $x=1/3, 1/2, 2/3$) have been investigated. The partial yield spectra and the constant-initial-state (CIS) spectra near the Pr 4d absorption edge indicate that the Pr ions are nearly trivalent in PSMO. The Pr 4f and Mn 3d partial spectral weight (PSW) distributions of PSMO have been extracted. They are found to be insensitive to x , reflecting the small overlap between Mn 3d and Pr 4f orbitals. The Pr 4f PSW exhibits a dominant hybridization peak near 2eV BE, indicating large Pr 4f-O 2p mixing. The spectrum near the Fermi level exhibits evidence for the metal-insulator transitions with varying x and temperature, as well as a charge gap formation for $x=1/2$. The Mn 3d partial density of states (PDOS) have been calculated for PSMO and compared to the experimental Mn 3d PSWs. This comparison suggests the localized nature of the Mn e_g electrons in PSMO, probably due to the lattice polaron formation.

Satellite-free O K emission spectra from O-bearing compounds

M. UDA (a,b), D. TERASHI (a), D. YAMASHITA (a), T. YAMAMOTO (c), H. OSAWA (a), K. KANAI (a),
R. PERERA (d)

(a) Department of Materials Science and Engineering, Waseda University, Ohkubo 3-4-1, Shinjuku-ku, Tokyo

(b) Laboratory for Materials Science and Technology, Nishiwaseda 2-8-26, Shinjuku-ku, Tokyo

(c) Institute of Physical and Chemical Research, Wako-shi, Saitama, Japan

(d) Center for X-ray Optics, Lawrence Berkeley Laboratory, University of California-Berkeley

A characteristic X-ray is generally emitted when one of inner shell electrons is ionized by bombardments of electrons, ions and photons with sufficient energies. However, multiply ionized states are also produced together with a singly ionized state. The former states emit the satellite X-rays whose energies are higher than that emitted from the latter. This makes the fine structures of the characteristic X-rays originating from molecular orbitals complicated.

A satellite-free characteristic X-ray reflects a partial density of state responsible for its X-ray emission. Then by appropriate selection of excitation photon energies, the singly ionized state alone was produced. Such an excitation condition was prepared by using the Advanced Light Source in Berkeley.

Molecular orbitals responsible for emitting O K emission were calculated by use of the DV-X alpha method for several oxygen-bearing compounds. Observed satellite-free X-ray spectra are well reproduced by calculated O 2p partial density of states

Characterization of Fe-bearing compounds in aerosol using Fe L emission spectra

M.UDA(a, b), D. YAMASHITA (a) and H. NAKAMATSU (c)

(a) Department of Materials Science and Engineering, Waseda University, Ohkubo 3-4-1, Shinjuku-ku, Tokyo

(b) Laboratory for Materials Science and Technology, Waseda University, Nishiwaseda 2-8-26, Shinjuku-ku,
Tokyo

(c) Institute for Chemical Research, 611 Kyoto

Chemical classification of S-bearing compounds in aerosol was successfully performed using S K emission spectra. Here S-bearing compounds can be used to diagnose the quality of an aerosol. The same is also true for Fe-bearing compounds in it.

The expected chemical formulae of the Fe-bearing compounds in the aerosol are Fe, $\text{Fe}_c\text{RO}_c\text{S}$, Fe_2O_3 and FeSO_4 which might originate from exhaust particles from cars, road dust, coal/oil combustion, industry and soil. The L X-ray spectra emitted from these compounds show significant difference in shape, suggesting the effective use of the spectra for chemical classification. However, the shape of the L X-ray spectra is much altered by change in the valence structures of the above compounds, though enough explanation has not yet been given based on quantum chemical calculations.

The DV-X alpha method was employed for estimating the fine structures of the molecular orbitals of the above compounds. The observed fine structures of the Fe L emission spectra are well compared with the calculated ones.

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XANES Spectra of Sesqui-oxides of Al, Cr and Fe

M. UDA (a,b), D. YAMASHITA (a), D. TERASHI (a), T. YAMAMOTO (c), H. OSAWA (a), K. KANAI (a),
R. PERERA (d)

(a) Department of Materials Science and Engineering, Waseda University, Ohkubo 3-4-1, Shinjuku-ku, Tokyo

(b) Laboratory for Materials Science and Technology, Nishiwaseda 2-8-26, Shinjuku-ku, Tokyo

(c) Institute of Physical and Chemical Research, Wako-shi, Saitama, Japan

(d) Center for X-ray Optics, Lawrence Berkeley Laboratory, University of California-Berkeley

The sesqui-oxides of Al, Cr and Fe with the corundum structure are crystallized in the form of hexagonal closest packing of oxygen ions. These oxides are chemically and thermally stable, and then are used as industrial materials. For further understanding of detailed nature of the oxides, near edge electronic structures are investigated by employing the XANES method. Here XANES spectra from O, Al, Cr and Fe were taken using the Advanced Light Source in Berkeley.

The observed XANES spectra are well compared with theoretical ones, where partial density of states responsible for X-ray absorption are calculated using the DV-X alpha molecular orbital calculation method.

High-resolution photoemission spectroscopy of CeSi single crystal

K. MIMURA[a], T. TAKASE[a], H. MIZOHATA[a], Y. TAGUCHI[a], K. ICHIKAWA[a], Y. TAKEDA[b],
M. ARITA [c], K. SHIMADA[c], H. NAMATAME[c], S. NOGUCHI[a], K. OKUDA[a],
M. TANIGUCHI[b, c], O. AITA[a]

[a]Graduate School of Engineering, Osaka Prefecture University, 1-1, Gakuen-cho, Sakai 599-8531, Japan

[b]Faculty of Science, Hiroshima University, Kagamiyama 1-3-1, Higashi-Hiroshima 739-8526, Japan

[c]Hiroshima Synchrotron Radiation Center, Hiroshima University, Kagamiyama 2-313, Higashi-Hiroshima
739-8526, Japan

CeSi with the orthorhombic FeB-type structure orders antiferromagnetically below the Néel temperature of 5.9 K [1, 2], and shows anisotropy along b-axis in the magnetic susceptibility and the electric resistivity [2]. The magnetic structure, derived by powder neutron diffraction, has been recently reported to be a 3D sinusoidally modulated incommensurate structure [3]. The resistivity along b-axis exhibits a small hump at the ordering temperature, indicating the change of density of states (DOS) [2]. In this study, we have investigated the valence-band electronic structure for CeSi single crystal by means of high-resolution photoemission spectroscopy (HR-PES).

HR-PES measurements were done using a spectrometer equipped with a hemispherical energy analyzer and a high-flux He discharge lamp. The sample temperature was controlled at 7 and 290 K. The clean surface of the sample was obtained in situ by scraping using a diamond file. The overall energy resolution was estimated to be 6 meV.

The HR-PES spectrum in the vicinity of Fermi level (EF), excited with He II resonance line (40.8 eV) at the sample temperature of 7 K, exhibits the peak structures at 50 and 280 meV, which are ascribed to the Ce $4f_{5/2}^f$ and $4f_{7/2}^f$ final states, respectively. For the structure of Ce $4f_{5/2}^f$ final states, in particular, it is characteristic that the photoemission intensity gently decreases as energy is headed from 50 meV to EF. This trend is different from those of conventional Kondo systems CeSix ($1.6 \leq x \leq 2$), which exhibit a sharp peak structure on to EF [4]. This result indicates that no Kondo effect is apparent or the Kondo temperature is very low (< 1 K) for CeSi, and corresponds to the results of the electrical and magnetic properties [1-3].

In order to obtain the change of spectral DOS, we have divided the He I spectra (21.2 eV) at 7 and 290 K by the Fermi-Dirac distribution function convoluted with the instrumental resolution. The spectral DOS at 290 K is structureless, while that at 7 K decreases between EF and 20 meV and increases between 20 and 100 meV in comparison with that at 290 K. These changes are ascribed to the change of DOS with magnetic ordering. This result is consistent with that obtained from the electric resistivity measurements [2].

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Electronic Structures of Organic Salts DMTSA-BF₄ Using Photoelectron Spectromicroscopy

Yuichi HARUYAMA[a], Toyohiko KINOSHITA[b], Kazuo TAKIMIYA[c],
Tetsuo OTSUBO[c], Chikako NAKANO[d] and Kyuya YAKUSHI[d]

[a]Laboratory of Advanced Science and Technology for Industry, Himeji Institute of Technology, Kamigori, Ako
678-1205, Japan

[b]Synchrotron Radiation Laboratory, Institute for Solid State Physics, University of Tokyo, Kashiwa 277-8581,
Japan

[c]Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

[d]Institute for Molecular Science, Okazaki 444-8585, Japan

The 1:1 charge-transfer organic salt DMTSA-BF₄, where DMTSA is 2,3-dimethyltetraseleno-anthracene, have attracted the interest of many researchers because of the high electrical conductivity and metallic physical properties above ~150K[1]. So far, it has been considered that the 1:1 charge-transfer salt becomes a Mott insulator due to the Coulomb interaction since the 1:1 charge-transfer salt has half-filled band. The origin of the metallic physical properties for DMTSA-BF₄ is not clear at present. In order to obtain the information on the electronic structures such as the band structure, density of states, and the orbital characters, we have performed the photoemission experiments for DMTSA-BF₄.

