

ELECTRONIC STRUCTURE

Experimental and theoretical studies of the electronic structures of AuAl₂ and PtGa₂

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Synchrotron-radiation-excited angle-resolved photoemission spectra for the (100) and (111) faces of AuAl₂ and (111) face of PtGa₂ are presented, along with derived experimental dispersion relations. These bands are compared with those obtained from the theoretical band-structure calculation, as shown in Figure 1 and Figure 2. The density-of-state curves, band hybridization, and charge transfer for AuAl₂ are calculated. The x-ray absorption near-edge spectra for PtGa₂ agree with the calculated site- and symmetry-decomposed partial density-of-state curves, and electrons transfer from Pt to Ga in forming the PtGa₂ compound. Extended x-ray absorption fine-structure spectra of PtGa₂ are analyzed to yield its structural parameters. The energy variation of the Au and Pt 5d bands for AuAl₂ and PtGa₂, respectively, shows atomic-like behavior in the photon-energy range of 80 to 200 eV.

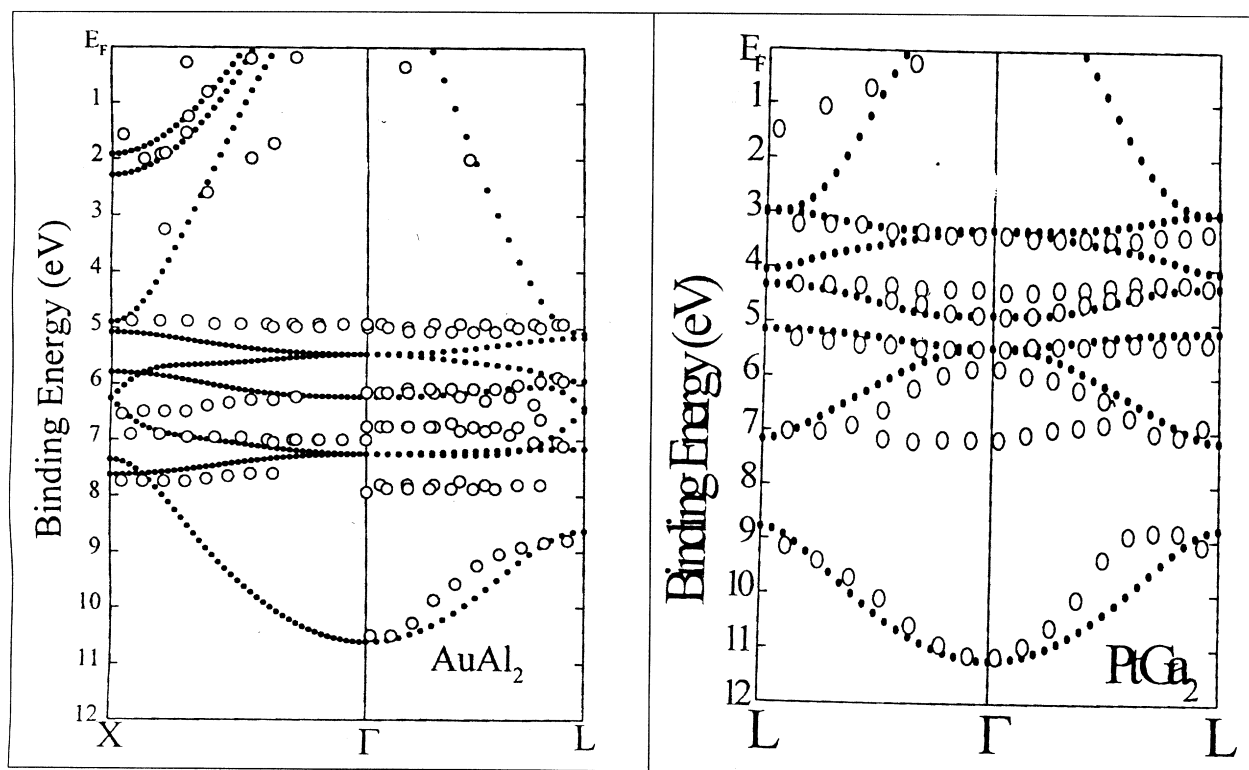


Figure 1: Experimental (open circles) and theoretical (closed circles) band structure of AuAl₂ along X-Γ-L.

Figure 2: Experimental (open circles) and theoretical (closed circles) band structure of PtGa₂ along Γ-L.

Resonant Photoemission Study of $R\text{Fe}_4\text{P}_{12}$ ($R = \text{La}, \text{Ce}, \text{Pr}$)

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Ternary intermetallic compounds $R\text{Fe}_4\text{P}_{12}$ ($R = \text{rare earth}$) with the filled skutterudite structure exhibit various interesting properties. According to the measurements using a high quality single crystal [1], $\text{CeFe}_4\text{P}_{12}$ shows the complex temperature dependence of resistivity unexpected for a simple single-gap semiconductor; $\text{PrFe}_4\text{P}_{12}$ exhibits the Kondo-like anomalies in the transport properties. In this study, we investigated the electronic states of $R\text{Fe}_4\text{P}_{12}$ ($R = \text{La}, \text{Ce}, \text{Pr}$) by the high-resolution resonant photoemission spectroscopy.

The photoemission experiments were performed using synchrotron radiation at the beam line BL-11D of the Photon Factory, High Energy Accelerator Research Organization (KEK). The instrumental resolution was about 65 meV. The samples were cooled to 20 K.

Figures 1 and 2 show the resonant photoemission spectra of $\text{CeFe}_4\text{P}_{12}$ and $\text{PrFe}_4\text{P}_{12}$, respectively. The intense band located at the binding energy of ~ 0.7 eV is mainly due to the Fe $3d$ band. The $4f$ spectra were obtained by subtracting the resonance minimum spectra ($h\nu = 114$ eV and 115 eV) from the resonance maximum spectra ($h\nu = 122$ eV and 124 eV). The solid lines in Figs. 1 and 2 indicate the Ce $4f$ and Pr $4f$ spectra, respectively. In the Ce $4f$ spectrum, the f^0 and f^1 peaks are located at the binding energies of ~ 2.8 eV and ~ 0.5 eV, respectively. The large intensity ratio of the f^1 peak to the f^0 peak indicates the strong hybridization between the Ce $4f$ and the valence band states. However, the $f_{5/2}^1$ peak located near E_F was not observed apparently. We performed the analysis of the Ce $4f$ and Ce $3d-4f$ absorption spectra [2] using a single impurity Anderson model. The number of $4f$ electrons was estimated to be ~ 0.85 . In the Pr $4f$ spectrum, the f^1 and f^2 peaks are located at the binding energies of ~ 4.6 eV and ~ 0.5 eV, respectively. The spectrum indicates that $\text{PrFe}_4\text{P}_{12}$ is a strongly hybridized system in Pr compounds. However, we could not observe a peak structure corresponding to the tail of the Kondo resonance peak in the vicinity of E_F .

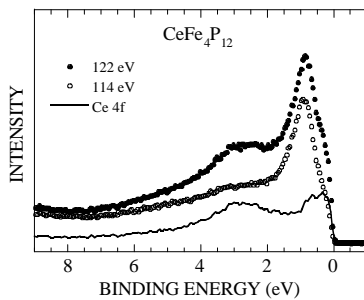


Figure 1: Resonant photoemission spectra of $\text{CeFe}_4\text{P}_{12}$.

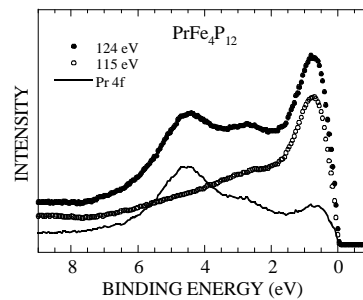


Figure 2: Resonant photoemission spectra of $\text{PrFe}_4\text{P}_{12}$.

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Electronic Structures of Linear Carbon Chain Molecules

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Carbyne is a name of linearly bonded carbon atoms and it can be classified into two categories by its bonding conditions; cumulene type having (=C=C=C=C=) bonds and polyynes type having $-C\equiv C-C\equiv C-$ bond [1]. Carbyne is believed to be unstable so that it cannot be isolated with macroscopic quantity. Because of this nature, carbyne has not been investigated intensively, but it is considered as an ultimate form of carbon nanotubes so that its application such as field emitter, molecular conductive wire and fibers with mechanical strength are expected. There could be a large difference in the electronic structures of these two types, but it is difficult to deal with them because of lack of the specimens. In order to clarify the difference we measure ultraviolet photoelectron spectra of their model compounds and examine their electronic structure with an aid of MO calculation.

Figure 1 shows photoelectron spectra of cumulene type model compounds terminated by phenyl groups. A spectrum of solid benzene [2] is also shown to distinguish the contribution from phenyl groups. Structures labeled B, C and D seem to be due to electrons derived from phenyl groups. Hence structure A, the smallest binding energy component, can be attributed to cumulene type carbon chain. The longer the chain length, the smaller the binding energy of the highest occupied molecular orbital (HOMO). This could be an indication that carbyne of long carbon chain is not stable. MO calculation also supports this binding energy tendency of the HOMO of cumulene type molecules.

Photoelectron spectra of polyynes type model compounds also revealed that the HOMO is attributed to polyyne chain. Chain length dependence of the HOMO energy level has not been examined yet, but MO calculation suggests that its decrease saturates when the number of the carbon atoms exceed more than ten.

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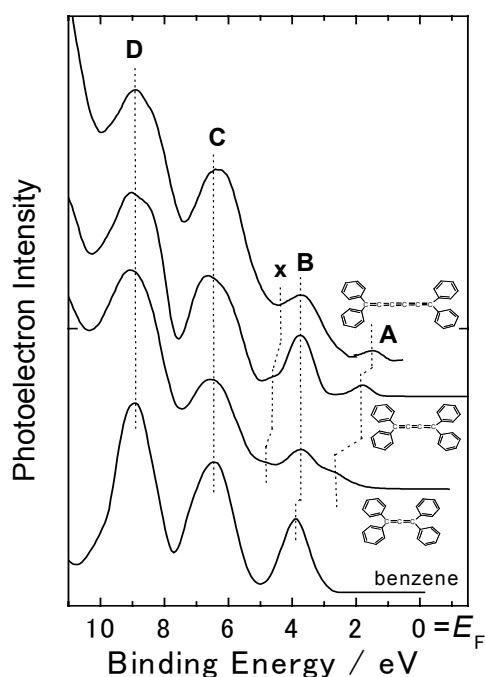


Figure 1: Photoelectron spectra of cumulene type carbyne model compounds and benzene.

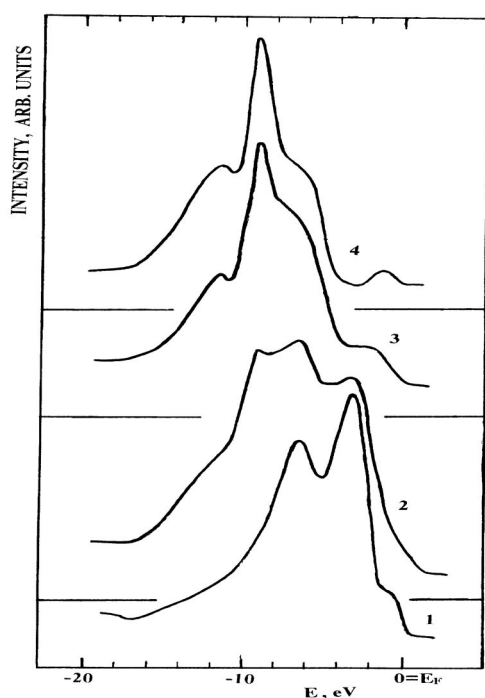
PHOTOELECTRON SPECTRA OF SUBMONOLAYER $C_{60}F_{48}$ FILMS ON D-METAL SUBSTRATES.

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Photoelectron valence band spectra of submonolayer (~ 0.1 - 1.0 ML) fullerene $C_{60}F_{48}$ films, evaporated in situ onto d- metal foils of Au, Pt, Ta, W (VB= 5d-6s), Ni (3d-4s), were obtained under He II- lamp excitation (40.8 eV) at the UHV set-up (property of the Spectromicroscopy beamline of ELETTRA) at RT. Spectral structure transformations versus film thickness and substrate material were under investigations (Fig.1) [1]. For film thickness starting from ~ 0.5 ML up to 1.0 ML the spectral features were found to be close to those measured for thick films (~ 5 - 10 ML and higher) [2]: with a main peak at a $E_b=9$ eV (below the Fermi-level) of a F2p origin and a broad peak at 11.4 eV (C2p or C2s), with a total VB width about 14 eV. However, a new small intensity band with a $E_b=1.5$ eV (FWHM ≈ 1.4 eV) was found to appear at film thickness of (0.4 - 0.5) ML and to decrease beyond 1 ML. This feature was absent in thick film spectra. It may be attributed to a strong ion-covalent bonding between d-metal and film at low coverage, thus giving rise to conduction band changes of the near surface metal layer, with a new antibonding state below E_f . The likely type of structure has been reported for several of C_{60} /Metal systems [3]. For film thickness exceeding 0.3 ML, our spectra were



found to be rather weakly dependent on substrate material, excepting for Ni where this new band was found at $E_b=1.7$ eV, correlating with a stronger C_{60} /M bonding found for Ni.

Figure 1. Typical photoelectron spectra taken at 300 K, $\sim 10^{-10}$ mbar, immediately after $C_{60}F_{48}$ film evaporation *in situ* from powder onto an Au foil (shown from bottom to top, $E=0$ corresponds to E_f): 1 - pure Au foil, 2 - about 0.1 ML of $C_{60}F_{48}$ coverage, 3 - 0.3 ML, 4 - about 1.0 ML: shown are a main peak at $E_b=9$ eV, a shoulder near 6.6 eV, a broad peak at 11.4 eV, and a new small intensity band at 1.5 eV.

(The energy resolution of a hemispherical electron energy analyser is about 150 meV.)

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THREE-DIMENSIONAL BAND MAPPING BY COMBINED VERY-LOW-ENERGY ELECTRON DIFFRACTION AND PHOTOEMISSION

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Mapping of the electronic band structure $E(\mathbf{k})$ resolved in the three-dimensional \mathbf{k} using angle-resolved photoemission (PE) spectroscopy has a principal constraint: the final state dispersion in the surface-perpendicular wavevector k_{\perp} must be known. As the final states are the time-reversed LEED states, the optimal method for their determination is Very-Low-Energy Electron Diffraction (VLEED): The critical points (CPs) in the final state k_{\perp} -dispersion like the edges of local band gaps are reflected by the extrema in the derived elastic electron transmission dT/dE (Fig. 1). Moreover, the final state lifetime can be determined from the VLEED spectral widths.

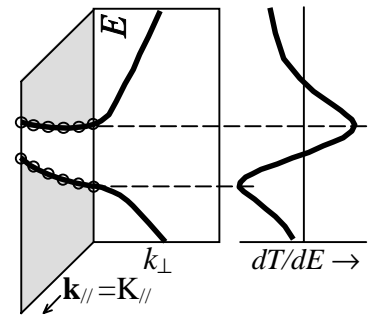


Fig. 1. Determination of the PE final bands by VLEED: the critical points are reflected by the dT/dE extrema.

The VLEED-PE three-dimensional band mapping can be realized, firstly, using model final bands fitted to the VLEED experimental CPs. This method has recently enabled consistent mapping of the valence band for some layered materials [1]. Alternatively, a direct angle-dependent method can be realized: The final bands are mapped directly along certain Brillouin zone symmetry lines by plotting CPs as a function of the incident $\mathbf{K}_{//}$; photoemission out of these bands is then used to map the valence bands in the Constant-Final-State mode. This method has recently been demonstrated on Cu [2] (Fig. 2). It gives an access to a variety of lines in the Brillouin zone using only one crystal surface. Both combined VLEED-PE methods, incorporating the non-free-electron and self-energy effects in the final states, enable accurate three-dimensional band mapping under control of the intrinsic accuracy.