As the size of needlelike shaped DMTSA-BF₄ synthesized by electrochemical reduction is not large enough to carry out the ordinary photoemission measurements, we used the photoelectron spectromicroscopy instrument (FISONS, ESCALAB-220i-XL)[2]. The typical sample size used here was less than 2×0.2×0.1mm³. The clean surface was obtained by scraping the sample surface using an edge of a razor.

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

Electron and Ion Fragment Momentum Correlation from Core Ionized CO Molecules*

A.L. LANDERS [a], T. WEBER [b], R. DOERNER [b], A. NAUERT [b], M. HATTASS [b], H. SCHMIDT-BOECKING [b], T. OSIPOV [c], I. ALI [c], C.L. COCKE [c], A. STAUDTE [d], M.H. PRIOR [d], A. CASSIMI [e]

[a] Dept. of Physics, Western Michigan Univ., Kalamazoo, MI 49008

[b] Institut fuer Kernphysik, Univ of Frankfurt, August-Euler Str #6, D-60486 Frankfurt Germany

[c] Dept of Phys, Kansas State Univ, Cardwell Hall, Manhattan KS 66506

[d] Chemical Sciences Division, Lawrence Berkeley National Lab., Berkeley CA 94720

[e] CIRIL/CEA/CNRS/ISMRA, U. de Caen, Rue C. Bloch, Box 5133, F-14070 Caen Cedex 5, France

The breakup of fixed-in-space CO by photo-fragmentation at and above the carbon and oxygen K edges has been investigated by measuring the complete momentum vectors of both fragment ions and the low energy photoelectron in coincidence. The method is based on an extension of the Cold Target Recoil Ion Momentum Spectroscopy (COLTRIMS) electron/ion coincidence technique to molecular target species. The photons were obtained at beam line 9.3.2 at the LBNL Advanced Light Source. We have measured the angle and energy distributions of the photoelectron, subsequent Auger electron(s), and molecular fragment pairs in coincidence, for photon energies from 0-30 eV above the C(1s) and O(1s) thresholds. Interference effects due to intramolecular scattering of the de Broglie electron wave from the nuclear centers of the fixed-in-space molecule have been observed. In addition, the data show fragment energy spectra differing substantially from that obtained from a simple Frank-Condon projection from the CO ground vibrational state onto a single C^+O^+ Coulomb potential curve. The fragment spectra show structure likely attributable to molecular CO^{++} levels which rapidly dissociate to separated C^+ , O^+ ions with either or both fragments in excited levels. Also observed are strong multiple (up to CO^{+4}) ionization channels. The data reveal the correlation between electron and fragment momenta for any orientation of the molecule with respect to the photon linear polarization axis at several photon energies in the range 0-30 above the K shell ionization thresholds.

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X-ray fluorescence measurements of advanced organic materials

E.Z. KURMAEV¹, A. MOEWES², K. ENDO³ and D.L. EDERER⁴

¹Institute of Metal Physics, Russian Academy of Sciences-Ural Division, 620219 Yekaterinburg GSP-170, Russia
²CAMD, Louisiana State University, 6980 Jefferson Highway, Baton Rouge, Louisiana 70806, USA

³Department of Chemistry, Faculty of Science, Kanazawa University, Kakuma-machi, Kanazawa, 920-1192 Japan

⁴Department of Physics, Tulane University, New Orleans, LA 70118, USA

The results of X-ray fluorescence measurements of advanced organic materials (irradiated polymers, organic semiconductors and superconductors, metal/polymer interfaces and organic magnets) are presented. The X-ray fluorescence measurements are performed at Beamline 8.0 of Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL, Berkeley) and the following results were found:

1. We observe a degradation for polyimide (PI) films that are implanted with ion concentrations above $1 \cdot 10^{14}$ ions/cm² into amorphous C:N:O systems. The filling of the band gap in these compounds¹ is monitored by changes in the fine structure of carbon Ka emission spectra.
2. We show that an enhancement in adhesion strength is observed in Cu/Al/PI system after ion-beam mixing. The enhancement is due to the formation of buffer CuAl₂O₄ layer².
3. X-ray fluorescence measurements of molecular superconductors (ET)₄Fe(C₂O₄)₃·C₆H₅CN·H₃O⁺ (T_c=8.5 K) and (ET)₄Cr(C₂O₄)₃·C₆H₅CN·H₃O⁺ (T_c~6 K) and molecular conductor (ET)₄Fe(C₂O₄)₃·C₅H₅N·H₃O⁺ containing paramagnetic 3d-ions show that the ratio the spectra intensities of I(Fe L₂ XES)/I(Fe L₃ XES) and I(Cr L₂ XES)/I(Cr L₃ XES) for (ET)₄Fe(C₂O₄)₃·C₆H₅CN·H₃O⁺ and (ET)₄Cr(C₂O₄)₃·C₆H₅CN·H₃O⁺, respectively, is found to be 2.8-3.1 times higher than in pure metals. This indicates that the paramagnetic 3d-ions are situated in highly insulating anionic layers³.
4. We have studied carbon, nitrogen, fluorine Ka and sulphur, copper L_{2,3} emission of organic semiconductors: thiophenes [regioregular poly(3-hexylthiophene (P3HT) and a,w-dihexylquaterthiophene (DHa4T)] and phtalocyanines [copper phtalocyanine (CuPc) and copper hexadecafluorophtalocyanine (F16CuPc)]. The obtained results are compared with UPS and XPS VB spectra and MO LCAO calculations of monomer-like molecules. It is found that carbon Ka XES of P3HT and DHa4T are almost identical indicating that the electronic structure of the p-system is not affected by the presence of the alkyl group. The ratio of the emission intensities of the peaks Cu L₂ to Cu L₃ is found to be two times less for CuPc and F16CuPc than for pure metal evidencing the strong covalency in phtalocyanines⁴.
5. Soft X-ray fluorescence spectra of a single crystal of organic antiferromagnet 2,4,6-triphenylverdazyl (TPV) are compared with X-ray photoelectron valence band spectra and MO LCAO calculations. It is shown that the interchain interactions are weak which provides a quasi-one-dimensional character of electronic structure of TPV crystal. We have found spectroscopic evidence of a delocalization of unpaired N 2p-electrons over the verdazyl ring⁵.

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Determination of the momentum-transfer dependence of the Fano parameters of the low-lying doubly excited transitions and first observation of nondipole autoionization resonances in He and Ar

X.W. FAN and K.T. LEUNG*

Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

The absolute generalized oscillator strength (GOS) of the lowest-lying doubly excited transition (1s1s to 2s2p) in He has been determined as a function of the momentum transfer for the first time by angle-resolved electron energy loss spectroscopy at 2.5 keV impact energy. The GOS profile is found to be dominated by a strong maximum at zero momentum transfer, characteristic of predominantly dipole interaction. The corresponding Fano parameters have also been determined as functions of the momentum transfer for the first time, which may be used to shed new light on the underlying matrix elements involved in the competing direct ionization and autoionization mechanisms. Furthermore, the presence of a nonoptical autoionizing resonance at 58.1 eV in He, predicted theoretically earlier, has now been confirmed at a higher momentum transfer. These electron energy loss studies have been extended to the low-lying doubly excited transitions in Ar, which exhibit some rather different and surprising behaviour.

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Pre-K-Edge structure of Resonant X-ray Scattering in LaMnO₃

M. TAKAHASHI[a], J. IGARASHI[a], P. FULDE[b]

[a]Gunma University, Kiryu 376-8515, Japan

[b]MPIPKS, 01187 Dresden, Germany

We study the pre-K-edge (PKE) structure of the resonant X-ray scattering (RXS) for forbidden reflections in LaMnO₃ using the band structure calculation based on the local density approximation. We also calculate the RXS intensity in the main-K-edge (MKE) region. The calculated MKE structure shows good agreement with the experiment[1,2]. It is found that the MKE structure is mainly generated by the Jahn-Teller distortion so that the idea that the RXS intensity in the MKE region is a direct reflection of the orbital-order is not correct in LaMnO₃ and the other systems with strong J-T distortion. It has been suggested that the observation of the RXS intensity in the PKE region is much suitable for detection of the orbital order.[3]

In the calculation of the RXS intensity in the PKE region we take account of not only the E1 transition but also the E2 transition in the photo-absorption processes, because the unoccupied 3d states make a narrow band in the concerning energy region. Result of the calculation shows that the RXS intensity appears mainly through the E1 transition process. The effect of the E2 transition is found to be negligible, slightly modifying the azimuthal-angle dependence.