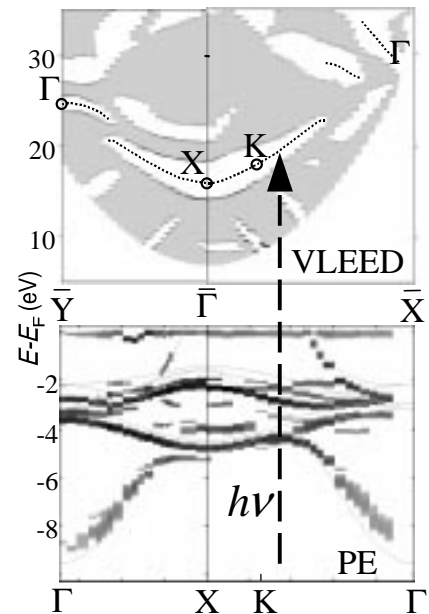


Fig. 2. Angle-dependent VLEED-PE band mapping on Cu(110): VLEED surface-projected final bands with the gaps along $\Gamma X K \Gamma$ indicated. Note non-free-electron dispersions at larger $\mathbf{K}_{//}$; PE valence band determined with the final state energies in these gaps.

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ELECTRONIC STRUCTURE OF Cu REVISITED: SELF-ENERGY EFFECTS IN UNOCCUPIED AND OCCUPIED STATES

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Quasiparticle dispersions $E(\mathbf{k})$ for unoccupied states above the vacuum level can be mapped using Very-Low-Energy Electron Diffraction (VLEED) [1]. This technique is based on the fact that the sharp changes in the elastic electron reflectivity $R(E)$ reveal the critical points in the k_{\perp} -dispersion of the bands effectively coupling to vacuum. Plotting the dR/dE extrema as a function of the incident electron \mathbf{K}_{\parallel} then directly yields $E(\mathbf{k})$ along certain symmetry lines in the Brillouin zone under full control of the three-dimensional \mathbf{k} . The VLEED derived unoccupied bands can then be used in photoemission (PE) spectroscopy to achieve three-dimensional mapping of the quasiparticle dispersions in the valence band.

We report on mapping of unoccupied and occupied bands in Cu, a prototype weakly-correlated system, under full control of the three-dimensional \mathbf{k} using, respectively, VLEED and PE. The experimental quasiparticle $E(\mathbf{k})$ was compared with a Density Functional Theory (DFT) calculation performed by a state-of-art full-potential LAPW method (Fig.1). The deviations are the self-energy corrections $Re\Delta\Sigma$ due to the difference of the excited-state exchange-correlation from the DFT ground-state one. They show a significant band- and \mathbf{k} -dependence such as e.g. a sign change between the valence d - and sp -bands. This behavior is correlated with the spatial distribution of the one-electron wavefunctions: strong localization in the core region of high electron density results in a stronger self-energy shift from the Fermi level [2]. The established view that for weakly-correlated Cu the excitation spectra are well described by DFT resulted thus from fortuitous inaccuracies of earlier calculations. An inclusion of the excited-state exchange-correlation within the GW approximation vastly improves description of the quasiparticle energies (Fig.1).

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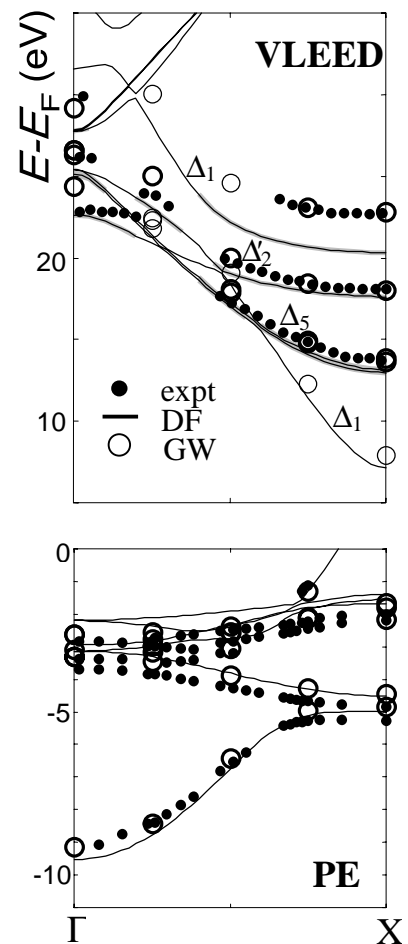


Fig. 1. Experimental $E(\mathbf{k})$ compared with the DFT results. The significant and band-dependent deviations are due to the self-energy effects. They are reproduced by the quasiparticle GW calculations.

DICHROISM IN THE RESONANT 4f PHOTOIONISATION OF ATOMIC EUROPIUM

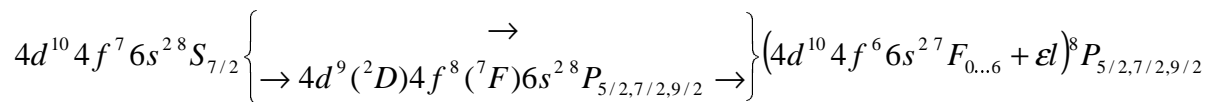
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In the vicinity of the $4d^{-1}$ photoionization thresholds the cross section of the europium $4f^1$ photoionization is dominated by the well known giant resonance, which is due to the interference between direct $4f^1$ photoionization and the excitation of a $4d$ electron into the $4f$ shell followed by a fast autoionization [1]:



Preparing oriented / aligned free europium atoms by optical pumping with circularly / linearly polarized laser radiation we probed the linear magnetic dichroism in the angular distribution (LMDAD) and the linear alignment dichroism (LAD) in the $4f$ photoionization spectra excited by linearly polarized undulator radiation at the BW3 beamline at HASYLAB.

Both the LMDAD and the LAD change dramatically when tuning the photon energy through the giant resonance. The characteristic features of the spectra can be explained by model calculations based on the description of the dichroism in the photoelectron spectra of polarized atoms [2] and Fano's [3] treatment of the interaction of discrete states with underlying continua.

The results of the model calculations are corroborated by HF-calculations which reproduce the energy dependence of the LMDAD / LAD in more detail. Our LMDAD spectra are in contrast to the corresponding spectra reported for solid Gd which display only small differences for excitation on and off resonance [4].

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Resonant photoemission from clean and Er-covered Si(100) surfaces

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A detailed investigation of the Er/Si(100) system, with Er coverages ranging from 0 to several monolayers, has been conducted by means of soft X-ray photoemission combined with low energy electron diffraction. The valence band (VB) spectra measured show the existence of resonances at both clean and Er-covered Si(100) surfaces.

For the clean (2x1)-reconstructed surface, a sharp resonant peak appears at 4.5 eV below VB maximum when the photon energy, $h\nu$, reaches above the Si 2p core-excitation threshold, namely, in the range of 110 – 120 eV. The phenomenon is quite different from a previous observation by Kobayashi *et al* [1] and is ascribed to Fano interference between the excitation of a valence s-p electron to the continuum and the core excitation from 2p to a 3d state. Momentum conservation holds for the transitions observed.

The presence of a thin Er overlayer brings in the VB spectrum a multiplet Er 4f component, whose intensity shows a typical Fano profile versus $h\nu$ in the vicinity of the Er 4d excitation threshold. While the 4f peaks are relatively broad for as-deposited surfaces, fine structure becomes observable upon annealing of the Er-covered samples moderately, which is indicative of the formation of a single erbium silicide species in the latter case.

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A NEGATIVE SPIN-POLARIZATION STRUCTURE OF NI(110): PROBED BY SPIN- AND ANGLE-RESOLVED PHOTOELECTRON SPECTROSCOPY

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Nickel is one of the typical itinerant ferromagnetic 3d transition metals and many experimental and theoretical studies have been performed so far. Spin- and angle-resolved photoelectron (SARPE) spectroscopy has been used to study its spin-dependent electronic states. However, all the measurements reported by other groups are performed only in normal-emission manner, which can only provides the information on the electronic states in a limited wave vector region, for Ni(110) the ΓK line ($\bar{\Gamma}$ point) of the bulk (surface) Brillouin zone.

We already reported the SARPE measurements of Ni(110), Ni(110)-p(2x1)O and Ni(110)-c(2x2)S along $\bar{\Gamma S}$ line of Ni(110) surface Brillouin zone using He I radiation [1]. We found that the structure at about 1.3 eV binding energy had unusual character near the \bar{S} point. Although the majority-spin state is located at higher binding energy than that of minority-spin ones, the spin polarization of this structure is observed to be negative, $-9 \pm 1 \%$, which means the intensity of minority-spin electrons is higher than that of majority-spin ones. After the adsorption of oxygen and sulfur on the Ni(110) surface, the degree of negative spin polarization is found to decrease.

Before we can clarify the reason of the negative spin polarization, we must answer the following questions:

- 1) Is this structure a surface or a bulk related state?
- 2) What is the spacial symmetry of this electronic structure?

To solve these questions, we have performed the SARPE measurements for Ni(110) using undulator radiation from BL-19A of Photon Factory along the LW line of its bulk Brillouin zone. The results will be reported.

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Electronic structures of carbon nanotubes aligned vertically on a SiC surface

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Introduction - Carbon nanotube (CNT) is another exotic and exciting form of carbon materials, which has an unprecedented electronic properties such as non-Fermi-liquid (NFL) behavior. Moreover, CNT attracts great technological interests due to numerous possibilities of elaborated applications. However, the experimental approach to CNT by conventional spectroscopy tools is significantly prohibited by the difficulties in preparing well-defined samples in macroscopic quantity.

Experiment and Calculation – We prepared a closely packed and vertically aligned multi-wall CNT on SiC single crystal substrate [1]. The electronic properties of the CNT are characterized by high-resolution photoemission and x-ray absorption using synchrotron radiation (on BL-7.3.1 of Advanced Light Source, Berkeley and on BL-8A1 of Pohang Light Source). Empirical and *ab initio* theoretical calculation was also done to understand the novel features of spectroscopic results.

Results – The C 1s photoemission of CNT are measured which exhibit characteristic satellite structures due to the interband transitions between the molecular levels. These satellite structures are discussed along with the C 1s near-edge absorption spectra, which reveals the unoccupied molecular levels. These data show the spectral features, which differs from those of the graphite for the first time. The valence band photoemission spectra also measured in a various photon energies. This series of valence band spectra exhibits the occupied electronic levels clearly and, in particular, the main π -band show a distinctive oscillation upon photon energy scan. Similar behavior was previously noticed for C₆₀ [2], which was interpreted as the topological quantization of the final states. The physical origin of the oscillation is discussed along with the elaborated *ab initio* calculations.

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Electron correlation effects on L X-rays following photoionization

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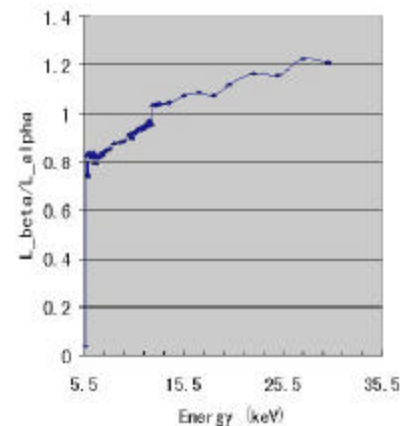
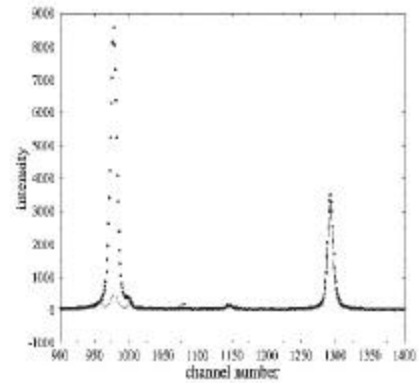
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Since L X-rays originate in electron transitions between L and M, N or outer shells, they can provide important information on inter-shell and intra-shell electron correlations in atoms. When studying line position, relative intensity and line shape dependence of the L X-rays on, for example, photon energy in photo-ionization, interesting information on the excitation and ionization dynamics can be obtained. In this experiment, we measured L_{η} , L_{α} and L_{β} X-rays following photo-ionization of Ba at synchrotron radiation (SR) photon energies between 5.6 and 30 KeV. Specific attention was paid to the threshold energies for single L electron ionization, single L electron plus M or N electron ionization and double L electron ionization. Some results are shown in the following figures. The top figure shows the L X-ray spectra below (line, at SR photon energy of 5.60 KeV) and above (dots, at SR photon energy of 5.64 KeV) the L_2 threshold. The bottom figure shows the intensity ratio of $L_{\beta 3} / L_{\beta 2,15}$. The sudden change in the ratio is considered to be from the contribution of L electron correlations. Further analysis is in progress and further discussion will be presented.



Low Temperature VUV Spectroscopy of Lithium Hydride Single Crystals

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The simple electronic structure of Li^+ and H^- ions, having $1s^2$ configuration, gives for LiH a special place among the numerous binary crystals and in many aspects it serves as an ideal model system for other ionic compounds. However, the study of electronic excitations in LiH crystals complicated due to its high reactivity. As a result LiOH , Li_2CO_3 and other compounds can be formed on the crystal surface. These circumstances lead to the considerable distortion of the measured optical properties of LiH. This is the reason that even such general characteristics as the reflection spectra (RS) in VUV range remain insufficiently studied and show controversial results up to now. The attempts of such measurements of RS in VUV region have been earlier undertaken several times [1-3]. However, the changes in the RS as a function of time after the cleaving were observed in all these works. Therefore, unfortunately no true RS have been measured and accordingly no reliable spectra of optical constants have been calculated for LiH crystal so far.

The aim of the present work was to measure the RS and excitation spectra for emissions of free excitons and impurity centers in LiH crystals in the energy range 4-35 eV at low temperatures. The experiments were performed at the SUPERLUMI station of HASYLAB at DESY. The LiH samples were cleaved directly before measurements in the ultrahigh vacuum of $2.3 \cdot 10^{-10}$ mbar at $T=9$ K. The RS were recorded simultaneously with time-resolved excitation spectra immediately after cleaving of the crystal. The first high intensity reflection peak at $E=4.950$ eV corresponds to the creation of an exciton with $n=1$. A group of broad peaks in the region of 6.3-14 eV are due to the transitions from the valence band to conduction band at the different points of the Brillouin zone. On the basis of the band structure calculations an approximate assignment of optical transitions for LiH can be made. The reflection coefficient has very small value in the region of 17-35 eV. This fact is stipulated by a "poor" structure of filled electronic states, that have only two $1s$ shells. The luminescence spectra of pure LiH crystals consist of emission peaks near the fundamental absorption edge. This luminescence is due to the radiative decay ($\tau < 1$ ns) of free excitons interacting with the LO-phonons. At energies above 15 eV ($E > 3E_g$), a considerable increase of luminescence intensity of free excitons as well as Bi^{3+} center emission is observed. Such a behaviour is interpreted as the manifestation of photon multiplication effect in LiH.

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ANISOTROPY OF EXCITON RELAXATION IN BeO CRYSTALS

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The creation, structure and evolution of self-trapped excitons (STE) in alkali-halide crystals (AHC) have been investigated in detail, whereas in oxides the properties of STE are under discussion. The STE are typical for oxide crystals with the low local symmetry of oxygen ions (SiO_2 , $\alpha\text{-Al}_2\text{O}_3$). The excitonic structure near the fundamental absorption edge is expressed poorly in such compounds. On the contrary, the well advanced excitonic structure and the edge luminescence of free excitons have been observed in high symmetry oxide crystals (MgO , CaO), where no intrinsic self-trapping of excitations takes place. Therefore, the analysis of STE creation and evolution is more difficult in oxides because the excitation spectra in the edge region are less informative than in AHC [1]. BeO crystals demonstrate the well-expressed excitonic structure in reflection spectra and the edge luminescence is observed also. The wide emission bands peaking at 4.9 and 6.7 eV are interpreted as radiative decay of two types of STE. The optical anisotropy of the BeO crystals (wurtzite type lattice) enables to take advantage from the polarization of synchrotron radiation.