This means that the PKE structure reflects the '4p' states not the orbitally polarized 3d states. These p-symmetric states strongly hybridize with the unoccupied 3d states on the neighboring Mn sites so that they sense the orbital order through the hybridization with the orbitally polarized 3d state. Therefore the RXS intensity in the PKE energy region is a reflection of the orbital order, although the relation is not a direct one derived from the effect of the E2 transition. We also calculate the absorption spectra in the PKE region. The result reproduces well the experimental spectra[4], which shows a two-peak structure.

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Nanospectroscopy on InAs Nanocrystals

Y. WATANABE[a], S. HEUN[b], B. RESSEL[b], TH. SCHMIDT[b], K. C. PRINCE[b]

[a] NTT Basic Research Laboratories, Atsugi-shi, Kanagawa 243-01 Japan

[b]Sincrotrone Trieste, Basovizza, 34012 Trieste, Italy

Spectromicroscopic measurements of InAs nanocrystals by soft x-ray photoemission electron microscopy (XPEEM) are presented. Measurements were performed with the spectroscopic photo emission and low energy electron microscope (SPELEEM) at beamline 6.2LL of ELETTRA in Trieste, Italy [1]. The InAs nanocrystals were fabricated on Se-terminated GaAs(100) surfaces by molecular beam epitaxy (MBE) in Tsukuba, Japan [2]. The samples were protected by an amorphous As capping layer deposited in-situ in the MBE chamber during transfer in air to ELETTRA. The capping layer was desorbed in the SPELEEM sample preparation chamber. Measurements on As-capping and decapping of InAs nanocrystals proved that the electronic properties of the samples were not changed by this procedure [3]. A statistical analysis of nanocrystal density and size distribution was performed.

Integral photoelectron spectra measured with the SPELEEM are in good agreement with literature data [4-6]. Chemical contrast in XPEEM images was readily obtained: XPEEM images measured at the photoelectron kinetic energy corresponding to the In 4d core level show the InAs nanocrystals brighter than the Se-terminated GaAs-substrate. The contrast is inverted at the energy of the Se 3d core level. Laterally resolved valence band spectra were obtained from stacks of XPEEM images. They clarify the band alignment between nanocrystals and substrate. Work function measurements on the nanocrystals indicate a dependence of work function on InAs overlayer thickness. Finally, laterally resolved core level spectra help to obtain a better understanding of the XPEEM images from the samples.

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Short Time Measurements of Full-Solid-Angle Photoelectron Diffraction Using a 180° Deflection Toroidal Analyzer*

S. SHIRAKI [a], H. ISHII [a], M. OWARI [b], Y. NIHEI [a]

[a] Institute of Industrial Science, University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106-8558, Japan

[b] Environmental Science Center, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Using a 180° deflection toroidal analyzer, the two-dimensional patterns of X-ray photoelectron diffraction (XPED) were measured in short acquisition times. This analyzer enables the simultaneous detection of the energy and polar angle distribution of electrons from solid surfaces. Therefore, a major feature is that the measurement over full solid angle can be performed rapidly by azimuthal rotation of the sample. Up to now, we have improved the focusing properties of the analyzer and examined the optimization of electron trajectory in the analyzer [1]. As for the two-dimensional patterns of Auger electron diffraction (AED), we have already reported electron-beam-excited O KLL and Mg KLL AED patterns from a MgO(001) surface, which were obtained in an hour or less [2]. In this study, we present the XPED pattern measured using a 180° deflection toroidal analyzer and high-power X-ray generation system. This generation system produces focused X-ray beam and high photon intensity, so we can rapidly gain the full-solid-angle XPED pattern. We also discuss about the obtained XPED patterns in comparison with theoretical results calculated by the multiple-scattering scheme.

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Water and Ammonia ices: Phase transition probed by NEXAFS

F. BOURNEL [a], M. TRONC [a], C. LAFFON [b], Ph. PARENT [b]

[a] Laboratoire de Chimie-Physique, Matière et Rayonnement, Université Paris 6, 11 rue P. et M. Curie, 75231 Paris Cedex 05, France

[b] Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Université Paris-Sud, Bât. 209d, BP 34, 91898 Orsay Cedex, France

Understanding the reactivity of and with ices surfaces is of considerable interest. In fact, the chemical reactions happening on interstellar icy dusts could be at the origin of life on earth. This chemistry also includes the basic reactions of pollution / depollution mechanisms in the polar stratospheric clouds (PSC).

We have performed X ray absorption experiments (Near Edge X ray Absorption Fine Structure, NEXAFS) on water and ammonia ice films. Ice films can be simulated in the laboratory when water (ammonia) is condensed on a cold substrate in UHV conditions. NEXAFS spectroscopy at O K-edge and N K-edge which probes empty electronic states is very sensitive to a modification of the electronic structure and to the environment of the excited atom. Our study points out the ice morphology changes with the condensation temperature. Thus, for temperatures below 80 K, water forms a microporous amorphous phase with a large specific surface which can enhance reactions with incoming molecules. A phase transition occurs when the temperature is raised and the hexagonal crystalline phase is present above 150 K. The NEXAFS spectra reveal this phase transition. The first two NEXAFS transitions attributed to O1s \rightarrow 4a1 and O1s \rightarrow 2b2 transitions (based on comparison with transitions in the gas phase) are similar in the amorphous and crystalline water ice phase. Only the third transition which corresponds to a transition to Rydberg states (B1 symmetry) is different between crystalline and amorphous ice. The same study has been carried out on ammonia ices (N K-edge). Once again NEXAFS is sensitive to a phase transition which arises around 40 K.

Development of a High Angle-Resolving Electron Energy Analyzer*

S. SHIRAKI, H. ISHII, Y. NIHEI

Institute of Industrial Science, University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106-8558, Japan

Angle-resolved photoelectron spectroscopy is well known as an important technique for surface and interface analysis. Particularly, photoelectron diffraction (PED) is used not only for the chemical state analysis but also for the study of atomic geometry. In PED measurements, angle-resolving aperture is often used, which is attached in front of the input-lens system. However, this angle-resolving aperture has a serious problem that the transmission rate inevitably decreases, as angle resolution is high. In this study, we constructed a high angle-resolving electron energy analyzer with the newly designed input lens system. In this lens system, an aperture is placed at the position where the diffraction pattern is created by lens action. Thus, electrons passing through the diffraction plane aperture are angle-resolved without detection loss. In addition the angle resolution is easily controlled by the size of diffraction plane aperture. Using trajectory calculation, we obtained high angle resolution of 0.3° when the diameter of diffraction plane aperture is 1 mm. On the other hand, since the spherical analyzer and 64 channel multi-detection system are used, high energy resolution and high speed measurement are performed.

Furthermore, details including some experimental results will be presented.

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Resonant Auger Spectroscopy of Poly(4-hydroxystyrene) at C and O K edges

J.-J. GALLET [a], F. BOURNEL [a], G. DUFOUR [a], F. JOLLY [a], F. ROCHET [a, b], F. SIROTTI [b] and P. TORELLI [b]

[a] Laboratoire de Chimie-Physique, Matière et Rayonnement, Université P. et M. Curie, 11 rue P. et M. Curie, 75231 Paris Cedex 05, France

[b] Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Université Paris-Sud, Bât. 209d, BP 34, 91898 Orsay Cedex, France

Valence Band Photoemission of Poly(4-hydroxystyrene) (PHS) is investigated at C and O K-edges. PHS consists of a saturated polyethylene backbone where a phenolic group substitutes one of the hydrogen atoms at every other carbon.

The C1s NEXAFS spectrum of PHS is dominated by two well separated π^* resonances attributed to C1s $\rightarrow \pi^*$ transitions of the phenolic group. The first one originates from the five carbon atoms not bonded to the OH group (five core levels within a 250 meV range [1]). The second one is for the carbon atom bonded to the alcohol function (core level 1.8 eV lower than the other carbon atoms). The photoemission spectra show a large dependence with the excitation energy. They all have a C-VV Auger-like stepped shape on which finer structures clearly appeared at both π^* NEXAFS resonances.

We have interpreted the resonant spectra in terms of a superposition of participator (1h final state) and spectator (2h1e final state) contributions. Spectator Auger contributions are observed at both C and O K-edges. It is discussed in terms of ground state symmetry and spatial extents of occupied and unoccupied molecular orbitals and in terms of interference effects in the Auger decay. We show up that the intensity of the resonant features is strongly dependent of the core hole site (carbon bonded or not bonded to OH). The localization of the spectator electron to the core-hole is measured with the spectator shift which is the same at both edges. In contrary, participator contribution is only observed at C K-edge meaning there is no correlation between the degree of localization of the spectator electron and the intensity of the participator channels.

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Graphite-like Structure of Carbon Nitride Films Prepared by Low Energy Ion Implantation

I. SHIMOYAMA, T. SEKIGUCHI W. GUOHUA, Y. BABA

Japan Atomic Energy Research Institute,
Tokai-mura, Naka-gun, Ibaraki 319-1195, Japan

Since the theoretical predict of hypothetical beta-C₃N₄ [1], carbon nitride has been an attractive material and many crystal structures have been proposed in the last decade. In spite of considerable efforts, the electronic structure of carbon nitride solids has not been explored well. Near edge x-ray absorption fine structure (NEXAFS) and x-ray photoelectron spectroscopy (XPS) are the most promising techniques to study the electronic structure. Especially, NEXAFS has great characteristic that polarization dependence measurement gives us information about an orientation of the system. In this work, we measured N 1s NEXAFS and XPS spectra of carbon nitride films which were prepared by low energy ion implantation onto graphite.

The NEXAFS spectra of carbon nitride film have shown obvious three sharp pi* and one broad sigma* resonances in the N K-edge energy region. The polarization dependence of first and third pi* resonances have shown similar tendency to that of the pi* resonance in C 1s NEXAFS spectra of graphite. While, the second pi* resonance has shown different behavior and the peak intensity has scarcely depended on incidence angle of x-ray. Furthermore, the polarization dependence of the third pi* resonance was enhanced by annealing above 1000 K. From the results, we concluded that the first, second, and the third pi* resonances originate from pyridine-like structure, cyanic structure, and graphite-like structure, respectively. The results show the clear experimental evidence that there exists a graphite-like structure in which some of the carbon atoms are substituted by nitrogen atoms. We will present the correlation between the NEXAFS spectra and the XPS spectra.

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Direct Surface Structure Technique based on the Vibrational Correlation

T. ABUKAWA[a], C. M. WEI[b], T. HANANO[a], K. YOSHIMURA[a] and S. KONO[a]

[a]Research Inst. Sci. Measurements, Tohoku University, Sendai 980-8577, Japan

[b]Inst. Phys., Academia Sinica, Nankang, Taipei, Taiwan 11529, Republic of China

Since the crystal atomic vibration is strongly correlated between neighbor atoms or within very short-range, the short-range coherency in the crystal diffraction may survive even if the thermal vibration destroys the long-range coherency. The short-range coherency should causes the broad structures in the thermal diffuse scattering (TDS). This condition is indeed realized on the Si surface when the medium energy electron diffraction is measured around the medium scattering angle [1]. The diffraction by the nearest neighbor atoms, which are strongly correlated in vibration, has been dominantly observed as a very simple oscillation of the diffuse intensity. This diffuse structure is termed correlated thermal diffuse scattering (CTDS) [1]. Since CTDS could be considered as the kinematical diffraction between the nearest neighbor atoms composing the crystal structure, the three-dimensional Patterson function is obtained by the simple Fourier transformation of the CTDS pattern three-dimensionally measured. When the surface sensitivity is enhanced by the grazing incidence, the building blocks of the surface structure, i.e. the length and the orientation of the all surface related bonds, can be directly obtained from the Patterson function [2]. The potential of CTDS will be demonstrated on the surface structure analysis of Si(001)2x1, Si(111)R3xR3-In and Si(111)4x1-In.

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X-Ray fluorescence holography*

G. FAIGEL[a], M. TEGZE[a], S. MARCHESINI[b], M. BELAKHOVSKY[b]

[a] Research Institute for Solid State Physics and Optics, 1525 Budapest, POB 49, Hungary

[b] DRFMC SP2M/IRS CEA, Grenoble, 38043 Cedex 9 France

In the last decade, hard x-ray holography using inside reference point has been developed for the study of 3D atomic arrangements in solids [1-3]. Two types of this method are used: "normal holography" in which the atoms serve as sources of x-radiation and "inverse holography" in which the atoms detect the interference field originating from the incident and scattered waves [4]. Beside the first two demonstration experiments [1,2], there have not been many measurements of this type. The cause of this is that there are serious technical difficulties and evaluation problems, which have to be solved before the wider application. Lately, many of these problems have been overcome; so hard x-ray holography became a useful tool for structural studies. Recent developments in the technique and the evaluation will be discussed and the capabilities of the method will be illustrated by examples.

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Symmetry-resolved density of states from valence band photoelectron diffraction

PH. HOFMANN [a], CH. SØNDERGAARD [a], CH. SCHULTZ [a], M. SCHØNNING [a],
S. LIZZIT [b], A. BARALDI [B]

[a] University of Aarhus, Denmark

[b] Sincrotrone Trieste, Italy

Understanding the electronic structure of new and complex materials is a major challenge in current solid state physics. The electronic states very close to the Fermi level are of particular interest because they are responsible for metal-insulator transitions, high T_c superconductivity and magnetoresistance. A promising approach for measuring the density of states (DOS) of complex materials is soft x-ray emission spectroscopy. This technique offers the possibility to determine chemically-resolved and symmetry-restricted partial densities of states (PDOS) if a suitable core level is available.

Valence band photoelectron diffraction (VBPED) could be a powerful alternative which combines the possibility of higher spectral resolution with stringent symmetry restrictions. In this talk it will be shown that VBPED can be used to determine the initial-state symmetry-resolved PDOS of solids. As an example, the density of states of aluminium is broken down into the s and p contributions. The results reveal a more s-like DOS at the bottom of the band and a more p-like DOS near the Fermi-level, in qualitative agreement with tight-binding calculations. A quantitative comparison does, however, show that the measured DOS contributions are narrower, i.e. more "atomic-like" than the calculated ones. Possible reasons are discussed.

High-resolution soft x-ray bulk sensitive photoemission from strongly correlated systems

Shigemasa SUGA and Akira SEKIYAMA

Department of Material Physics, Graduate School of Engineering Science, Osaka University
Toyonaka, Osaka 560-8531, Japan F/T:+816-6850-2845, e-mail:suga@mp.es.osaka-u.ac.jp

Electronic states of highly correlated electron systems near the Fermi level have so far been studied by high resolution photoemission spectroscopy (HPES) including the angle resolved measurements. Most of the HPES have been done in low photon energies near 100eV down to 40.8(He \uparrow U) or 21.2eV(He \uparrow T). In the case of rare earth (RE) compounds, the photoionization cross section of the 4f states is very low for He \uparrow U and He \uparrow T. Therefore most experiments for RE compounds are done by means of resonance photoemission for the 4d-4f excitation near 100eV. However, the photoelectron mean free path has a minimum between 20 and 200eV of the electron kinetic energies (E_K). Then the photoemission results in this regime represent the surface electronic states and do not necessarily provide information on the bulk electronic states. If one does the PES for E_K near 1keV, the mean free path becomes up to 15Å. The valence band XPS done by conventional Mg and Al K α sources is thus a bulk sensitive method. However, its resolution is not satisfactory for detailed studies of correlated electronic states even when an additional crystal monochromator is used.

We made a breakthrough in this field by commissioning a very high resolution soft X-ray monochromator at BL25SU of SPring-8, installed on a twin-helical undulator. Photon resolution down to 50meV is realized near 1keV. A SCIEN TA SES200 analyzer is used for HPES. Then the total PES resolution better than 80meV is achieved at 870eV. First we have done the HPES measurements for Yb compounds such as Yb $_4$ As $_3$. The surface components overlapping with the bulk Yb $^{2+}$ components in the measurements near $h\nu=100$ eV are almost suppressed near $h\nu=1$ keV. Thus the bulk Yb $^{2+}$ spectra can be directly analyzed without resorting to deconvolution. In the case of Ce compounds, the tail of the Kondo resonance is observable in HPES. However, there has been a strong controversy over a decade on the 4f spectral shape derived from the 4d-4f resonance near 120eV. The deconvolution is rather critical in the Ce systems because the surface and bulk components are completely overlapping. In our measurements, bulk electronic states are directly obtained.¹⁾ The spectra are found to be reasonably scaled by the Kondo temperature²⁾. Most controversies are now solved by our bulk sensitive HPES. Even in studies of transition metal(TM) compounds, importance of the bulk sensitive HPES is demonstrated.