In this work the pathways of creation and radiative relaxation of the triplet and singlet STE are investigated in detail for the oriented BeO crystals. The time-resolved emission (2.5-10.2 eV), luminescence excitation and reflection spectra measured at low temperatures under selective VUV-excitation (8-35 eV) were studied using synchrotron radiation from the DORIS storage ring at the SUPERLUMI station of HASYLAB, DESY. For the $\mathbf{E}_{\text{SR}} \parallel \mathbf{C}$ orientation of BeO crystals the excitonic relaxation from the $n=1$ state forms the STE with characteristic emissions at 5.0 eV ($\tau=4.4$ ns) and 4.7 eV ($\tau \approx 54$ ns) at $T=10$ K. The excitons with the $n=2,3$ states predominantly relax to the STE state with the emission band at 4.0 eV ($\tau=2.2$ ns) and simultaneously exhibit a VUV-emission peaking at 6.7 eV ($\tau=340$ mcs). The situation is different for the $\mathbf{E}_{\text{SR}} \perp \mathbf{C}$ orientation of BeO crystals. In this case, only the VUV-luminescence at 6.7 eV is the most effectively excited in the region of $n=1$ excitons, while the UV-luminescence forms a single band at 4.6 eV ($\tau \approx 58$ ns). The fast component of decay kinetics is revealed more weakly as well. The emission band at 4.0 eV has the biggest Stokes shift in BeO and its spectral position is close to the known F^+ -center luminescence peaking at 3.92 eV. From this viewpoint, the assumption concerning the existence of short-live colour centers, the pathways of the creation and variety of STE states in BeO will be discussed. The influence of crystal orientation on the optical properties is observed also at creation of electron-hole pairs, including the region of photon multiplication >23 eV.

This work is partially support by RFBR (grant №00-02-16206), Russian Ministry of Education (grant №992886) and the Deutsche Forschungsgemeinschaft (grant ZI-159/4-1).

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Electronic structures of the nitrogen and boron doped diamonds by photoemission spectroscopy

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The valence-band photoemission spectroscopy measurements have been performed for nitrogen (N-) and boron (B-) doped diamond films with various N(B) concentrations. The valence-band photoemission spectra of N-doped diamond films are very similar to those of B-doped diamond films, indicating that N-doped diamond films have similar valence-band electronic structures to those of the B-doped diamond films. The valence-band photoelectron spectra reveal that N(B) dopants cause the broadening of both σ - and π -bond features and the enhancement and reduction of the σ - and π -bond features, respectively.

Surface photovoltage effect on GaAs-GaAsP super-lattice studied with combination of synchrotron radiation and laser

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The negative electron affinity (NEA) surfaces of a p-type GaAs and its super-lattice have been attracting much interest, since they are useful as electron sources with high quantum yield and high degree of spin-polarization, respectively. In studies of GaAs photo-cathodes, it has been pointed out that the electron density saturates when photo-cathodes are excited with intense pulsed lasers. It is suggested that the surface photovoltage (SPV) effect plays an important role to cause the saturation. Togawa et al. [1] proposed the use of super-lattice photo-cathodes with a heavily doped overlayer as polarized electron sources, since quantum wells are expected to suppress the transport of photo-carriers and the overlayer promotes the fast recovery of the photo-carriers. Hence, the purpose of the present work is to investigate the SPV effect on the super-lattice from a viewpoint of basic surface science.

The core-level photoelectron spectroscopy with VUV radiation is one of the most powerful tools to investigate the surface electronic properties, since the escape depth of the photoelectrons is very small in the range of some tens of eV. We apply this spectroscopy to observe the laser-induced core-level shift due to the SPV effect. In this study, we present the energy shifts of Ga-3d and As-3d photoelectrons on clean and NEA surfaces of a GaAs-GaAsP super-lattice. The time-dependence of the core-level shifts is also shown to study the dynamical behavior of the SPV effect.

The experimental system was constructed at BL5A of the UVSOR facility. The Ti:Sapphire lasers (Mira 900-F and RegA) were used as the exciting light sources to cause the SPV effect. The laser light was transported to the view-port of the main sample chamber using an optical fiber and focused on the sample surface using a quartz lens. SR was monochromatized by an SGM-TRAIN type monochromator and then SR photons of about 100 eV were introduced on the sample surface to observe the photoelectron spectra. By using the timing circuits, shutter and time-to-amplitude converters, the time-dependence of the SPV effect was also observed.

It was found that the core-level shift of the super-lattice surface is remarkably smaller than that of the bulk GaAs(100) surface. It is confirmed that the SPV value of the super-lattice is suppressed as compared with the bulk GaAs. It was also observed that there are at least two components in the recover process of the SPV effect on the clean super-lattice surface, while only one component exists on the NEA surface. It is suggested that the SPV effect originates from both of bulk and surface electronic structures.

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Forbidden C 1s Natural Circular Dichroism

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The coupling of the polarisation of the light with the symmetry of molecules and solids plays a great role in the study of the electronic and structural properties. Natural Circular Dichroism (NCD) since the work of Pasteur is a well established technique in the Infra Red - Ultra Violet range giving information on the stereochemical properties of the molecules. In the last years with the construction of synchrotron insertion devices able to produce circularly polarised light it was possible to begin the extension of the experimental methods and the theoretical interpretation of the Natural Circular Dichroism in the X-Ray region. The X-Ray Absorption Spectroscopy gives information on the local electronic and structural properties via the atomic character of the core excitation. In the XNCD the final goal is to characterise the local chirality.

Natural Circular Dichroism [1] is the difference between absorption spectra with right and left circular polarised light. It arises as a second order process in two distinct terms in the development of the light-matter interaction Hamiltonian. The first one is the interference electric dipole-electric quadrupole (E1·E2), the second is the electric dipole-magnetic dipole (E1·M1). The E1·M1 term is present in oriented and non oriented systems, E1·E2 only in the oriented. Because of the pseudotensor/pseudoscalar character of the matrix elements the effect vanishes in molecules or crystals whose point symmetry group includes rotoreflection elements.

The XNCD was detected in enantiomeric systems only in the E1·E2 interference term [2]. We propose the first enantiomeric measurements of XNCD in the E1·M1 term, which has the advantage to be present also in unoriented systems. The measurements were performed at the 4.2 Circular Polarisation beamline at ELETTRA (Trieste) with the electromagnetic elliptical wiggler driven in alternate current mode. In the X-NCD the source of the symmetry breaking is only the inversion of the helicity of the light. The inversion of the helicity with frequency 0.1 Hz gives the possibility to measure the dichroism at each photon energy to maximise monochromator reproducibility and minimise beam instabilities errors. The absorption spectra of optical isomers of some organic compounds were measured in the gas phase at the C 1s edge with a Samson absorption cell. The asymmetry ratio is of the order of magnitude of 10^{-3} . The XNCD is forbidden by the zero magnetic dipole associated to a $s \rightarrow p$ transition. However if the hybridisation between the C 1s and the valence states is considered, the net magnetic dipole is not negligible.

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Na K PHOTOABSORPTION AND RESONANT KLL AUGER SPECTRA IN NaF AND NaCl

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The aim of this study is to obtain the experimental evidence for the existence of the core excitons in the Na 1s photoabsorption spectra of sodium halides. For this purpose the resonant Auger spectroscopy has been used because it gives a possibility to separate the decay products of core excited and core ionized states. In case of the excited state the additional “spectator” electron screens the outgoing Auger electron from the core hole and kinetic energy of resulting electron is higher than the energy of the Auger electron, originating from the decay of core ionized state.

The experiments were performed at beamline D1011 at the MAX-II storage ring. The beamline is equipped with the Zeiss SX-700 monochromator and Scienta SES-200 electron spectrometer. The samples were *in situ* evaporated thin films with thickness about 10 nm. The photoabsorption was measured as the current through the sample holder.

As an example we present at Figure 1 the KLL Auger spectra of Na in NaF, measured in the vicinity of the Na 1s threshold. It can be seen that at excitation energies around 1074 eV and at 1076.8 eV there are the additional peaks in the energy spectrum of Auger electrons. Such an additional peak at low binding energy side of the Auger peak is typical for the decay of core excited state, where additional electron acts as “spectator”. As the 1s photoexcitation of atomic Na and Ne is dominated by the 1s→3p transitions, we suggest that the stronger “spectator” structure in Auger spectra at 89 eV binding energy is due to the sequence of transitions 1s²→1s3p→1s²2p⁴3p. The weaker “spectator” structure at 85 eV binding energy is most probably due to the transitions 1s²→1s3s→1s²2p⁴3s and 1s²→1s3d→1s²2p⁴3d.

In conclusion, our results show that the core excitons play important role in the near edge structure of K photoabsorption of Na. In case of NaF, where photoabsorption has a broad threshold peak, core excitons have identified through their decay products.

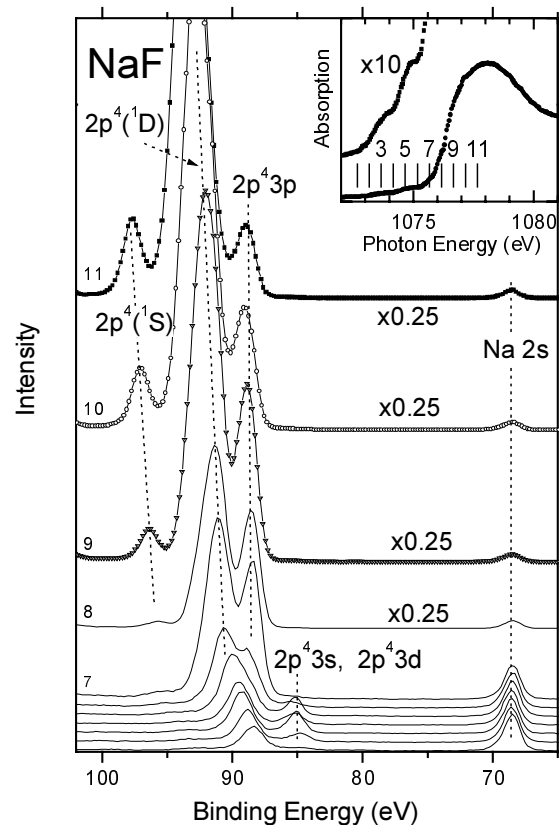


Figure 1. Na KLL resonant Auger spectra of NaF. The Na K photoabsorption spectrum is shown in the inset. The number at each spectrum corresponds to the vertical bar with the same number in the inset and shows the photon energy used.

ATOMIC AND ELECTRONIC STRUCTURE OF *i*-Al-Pd-Mn QUASICRYSTAL SURFACES

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An electronic structure study of icosahedral (*i*) Al-Pd-Mn quasicrystal [1] surfaces using ultraviolet photoemission spectroscopy (UPS) was performed in combination with an atomic structure survey of the surfaces using X-ray photoelectron diffraction (XPD), low-energy electron diffraction (LEED) and electron backscattering diffraction (EBSD). In structural surface studies it has been noticed that different surface terminations are possible depending on the sample preparation: sputtering, heat treatment, It is, however, not clear what are the electronic structure fingerprints of such differently prepared surfaces. Therefore we present a combined geometrical and electronic structure study on differently prepared *i*-Al-Pd-Mn monograin surfaces. Surfaces with drastically different electronic properties, ranging from crystalline to quasicrystalline behaviour, and atomic surface arrangements -disordered or ordered with crystalline or quasicrystalline structures- have been prepared using Ar⁺ sputtering and subsequent annealing of different faces (cut perpendicularly to 2-, 3- and 5-fold symmetric axes) of *i*-Al-Pd-Mn [2]. Furthermore, we studied the oxidation of the different possible surface phases. It appears clearly that the alloy constituting metals oxidize less in a quasicrystalline environment [3].

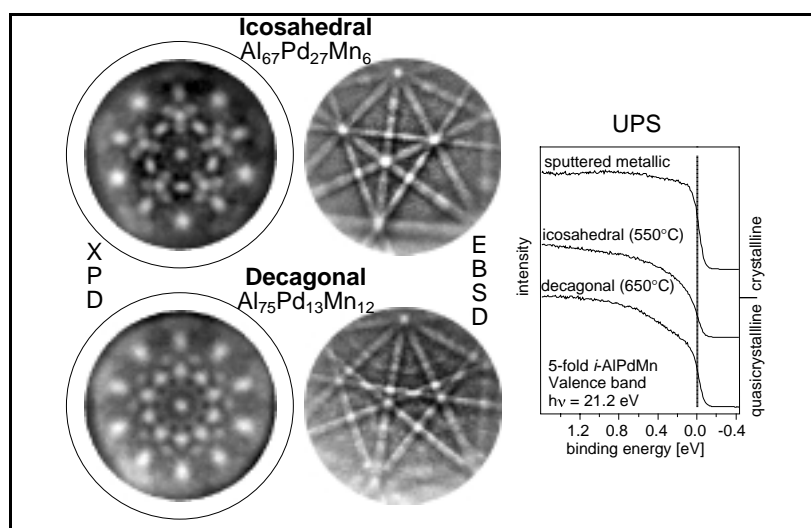


Figure 1: Icosahedral and decagonal quasicrystalline phases on the 5-fold symmetric surface of an icosahedral Al-Pd-Mn quasicrystal and measured with XPD, EBSD and UPS.

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EXPERIMENTAL SURFACE STATES DISPERSION OF THE Ba INDUCED Si (111) RECONSTRUCTED SURFACES

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The geometrical and electronic structures of the alkali metal(AM) or alkali earth metal(AEM) induced Si(111)3×1 surface have not reached to consensus in spite of the extensive investigation more than a decade. One of the most interesting issue of the surface is the semiconducting character of the AEM induced 3×1 surface despite the odd number of surface electrons with 1/3ML coverage[1]. In order to solve the problem, we have performed the detailed investigation of the surface-state band structure of the single domain Si(111)3×1-Ba surface by means of the angle-resolved photoelectron spectroscopy(ARPES) using synchrotron radiation.

All the ARPES measurements have been done at the BL-18A of Photon Factory (KEK, Tsukuba) applying the different photon energies($h\nu = 12.5, 21.2,$ and 27.0 eV) and experimental geometry($A_{//}$ and A_{\perp} , see inset of the figure). The single domain surface was obtained by depositing Ba onto the vicinal n-type Si(111) wafer (20-30 Ω cm) from getter source.

Figure shows the experimental band dispersion of the prominent surface states (circles and squares with solid curves) as well as that of the calculated ones (dashed curves) for the honeycomb chained channel(HCC) model by Erwin and Weitering[2]. Nearly perfect agreement of the experimental surface states($S_1, S_2,$ and S_3) with the calculated ones ($S_1^-, S_2^+,$ and S_1^+) suggests that the HCC model is one of the promising model for the Si structure of the 3×1 surface. However, the theoretically predicted metal state (S_1^- in the figure) resulting from the odd number of electrons with the 1/3ML Ba on the 3×1 surface is hardly observed in our measurement. The inconsistency can be explained by the idea that the coverage of AEM is half of that of AM on the 3x1 surface, *i.e.* 1/6 ML.

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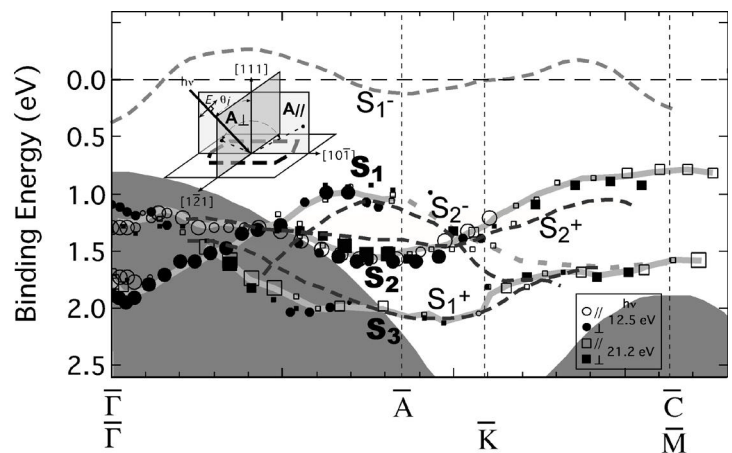


Figure. Summary of the band dispersion of the surface states(circles and squares with solid curves) as well as those of calculation (dashed curves from ref.[2]). Dark shaded area is bulk band projection and inset is the experimental geometry.