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Magnetic effects in the band structure of ferromagnetic and antiferromagnetic lanthanide metal films

C. SCHUESSLER-LANGEHEINE [a], E. WESCHKE [a], H. OTT [a], A. YU. GRIGORIEV [a,b], A. MOELLER [a], R. MEIER [a], C. MAZUMDAR [a], G. KAINDL [a]

[a] Institut fuer Experimentalphysik, Freie Universitaet Berlin, Arnimallee 14, D-14195 Berlin, Germany

[b] Institute of Physics, St. Petersburg State University, 198904 St. Petersburg, Russia

The influence of ferro- and antiferromagnetic order on the band structure of local-moment systems like lanthanide metals is a current topic of discussion. Concerning temperature-dependent magnetic splitting and spin polarization, theory predicts a strong relation to the degree of localization of the respective valence state. Delocalized states being sensitive to long-range ferromagnetic order should show a splitting that is essentially proportional to the sample magnetization, whereas localized states should be polarized by the local moment leading to a temperature-independent contribution to the splitting even in the paramagnetic phase [1]. From theoretical considerations, magnetic splitting may also be expected for helical antiferromagnetic structures with sufficiently large helix period [2]. As an example for a delocalized state, we performed a systematic photoemission (PES) study of the Δ_2 -band splitting for the series of the heavy lanthanide metals Gd, Tb, Dy, and Ho. In all magnetically ordered phases, a temperature-dependent splitting of the Δ_2 band with a Stoner-like decrease can be observed. The low-temperature splitting scales linearly with the 4f moment and the temperature scale is defined by the respective highest ordering temperature independent of the type of magnetic order. This result can be related to an anisotropic localization of the respective band states [3].

A valence state expected to show a temperature-independent splitting is the localized d_{z^2} surface state that can be found on the close-packed surfaces of all lanthanide metals. In ferromagnetic systems, this state is known to be exchange split with only the majority component being occupied. The splitting is therefore not accessible by PES. A fully occupied surface state with very similar properties can be prepared, however, by oxygen deposition at room temperature on heavy lanthanide metals. This oxygen-induced state can be readily investigated by PES, revealing a temperature-dependent magnetic splitting, however, with a constant residual splitting even in the paramagnetic phase. Both, the low-temperature and the residual splitting in the paramagnetic phase scale with the 4f spin moment in accordance with the picture of local exchange between 4f and valence electrons.

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X-ray Spectromicroscopy Studies of Polymer Microstructure

I.N. KOPRINAROV[a], A.P. HITCHCOCK[a], T. TYLISZCZAK[a], H. STÖVER[a], W.H. LI[a], J. R. DUTCHER[b], C. MURRAY [b], K. DALNOKI-VERESS[b] AND H. ADE[c]

[a] BIMR, McMaster University, Hamilton, ON, Canada L8S 4M1

[b] Physics, University of Guelph, Guelph, ON, Canada N1G 2W1

[c] Physics, North Carolina State University, Raleigh, NC 27695 USA

Scanning transmission X-ray microscopy (STXM) is emerging as a powerful synchrotron based technique for quantitative studies of the chemical composition and morphology of spontaneous and artificially generated polymer microstructures at 100 nm or finer spatial scales. Examples to be presented include core-shell polymer microspheres [1] and free-standing confined polystyrene-polyisoprene-polystyrene (PS-PI-PS) trilayer thin films [2].

The core-shell polymer microspheres, prepared by precipitation polymerization, have polydivinylbenzene cores, and shells consisting of poly(divinylbenzene-co-ethyleneglycol-dimethacrylate (DVB-EGDMA)) where the EGDMA content ranges from 0 - 90%. Analysis of the C 1s spectral response of the ~300 nm wide shell regions of the polymer microspheres gives compositions in good agreement with those predicted from the synthetic procedures.

Variable energy STXM of lateral patterns that develop in initially unstructured PS-PI-PS thin films which are annealed below T_g of polystyrene allows independent mapping of the thickness variation of the PS and PI layers. These results are being used to aid development of detailed models of the long range dispersion forces believed to drive the self-organization of these structures.

In discussing both examples the presentation will emphasize the importance of data analysis methods (stack-fit [3], singular value decomposition) that take advantage of spatial and spectral domains simultaneously.

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Resonant magnetic x-ray scattering from ultrathin lanthanide-metal films down to a few atomic layers

C. SCHUESSLER-LANGEHEINE [a], E. WESCHKE [a], A. YU. GRIGORIEV [a,b], R. MEIER [a], C. MAZUMDAR [a], C. SUTTER [c], G. GRUEBEL [c], D. ABERNATHY [c], G. KAINDL [a]

[a] Institut fuer Experimentalphysik, Freie Universitaet Berlin, Arnimallee 14, D-14195 Berlin, Germany

[b] Institute of Physics, St. Petersburg State University, 198904 St. Petersburg, Russia

[c] European Synchrotron Radiation Facility, B.P. 220, 38043 Grenoble-Cedex, France

Investigations of the magnetic structure of ultrathin films in the nm-thickness range are of high interest both for technological applications and from a fundamental point of view. Especially antiferromagnetic structures can be readily investigated using magnetic x-ray diffraction due to the separation of charge and magnetic diffraction signals in momentum space. Such structures are found, e.g., among lanthanide metals with a comparably large magnetic period. In these systems, finite-size effects can be expected if the film dimensions become comparable to the magnetic period. A characterization of the magnetic structure of Lanthanide metal films is also interesting from another point of view: Experimental band-structure studies of these systems are almost exclusively performed on epitaxially grown films which provide the atomically clean surface needed for, e.g., photoelectron spectroscopy. In order to interpret the band-structure data in terms of the magnetic structure, the latter has to be known, because a bulk-like structure cannot be anticipated, but may be altered in thin films by finite-size effects and substrate-induced strain.

We therefore performed magnetic x-ray scattering studies in the hard x-ray range on in-situ grown thin epitaxial lanthanide-metal films, which were prepared in a special UHV equipment small enough to be attached to a usual x-ray diffractometer. A magnetic structure similar to the bulk could be observed in Ho films grown on W(110) down to 33 ML thickness. But even by making use of the approx. 50-fold resonant enhancement at the Ho-L₃ absorption edge and performing a polarization analysis, a detailed investigation of the temperature dependence of the magnetic structure appeared impossible because of the strong charge-scattering background.

The situation turned out to be more favorable in the soft x-ray range. At the Ho-M₅ edge, the resonant enhancement of the magnetic scattering cross section amounts to more than 5 orders of magnitude, and experiments on films with thicknesses as small as the helix period (approx. 10 ML) and less become feasible even without polarization analysis. Furthermore, the strong change of the photon absorption length across the resonance can be used to tune the probing depth. For Ho metal, we find that films down to a thickness of 14 ML still show a helix period similar to bulk single crystals, but the magnetic structure in a 10-ML film is distinctly different. This change is accompanied by a change of the c-axis lattice parameter and may be an effect of the film thickness being just one period of the bulk magnetic structure.

Transient ISEELS: a new probe of chemical reactions

A.P. HITCHCOCK, L.E. ENNIS, J.F. LEHMANN

Dept. of Chemistry, McMaster University, Hamilton, ON, L8S 4M1, Canada

Photoelectron spectroscopy has long been used as a probe of transient species generated by a variety of means, such as thermolysis, photolysis, plasma decomposition, and homogeneous or heterogeneous chemical reactions. The detailed information on occupied electronic structure provided by transient-PES has long been used to help identify novel species and understand reaction mechanisms. Site specific core excitation probes unoccupied electronic structure in ways which are very complimentary to photoelectron spectroscopy. Thus it is reasonable to consider applying core excitation spectroscopy to transient studies. Recently we have begun to apply gas phase Inner Shell Electron Energy Loss Spectroscopy as a probe of transient species. ISEELS was used to study HBS, HBO and $H_3B_3O_3$ [1] which were generated by reaction of H_2S and H_2O with crystalline boron in a quartz tube. All three species are very reactive; they have only a transient existence before further reacting with their environment. Inner shell excitation spectra and mass spectrometry of the products of the H_2S reaction at $\sim 1100^\circ C$ identified the known product thioborine (HBS). Surprisingly, when the H_2S reaction was carried out at $\sim 1200^\circ C$, a new, non-S containing species was produced. Inner shell excitation spectra, mass spectrometry and comparison to GSCF3 *ab initio* calculations allowed us to identify this species as borine (HBO). The reaction of H_2O vapor with crystalline boron in a quartz tube at $\sim 1200^\circ C$ was also carried out to produce boroxine ($H_3B_3O_3$) which has a distinctly different spectrum from HBO. A reaction scheme is proposed for the generation of HBO from the reaction of H_2S and boron in a heated quartz tube. Other transient studies involving *in situ* generation of carbenes and reaction of a silylene with N_2O will also be discussed.