GAPS IN DIVALENT AND MIXED VALENT HEXABORIDES

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We present the first experimental views of the global band structure of divalent cubic hexaborides SrB_6 and EuB_6 , and of mixed-valent SmB_6 using angle-resolved photoemission (ARPES) and x-ray emission spectroscopy. The divalent hexaborides, surprisingly, do not show the expected bulk semi-metal band-structure consisting of small electron- and hole-band overlap at the X-point. Instead an X-point electron pocket separated by ≈ 1 eV from a filled “hole” band is measured (Fig. 1). While surface effects may play an important role in these hexaboride systems [1], there is recent theoretical support [2] for the interpretation of this photoemission result as showing a true bulk band gap at the X-point with near-surface electron doping. This result has important consequences for the understanding of the novel electronic properties of these divalent hexaborides, including the high Curie temperature ferromagnetism in La-doped CaB_6 [3].

In contrast, transport and optical spectroscopy of mixed valent SmB_6 , $n_f \approx 2.6$, have long suggested a small gap for which various mechanism have been proposed, including 4f-5d hybridization gap reduced by Kondo renormalization and an excitonic gap due to the 4f-5d Coulomb interaction. Using high-resolution ARPES, the localized 4f and 5d band ingredients of these models have been directly observed, with an ≈ 16 meV gap between E_F and the lowest lying final state $4f^6 \rightarrow 4f^5$ multiplet.

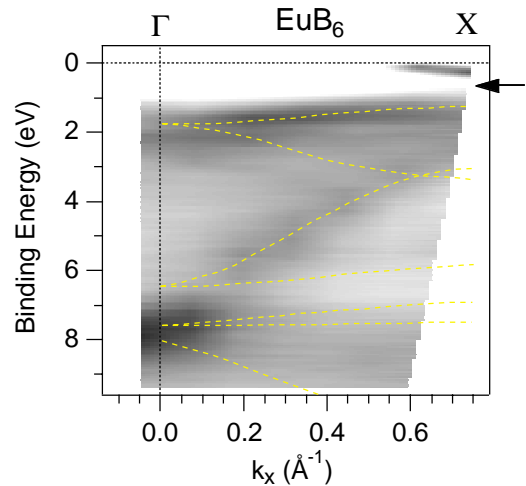


Figure 1: Experimental band structure of EuB_6 showing a 0.8 eV band gap (arrow) just below an X-point electron pocket.

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Electronic Structure of CoSe₂

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The valence-band and conduction-band electronic structure of pyrite-type CoSe₂, which is an exchange-enhancement Pauli paramagnet, has been investigated by means of ultraviolet photoemission, synchrotron-radiation photoemission and inverse-photoemission spectroscopies (UPS, SRPES and IPES). The UPS spectra were measured using a He discharge lamp ($h\nu=21.2$ and 40.8 eV), while the IPES spectrum was obtained by monitoring the emitted photons centered at 9.4 eV. The SRPES experiments were carried out at BL-3B of KEK-PF.

Figure 1 shows the UPS spectrum measured at $h\nu=21.2$ eV (He I), SRPES spectrum at $h\nu=50$ eV and IPES spectrum of CoSe₂ at room temperature. Energy is referred to the Fermi level. In the valence bands, the structures at -1.0, -3.0 and -6.3 eV and a shoulder in the shallower energy side of the main peak at -1.0 eV are observed. The main peak and the shoulder in the SRPES spectrum are prominent in comparison with the UPS spectrum. Due to the photo-ionization cross sections of the Co 3d and Se 4p states [1], the main peak and shoulder are attributed to be the Co t_{2g} and e_g states, respectively, while the Se 4p states mainly contribute to the structures at -3.0 and -6.3 eV. The feature of the SRPES spectrum is very similar to that of CoS₂ [2], although the band-structure calculation predicts the energy shift of the t_{2g} -bands between CoS₂ and CoSe₂ [3]. Self energy corrections to the theoretical calculations suggest that the electron correlation effect is more important for CoSe₂ than CoS₂. On the other hand, in the conduction bands, the structures at 0.6 and 2.0 eV are observed. In comparison with the bremsstrahlung isochromat spectrum of CoS₂ with the emitted photon energy of $h\nu=1486.6$ eV, the structure at 0.6 eV is mainly due to the unoccupied Co e_g -bands, while that at 2.0 eV to the Se 4p bands. This indicates that the Co e_g -bands contribute to the Fermi level.

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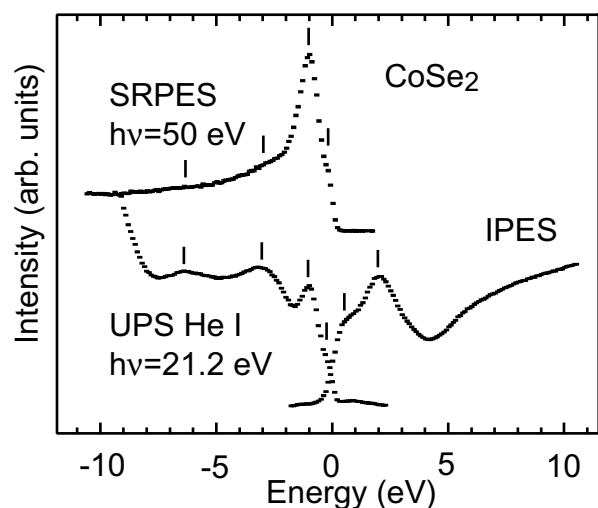


Figure 1: UPS, SRPES and IPES spectra of CoSe₂.

ANGLE-RESOLVED SOFT X-RAY PHOTOEMISSION FOR THE VALENCE BAND OF GRAPHITE

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The angle-resolved photoemission in the soft X-ray region has been so far used to the photoelectron diffraction to study the crystal (surface) structure. In this energy region, the observation of the band structure was considered to be difficult, because the momentum of the incident photon can not be negligible, the emitted electron is strongly influenced by the electron diffraction effects, and the cross section of the valence band is very small. But it was reported that the band near the Fermi level can be observed in this regime[1]. We observed the photoemission spectra of valence band of HOPG (highly oriented pyrolytic graphite). The HOPG is not a single-crystal but it has a highly oriented layer structure. We can then obtain the projection of the valence bands. The measurement was carried out at $T=200\text{K}$ and the photon energy was 980eV . The nearly normally emitted photoelectrons were detected. The measurement was carried out on BL25SU in SPring-8 by use of an electron analyzer SES200. The bright light source and the very good performance of the analyzer have enabled the observation of the band structure.

Figure 1 shows the experimental results. The white area in figure 1 corresponds to the graphite bands. The intensity depends strongly on both energy and angle of the photoelectron. Figure 2 is the band structure of the kish-graphite (single-crystal). The photoemission diffraction effects may be negligible in this experimental configuration and the results can be understood on the basis of the band model.

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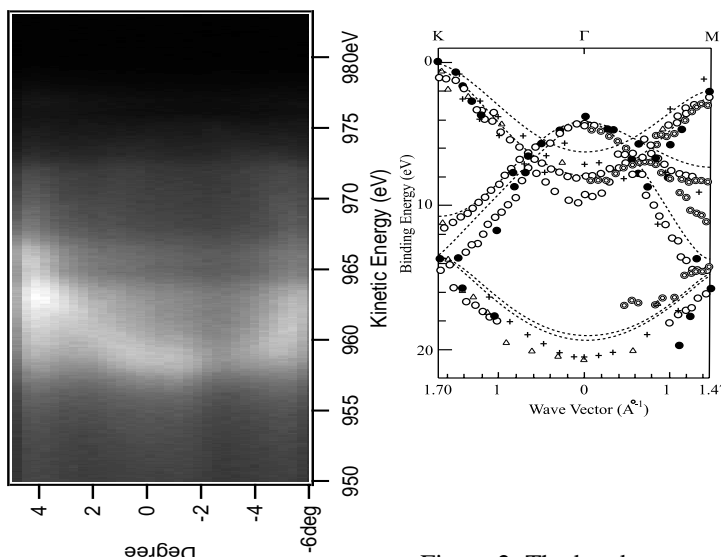


Figure 1: the experimentally obtained band structure of graphite.

Figure 2: The band structure of kish-graphite[2].