*Work supported by NSERC (Canada)

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Generalized Oscillator Strength Profiles for Inner Shell Excitation of CO₂ Derived from Variable Angle Electron Energy Loss Spectroscopy

A.P. HITCHCOCK[a], I.G. EUSTATIU[a], T. TYLISZCZAK[a], C.C. TURCI[b], A.B. ROCHA[b] and C.E. BIELSCHOWSY[b]

[a] Dept. of Chemistry, McMaster University, Hamilton, ON, L8S 4M1, Canada

[b] Instituto de Quimica, Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ 21910, Brazil

In the regime of weak to moderate interaction, inelastic electron scattering can be treated in the Bethe-Born model, which describes the scattering intensities at a given momentum transfer in terms of a generalized oscillator strength (GOS). While the GOS profiles for valence electron excitation have been extensively explored, very few systematic studies of the GOS profiles of inner shell excitations have been reported. As part of such a systematic program we have measured the inner shell electron energy loss spectra of CO₂ in the region of C 1s and O 1s excitation over a wide range of scattering angles (out to 40°), corresponding to momentum transfers (K) as high as 8.4 a.u. [1]. The relative scattering intensities have been converted to absolute GOS values with careful consideration of minimization of systematic errors. This treatment has enabled detection of the weak dipole forbidden C 1s $\sigma_g \rightarrow \sigma_g^*$ transition (298 eV) for the first time. Theoretical GOS were computed within the first Born approximation, using *ab-initio* configuration interaction wave functions for the C 1s transitions and *ab-initio* generalized multi structural wave functions for the O 1s transitions. The theoretical and experimental results are in good agreement indicating that the first Born approximation holds to a surprisingly large momentum transfer for the core excitations studied. This is significantly different than the valence excitation regime where deviations from the first Born approximation are often apparent by $K \sim 3$. A rationale will be presented.

Theory predicts large quadrupole contributions to the GOS for O 1s excitations, for which there is some supporting experimental evidence. The computed GOS for O 1s $\rightarrow ns\sigma$ and $np\sigma$ Rydberg states (~539 eV) clearly show oscillations which are believed to arise from interference between core excitations localized on the left or right oxygen atom of CO₂. Recent measurements provide experimental support for the existence of these oscillations in the GOS for the 539 eV signal.

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Photoemission from Pt(111)-(hex)Rb and Pt(111)-(4x1)RbO using Polarized Synchrotron Radiation*

J. MORAIS[a], A. OELSNER[b], G. SCHOENHENSE[b], R. LANDERS[c],
A. DE SIERVO[c], G.G. KLEIMAN [c], G.H. FECHER[d]

[a] Instituto de Fisica - Universidade Federal do Rio Grande do Sul
(UFRGS), Caixa Postal 15051, Porto Alegre, 91501-970, RS, Brasil.

[b] Johannes Gutenberg - Universitaet, Institut fuer Physik,
D-55099 Mainz, Germany.

[c] UNICAMP - Instituto de Fisica "Gleb Wataghin", Caixa Postal 6165,
Campinas, 13083-970, SP, Brasil.

[d] Institute of Physics, Academia Sinica, Nankang, Taipei 11529, Taiwan.

In various experiments it was proven that the circular dichroism in the angular distribution of photoelectrons (CDAD) is not only observed from oriented initial states (aligned adsorbed molecules or magnetized samples), but also as a consequence of the scattering of photoelectrons at the surrounding atoms in a solid or an adsorbate. In this work we will show first measurements performed at the SGM-beamline of the Brazilian Synchrotron Light Source (LNLS) on a (4x1) superstructure of 1ML RbO adsorbed on Pt(111). The angular and photon energy dependency of core level photoemission for all elements involved was measured by means of an one-axis goniometer electron analyzer built in an UHV chamber. Measurements from the 4p semi-corelevel of Rb and RbO adsorbed at Pt(111) were performed at the 6.5m NIM beamline at BESSY (Germany). The analysis of the 4p emission from clean Rb is complicated due to the high probability for plasmon excitations. The plasmon excitations vanish in the case of RbO, as expected. The measured angular variations of the intensity, spin-orbit branching ratio and CDAD are interpreted in terms of photoelectron diffraction. Differences are observed if using linearly instead of circularly polarized photons. The results will be used to discuss the possibility of photoelectron holography using circularly polarized light. The CDAD contains only intensity from mixed products of the directly emitted and scattered final state partial waves, which carry the full phase-information. Due to the angular momentum transformation the anisotropic nature of photoelectrons is taken automatically into account.

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High Resolution Pulsed Field Ionization Photoelectron-Photoion Coincidence (PFI-PEPICO) Studies of some Hydrides and Halogenomethanes

X.M. Qian[a], Y. Song[a], W. Chen[b], J. Liu[b] and C.Y. Ng[a]

[a]Ames Laboratory, USDOE and Department of Chemistry, Iowa State University, Ames, Iowa 50011

[b]Chemical Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

The availability of accurate thermochemical data for small organic species is important for the determination of energetic properties of larger molecular species. Recently, we have developed a novel pulsed field ionization photoelectron-photoion coincidence (PFI-PEPICO) detection scheme using synchrotron radiation. This development allows significant improvement in the energy resolution for state- or energy-selected unimolecular dissociation studies of cations. This new method achieves a resolution of $\sim 4\text{-}8\text{ cm}^{-1}$, which is more than 10 fold better than that achieved in conventional threshold PEPICO measurements. Using this new PFI-PEPICO scheme, together with pulsed field ionization photoelectron measurements, we have been able to obtain bond dissociation energies for small neutral molecules and their cations with unprecedented accuracy.

We have examined the H/D loss channels in the dissociative photoionization of NH_3 , ND_3 , CH_4 , and CD_4 , yielding the accurate 0 K dissociation thresholds for NH_2^+ , ND_2^+ , CH_3^+ and CD_3^+ from these neutral molecules to an uncertainty within 8 cm^{-1} . For the chlorine loss from Freon22 and Freon21, the 0 K dissociation thresholds have been determined with an accuracy 100 times better than the literature value^[1]. The PFI-PEPICO studies of CH_3I and CH_3Br , when combined with work on CH_4 dissociation, give a highly accurate value for the 0 K heat of formation of CH_3^+ . By comparing the PFI-PEPICO data for CH_2Cl_2 with CH_2ClBr , we have obtained accurate 0 K heats of formation for the important cation CH_2Cl^+ and CH_2ClBr molecule. We have obtained accurate C-Cl bonding energies in different halohydrocarbons. This measurement is relevant to the understanding of the atmospheric ozone chemistry involving the ozone depletion by chlorohydrocarbon compounds.

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**X-Ray Absorption Fine Structure and X-Ray Photoelectron Spectroscopy Study of Mixed Oxides
Obtained by Sol-Gel Processing Method**

J. E. GONCALVES[a], Y. GUSHIKEM[a], A. Y. RAMOS[b,c], M. C. M. ALVES[b], S. C. DECASTRO[d]

[a]Universidade Estadual de Campinas - Instituto de Quimica, Unicamp, CP 6154, 13083-970, Campinas, SP,
Brazil

[b]Laboratorio Nacional de Luz Sincrotron, CP 6192, 13083-970, Campinas, SP, Brazil

[c] Laboratoire de Mineralogie-Cristallographie, CNRS-Paris VI, 4 Place Jussieu, 75252, Paris Cedex 05, France

[d] Universidade Estadual de Campinas - Instituto de Fisica, Unicamp, CP 6165, 13083-970, Campinas, SP, Brazil

Binary oxides of $\text{SiO}_2/\text{TiO}_2$ prepared with different Ti concentrations were investigated by x-ray absorption spectroscopy (XAFS), including x-ray absorption near edge spectroscopy (XANES) and extended x-ray absorption fine structure spectroscopy (EXAFS). Ti oxides have a great number of applications in many fields, including catalysis. Their efficiency as a catalytic material depends on the morphology: a high surface area and porosity are needed. In addition, glasses containing TiO_2 are receiving great attention due to the high optical quality presented. Several studies were carried out trying to determine how Ti is coordinated: this coordination seems to account for the non stoichiometric characteristics of these glasses [1].

In this work Ti local order was investigated. XAFS analysis were performed on the Ti K edge. The x-ray absorption near-edge structure (XANES), compared to reference samples, proved Ti to be in octahedral environment for all sol-gel samples. EXAFS spectra confirmed XANES data, giving the medium Ti-O distance (1.92 Å) in the first coordination sphere. On the silica-titania oxides antimonate ion was adsorbed. The samples were analysed by x-ray photoelectron spectroscopy (XPS) together with reference compounds. According to XPS spectra Ti is present as TiO_2 and Sb as Sb_2O_5 .

No evidence was found of Ti in tetrahedral sites, as reported in the literature [2].

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Initial Stages of Pd Growth on Cu (111) by Photo-electron Diffraction

A. DE SIERVO, R. LANDERS, T.A. FAZAN AND G.G. KLEIMAN

UNICAMP -- IFGW Caixa Postal 6165 Campinas SP, Brasil

The PdCu alloy system, which has important catalytic properties, has been the object of many experimental and theoretical studies with many techniques. Nevertheless, some questions remain concerning the interaction of Pd with the Cu (111) surface.

There is no full agreement among results of theoretical calculations: both moderate Pd segregation [1] and Cu surface enrichment [2] have been predicted. Scanning tunneling microscope (STM) [3] studies have shown that Pd deposited onto the (111) surface of Cu tends to diffuse into the crystal if the coverage is greater than 15%. X-ray Photoelectron Diffraction (XPD), which is element and surface sensitive, is ideally suited to this kind of study because of its ability to determine the relative position of atoms. To date, no XPD study of this surface has been reported. Here we report the application of XPD to determine the structure of ultra thin epitaxial Pd films evaporated on Cu (111) single crystal surfaces.

The Cu crystal was cleaned in-situ by repeated cycles of Ar ion bombardment and annealing at around 800K under ultra high vacuum (base pressure 6×10^{-11} mbar). The cleanliness was checked by XPS and the surface crystallinity by LEED. Pd was evaporated from the tip of a wire heated by electron bombardment; the deposition rate was 0.5 monolayer/minute; and the pressure never exceeded 10^{-9} mbar during deposition.

In measurements of the Pd 3d and Cu 3p peaks, the axial angle was varied over a range of 150 degrees at intervals of 3 degrees. The exciting photon's energy was 800 eV from the SGM beam line at the Brazilian Synchrotron Light Source (LNLS).

Analysis of the data was performed [4] with a basic cluster size of 131 atoms arranged in 5 layers (8 multiple scatterings were adequate for this analysis). Many different types of structure were tried, and the only one to give a good agreement with both the Pd and Cu diffractions corresponded to a capping layer of pure Cu and a second layer mainly of Pd, both of (111) symmetry. Bulk Cu values of the interlayer and intralayer distances (within the precision of the calculations) describe the data well.

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Spectromicroscopy: Present and Future

E. BAUER

Department of Physics and Astronomy, Arizona State University, Tempe, AZ 85287-1504

The high brilliance of the third generation synchrotron radiation sources has opened the door to X-ray photoelectron microscopy (XPEEM), spectroscopy and diffraction with high lateral resolution using non-scanning cathode lens instruments. The resolution of these instruments is not limited by the spot size of the photon beam as in scanning XPEEM but by the quality of its electron optics. As a consequence, the evolution of the field has not only been determined by the improvements of the source brightness but to a large extent by the development of better electron optics. The photon energy range used in this work is up to 1000 eV. A brief review of the short history of the field will be followed by a discussion of the present state of the art with respect to instrumentation, methodology and applications. Instruments without energy filter use secondary electrons for imaging, those with energy filter in addition energy-selected true photoelectrons. The energy filter allows also fast photoelectron spectroscopy and diffraction from small areas. The addition of an illuminating electron beam and of a beam separator adds fast structural characterization by low energy electron microscopy (LEEM) and diffraction (LEED) so that a comprehensive structural characterization with presently 10 nm resolution is possible [1,2]. These possibilities will be illustrated by application examples to semiconductors, magnetic materials, polymers and biological materials from various groups. At present spectromicroscopy is limited by the aberrations of the cathode lens which limit resolution and transmission and by the fact that most XPEEMs lead a rather parasitic life on multi-end station beamlines. This situation will soon change with the development of aberration-corrected instruments such as the SMART at BESSY II [3] or a similar instrument at ALS and with the construction of high brightness beamlines specifically for spectromicroscopy. Resolution and brightness is expected to increase then by a factor of 10, opening up a much wider field of application.

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Quasi-Atomic MVV Auger Spectra of Pd Metal: Cascade Processes*

A. DE SIERVO, R. LANDERS, M.F. CARAZZOLLE AND G.G. KLEIMAN

Instituto de Física, Universidade Estadual de Campinas
13083-970 Campinas, São Paulo Brasil

One of the most interesting aspects of metallic valence band Auger spectra involves the connection between screening, correlation of the final-state holes and the form of the spectra. When the holes' effective Coulomb interaction (U) (or Auger parameter) is strong (as compared to the bandwidth) the MVV spectrum is quasi-atomic, as in the case of Ag. When it is weak, the spectrum does not present atomic multiplet structure, as in the case of Pd. For metals with more d -band holes, such as Rh, the MVV spectrum is band-like. The nature of the valence electron screening determines the strength of U : d -electrons screen the holes in Ag rather ineffectually, while s -electrons screen those of Pd (and Rh) much more effectively.

In alloys, quasi-atomic Pd MVV spectra have been observed [1], indicating a full Pd d -band. The complete screening model mentioned above, in which the screening electron is added self-consistently to the atom, has been used to interpret Auger parameter trends [2], and is normally assumed to be valid in analyses of spectral shapes. Nevertheless, the filling of the Pd metal d -band by s -screening electrons has never been directly demonstrated to produce quasi-atomic spectra. Indeed, for this to occur, it would be necessary for the final state to correspond to a full d -band.

We present results for the XAES MVV spectra of Rh, Pd and Ag measured, with synchrotron radiation, before and after ionization of the respective L_3 levels. The respective spectra change dramatically upon ionization and we attribute the extra structure produced after ionization as corresponding to the $M_{45}M_{45} \rightarrow M_{45}VV$ transition, which is subsequent to the $L_3M_{45}M_{45}$ transition. The extra structure for Pd is markedly similar to that of Ag and different from that of Rh, indicating its quasi-atomic nature. Results of atomic calculations for this rather complicated transition agree quantitatively with the experimental spectra of Pd and Ag. These results allow us to interpret the extra spectral structure of Pd as quasi-atomic. We attribute the quasi-atomic form to a bound state of the two final-state holes in the full Pd d -band. We believe the filling of the band to be produced by s -valence electrons which screen the two initial M_{45} holes. These findings represent the first observation of the influence of complete screening on spectral features.

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Photon Stimulated Ion Desorption for PMMA Thin Film in the Oxygen K-Edge Region Studied by Auger Electron-Photoion Coincidence Spectroscopy *

E. IKENAGA[a], K. ISARI[b], K. KUDARA[b], K. KUSABA[b], S. A. SARDAR[b], S. WADA[b], K. MASE[c], T. SEKITANI[b], K. TANAKA[b]

[a]Hiroshima Synchrotron Radiation Center, Hiroshima University, Higashi-Hiroshima 739-8526, Japan

[b]Department of Physical Science, Faculty of Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan

[c]Institute of Materials Structure Science, Tsukuba 305-0801, Japan

A study of surface photochemical reactions induced by core excitation has been developed with the advance of the synchrotron radiation technique in a soft X-ray region. In particular, site-specific reaction was found in photon stimulated ion desorption (PSID) following core resonant excitation for PMMA (poly-methylmethacrylate) thin films [1]. One of the probable models for PSID is the Auger stimulated ion desorption (ASID) mechanism. The Auger final state is directly related to the ion desorption in this mechanism. The coincidence measurement of energy-selected electrons and mass-selected ions is powerful technique for study of PSID mechanism, because the intermediate electronic states leading to ion desorption is directly identified by an energy analysis of the emitted electron. We constructed a new electron-ion coincidence apparatus at Hiroshima Synchrotron Radiation Center (HiSOR) in Hiroshima University, and recently applied it for ion desorption for PMMA thin films induced by carbon core excitation. The results of the Auger electron-photoion coincidence (AEPICO) measurements indicated that the ion desorption strongly depends on Auger final state. In this work, we performed AEPICO measurements for PMMA thin films at various resonant oxygen core excitations. The dominant productions of CH_3^+ and CH_2^+ ions were observed at resonant excitation to O- CH_3 anti-bonding state, and OCH^+ ion was observed at resonant excitation to C-O CH_3 anti-bonding state. Their coincidence yields were strongly dependent on Auger electron kinetic energy. The results show that the ion desorption depends on the bonding/anti-bonding character, and the localization character of the Auger final state. We will discuss the correlation between ion desorption and Auger final state for PMMA thin films.

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PEEM and MEEM of Chloroaluminum Phthalocyanine Ultrathin film on MoS₂

H. Yasufuku[a], T. Ibe[b], M. Okumura[a], S. Kera[a], K. K. Okudaira[a,b,c], N. Ueno[a,b,c], Y. Harada[d]

[a]Graduated School of Science and Technology, Chiba University

[b]Department of Materials Technology, Faculty of Engineering, Chiba University

[c]Center for Frontier Science, Chiba University, Inage-ku, Chiba 263-8522, Japan

[d]Life Culture Department, Seitoku University, Iwase, Matsudo 271-8555, Japan

Electronic states at organic/inorganic interfaces, which dominate properties of molecular devices, depend on either molecular orientation or the film thickness. Imaging techniques with high surface sensitivity are useful for directly detecting topological variation of surface electronic states. Photoelectron emission microscopy (PEEM) gives the lateral information of electronic states of solid surfaces ranging from the valence top to the inner shell. Especially, PEEM using photons of threshold ionization energy provides the ionization potential differences of the surface sensitively, while metastable electron emission microscopy (MEEM) offers the information of valence band of the outermost surface selectively. In this work, we could image the difference between the surface electronic states of monolayer and doublelayer regions of chloroaluminum phthalocyanine (ClAlPc) on a MoS₂ single crystal by PEEM and MEEM.

The specimen was prepared by depositing ClAlPc monolayer on the MoS₂, and further depositing second layer through a mesh to obtain doublelayer regions. On the MoS₂ surface, the molecules in the monolayer are oriented flat with the Cl atoms protruding outside the film, and the molecules in the second layer are turned over [1].

In the PEEM image, the monolayer region was bright, while the doublelayer region was dark. It directly indicates that the ionization potential of the monolayer is smaller than that of the doublelayer. On the other hand, It was reported that the work function of the monolayer is larger than that of the doublelayer [2]. The PEEM result cannot be understood from this work function difference. It suggests that the energy position of the valence top of the film largely depends on the film thickness. MEEM results will be shown at the conference.

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A State-Selective Photofragment Translational Spectroscopy Study of Ethylene Sulfide Probed via Tunable VUV Light Source

Fei Qi and Arthur G. Suits

Chemical Sciences Division
Ernest Orlando Lawrence Berkeley National Laboratory
Berkeley, CA 94720

Recent work on Endstation 1 at the Chemical Dynamics Beamline has revealed two new channels in the photodissociation of ethylene sulfide, $c\text{-C}_2\text{H}_4\text{S}$, that have fundamental chemical significance. Previous studies using traditional universal detection or laser probing of the photoproducts have shown the importance of a process yielding electronically excited sulfur atoms and the ground electronic state of ethylene, the reverse of the corresponding insertion reaction. However, recent work at the ALS exploits the tunable vacuum ultraviolet undulator radiation as a universal but selective probe of the reaction to reveal new aspects of the photodissociation dynamics. These new studies have shown, in addition to the established products, a channel representing the production of H_2S with a vinylidene radical, the H_2CC : isomer of acetylene. This implies reaction involving the 1,1 hydrogens in the course of H_2S elimination. Furthermore, a multimodal translational energy distribution is observed in the sulfur atom, and selective probing allows discrimination of the singlet and triplet components of this distribution. The second component of the ground state sulfur atoms are formed at energies corresponding to the production of the excited triplet state of ethylene. This implies a mechanism involving two C-S bonds scission synchronously, followed by spin-conserving elimination of the ground state sulfur atom to yield triplet ethylene. The energetics for this process can be used to provide the first experimental insight into the properties of triplet ethylene near its equilibrium geometry. This region of the potential energy surface is inaccessible to spectroscopic study since there is no Franck-Condon overlap between the planar ground state of ethylene and the triplet state, in which the two CH_2 groups are believed to lie in perpendicular planes.

Real-time monitoring of the growth and decomposition of SiO₂ layers on Si(001) by a combined method of RHEED and AES

Y. TAKAKUWA, F. ISHIDA

Research Institute for Scientific Measurements, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577,
Japan

In order to clarify the reaction model of Si thermal oxidation, which is of industrial importance to get high quality gate insulator films in a few nm scale for MOSFET devices, the growth and decomposition kinetics of very thin SiO₂ layers on Si(001) were investigated by a real-time monitoring method of reflection high energy electron diffraction combined with Auger electron spectroscopy (RHEED-AES). In the RHEED-AES measurement [1], O KLL Auger electrons excited by a grazing-incidence 10-keV electron beam for the RHEED observation are detected, so that the time evolutions of the SiO₂ coverage and interface morphology are obtained simultaneously. We demonstrate that the correlation between them is very useful for connecting the morphological change of the SiO₂/Si interface with the reaction model of Si thermal oxidation.

The Si(001) surface with a miscut angle of 0.4° was thermally oxidized by O₂ of 99.9% purity in a temperature region of 500-900°C. From the time evolution of the O KLL Auger electron intensity I_{O-KLL} , the Si thermal oxidation is divided into two temperature regions: SiO₂ growth and etching at ~750°C. Furthermore the SiO₂ growth is divided into two temperature regions: Langmuir-type adsorption and two-dimensional (2D) growth at ~650°C. In the 2D growth region, RHEED spots of Si bulk diffraction appear, indicating the roughening of the interface, while such spots are hardly observed in the Langmuir-type adsorption region. The correlation between the I_{O-KLL} and RHEED bulk diffraction spot intensity shows that the interface roughening occurs rapidly with the SiO₂ coverage up to ~30% and then saturates. On the other hand, the RHEED specular and half-order spot intensities decreases gradually with the SiO₂ coverage up to 100%. The interface roughening observed for the 2D SiO₂ island growth is considered in terms of the competitive consumption of Si adatoms (ad-Si) by SiO desorption, $2ad-Si + O_2 \rightarrow 2SiO$, and SiO₂ growth, $ad-Si + O_2 \rightarrow SiO_2$ [2].

When the Si(001) surface was completely oxidized, isothermal decomposition of the grown SiO₂ layer was started. Then the roughness was not reduced but enhanced further with the removal of SiO₂ layers. This is ascribed to the SiO desorption following the decomposition reaction: $SiO_2 + ad-Si \rightarrow 2SiO$.

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Local Electronic States of Oxygen on Ni (111) Surface Studied by Metastable Atom Electron Spectroscopy*

M. AOKI, H. TAOKA, T. KAMADA, S. MASUDA

Department of Chemistry, Graduate School of Arts & Sciences, The University of Tokyo, Komaba, Meguro,
Tokyo 153-8902, Japan

Interaction of oxygen molecule with a Ni surface has attracted considerable attention as a prototype for understanding dissociative adsorption, oxidation reaction, etc. However, information on the electronic states at the outermost surface layer seems very limited. In this study, we report the local electron distribution of oxygen adsorbed on Ni(111) surface using metastable atom electron spectroscopy, which is based on energy analysis of electrons ejected by thermal collision of rare gas metastable atoms such as He*(2³S) with a solid surface [1]. For systematic comparison, we measured the spectra for oxygen in various phases, i.e., gaseous O₂, chemisorbed O, physisorbed O₂ at low temperature, and NiO(111). Our results are summarized as follows:

- (i) The He* atoms deexcite on clean and chemisorbed surface via resonance ionization + Auger neutralization, while the decay channel changes into Penning ionization on the oxidized layer and NiO(111) owing to their insulating nature.
- (ii) Penning ionization also takes place on the physisorbed O₂ layer at 20 K, where the relative intensity of the π -derived bands

Multilayer X-ray Mirrors with Carbon Layers

I.I.LYAKHOVSKAYA [a] and E.A.BUGAEV [b]

[a] Institute of Physics, St.-Petersburg University, St.-Petersburg, 198904, Russia

[b] Kharkov Politechnical University, Kharkov, 310002, Ukraine

Progress in X-ray optics is connected with the increasing significance of optical elements for control of X-ray radiation beams such as X-ray interference mirrors. These mirrors have very perspective applications as the reflective and dispersive elements for soft X-ray radiation as well as for slow neutron beams.

The multilayer periodic nanostructures under investigation with the period of 5 nm consist of carbon layers alternated with metal chromium or chromium boride compound films evaporated on the polished silicon plates. The multilayer interference mirrors were produced by magnetron sputtering method from bulk material targets. The special attention was paid to the technological aspects during the preparation of the mirrors. The stabilized voltage sources were used. The distance between the targets and the substrates can be varied from 4 to 13 cm. Besides the temperature of the substrates was changed in the interval from 60 to 300 °C.

Various methods were used to investigate the structure of the layers and interfaces in the multilayer covering: electron spectroscopy of cross-section of the films and X-ray diffraction method. It was proved that the structure of metal layers and the quality of the X-ray mirrors strongly depended on the temperature of the substrates in the process of preparation.

For the X-ray interference mirrors indicated above the angular dependences of reflection power were measured in two wavelength intervals: on monochromatic radiation of Cu K α -line (0.154 nm) (X-ray diffractometer) and on C K -radiation (4.47 nm) (soft X-ray spectrometer). It must be emphasized that the absolute values of the reflection coefficients were obtained taking into account the relative efficiency of the detectors for incident and reflected intensities. The obtained maximal value of the reflection coefficient for the carbon K-radiation, 21 %, must be considered as very promising.

Being used for the powerful synchrotron radiation beams these optical elements are subject to an intensive heating that leads to rapid degradation of X-ray mirrors. The influence of thermal annealing was also considered in our studies. One of the important results was that the optical characteristics of CrB₂ – C interference mirror were found to be stable up to 1070 °K.

The theoretical evaluation of the reflection coefficients for measured multilayer nanostructures were also performed in this investigation and exposed the satisfactory correlation with our experimental results.