THE X-RAY ABSORPTION SPECTROSCOPY IN NaCo_2O_4 , LaCoO_3 AND SrCoO_3

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The soft X-ray core-level absorption spectroscopy is a powerful tool in the investigation of the electronic structure. We can obtain the information of electronic structure for the interested atom. The NaCo_2O_4 has particular properties of electronic states[1-5]. The crystal structure of NaCo_2O_4 has layer structure and the Co atom is surrounded by six oxygen atoms under distorted octahedral coordination. It is considered that NaCo_2O_4 consists of equal amounts of Co^{3+} and Co^{4+} ions.

We observed the XAS to investigate the electronic structure of Co site. The measurements were carried out at a soft X-ray beamline BL23SU of SPring-8. The XAS was obtained by measuring the total electron yield of the sample. The XAS spectra of LaCoO_3 and SrCoO_3 were also measured under the same condition to compare. LaCoO_3 and SrCoO_3 contains Co^{3+} and Co^{4+} , respectively. Co $2p$ XAS spectra of NaCo_2O_4 , LaCoO_3 and SrCoO_3 are shown in Fig. 1. The spectra of NaCo_2O_4 is different from both other spectra, but it resembles SrCoO_3 rather than PrCoO_3 . It may imply that NaCo_2O_4 has nearly Co^{4+} state.

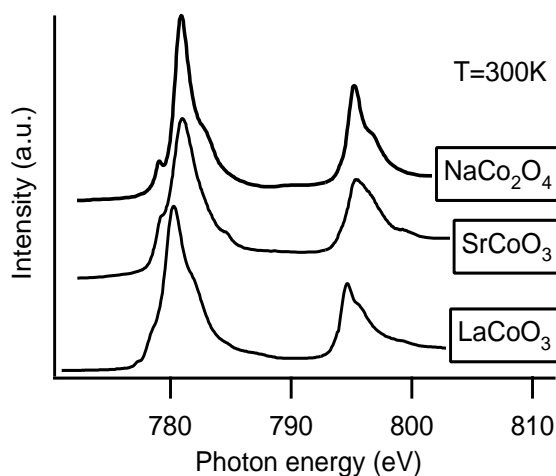


Figure 1: The XAS spectra of NaCo_2O_4 , LaCoO_3 and SrCoO_3 .

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Photon energy dependence of umklapp scattered transitions and three-dimensional band dispersion of Kish graphite

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The band structure of single-crystalline graphite (Kish graphite) from the entire Brillouin zone has been directly measured by using a two-dimensional display-type spherical mirror analyzer with a linearly polarized synchrotron radiation. Figure 1 shows the stereoscopic plot of π and σ bands. Two bands are intersecting at the binding energy of 4 ~ 5 eV. Due to the angular dependence of the dipole transition probability, σ band appears preferentially within the plane perpendicular to the polarization [1]. For the same reason, π band intensity is expected to diminish within this plane [2], however, a small intensity can still be identified. This can be understood as the result of the umklapp scattered transitions from other K symmetry points. Photon energy dependence of such transition intensity is analyzed in detail.

Furthermore, the evolution of photoemission patterns with the photon energy change is investigated. Figures 2(a) and (b) show the typical two-dimensional patterns of π band at binding energy of 2.0 eV. Remarkable difference in the features around K symmetry points is observed. This is related to the change in the transfer integrals among $C2p_z$ atomic orbitals, which can be explained in terms of the band dispersion along the surface normal direction.

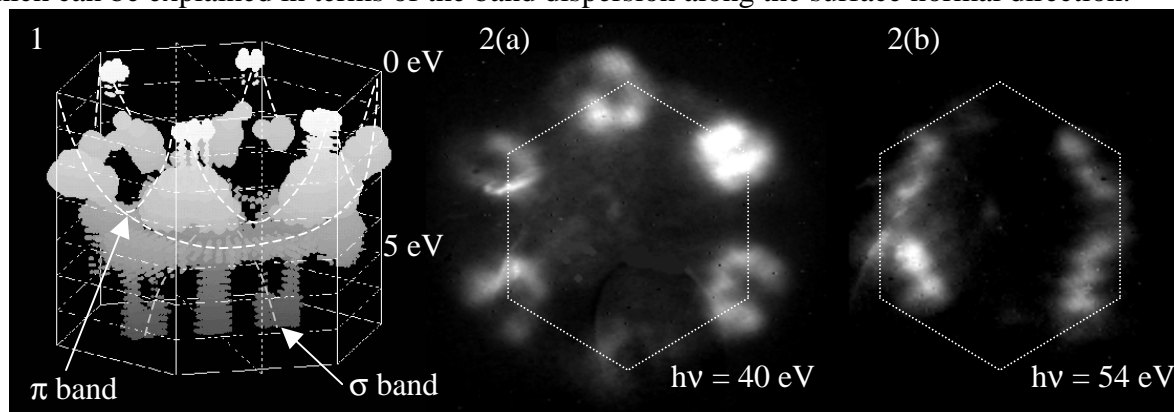


Figure 1: Valence band dispersion of single-crystalline graphite plotted in three dimensions. Photon energy of 40 eV is used for the excitation. Hexagonal lines represent the first Brillouin zone. Polarization plane is indicated by vertical dotted lines.

Figure 2: Observed two-dimensional photoemission angular dependence patterns from valence band of single crystal graphite at the binding energy of 2.0 eV with the photon energies of (a) 40 eV and (b) 54 eV. Dashed lines connect K symmetry points. The band dispersion along the surface normal direction leads to the difference in the features of π band.

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EXCITONIC SIDE BANDS OF INNER-SHELL EXCITATIONS IN RARE-GAS SOLIDS

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The creation of secondary valence excitons in rare-gas solids has been investigated recently with time-resolved photoluminescence techniques [1]. Following selective excitation with photons exceeding the band gap energy E_g , above a threshold $E_{th} = E_g + E_{ex}$ (E_{ex} : energy of valence exciton), 'simultaneous' creation (within experimental time resolution) of a free electron-hole pair and an exciton has been established. In the present work, the techniques have been applied to inner-shell excitations, in particular to Xe $4d$, Kr $3d$ and Ar $2p$ excitations. The measurements were performed with synchrotron radiation at beamline BW3 of HASYLAB/DESY.

Although the inner-shell excitations spectrally overlap with the valence continuum, the peculiarities of the time-resolved luminescence of valence excitons allows for a discrimination between *prompt* secondary excitons, and excitons originating from *delayed* electron-hole recombination. The luminescence of *prompt* valence excitons yields a pronounced resonance with a threshold $E_{th, core} = E_i + E_{ex}$ (E_i : ionization energy of the core level), superimposed on the background of the valence continuum (Figure 1). The resonance is split into two components originating from the spin-orbit splitting of the core state.

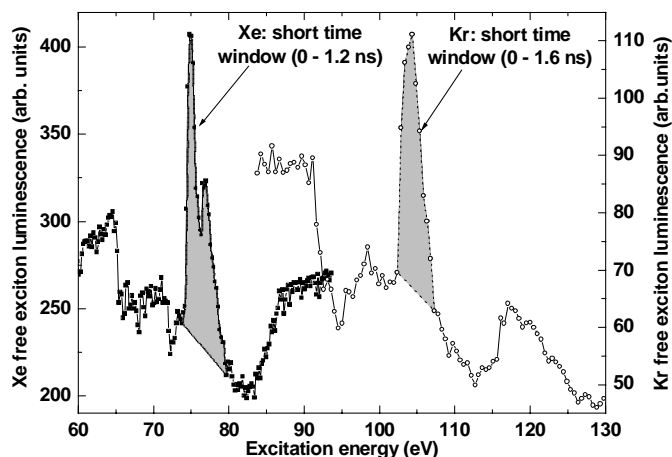


Figure 1: Time resolved excitation spectra of the free exciton emission in solid Xe (60-95 eV) and Kr (85-130 eV). The resonances are shaded.

The resonances are ascribed to elementary excitations consisting of simultaneous core ionization and creation of a valence exciton. This type of excitation was already predicted by Devreese *et al.* [2]. It is superimposed on ordinary inelastic scattering of photoelectrons with sufficient kinetic energy to create (within the experimental time resolution) prompt secondary excitons as well. There is experimental evidence that additional exciton side bands exist, indicating more complex elementary excitations consisting of a core ionization accompanied by more than one valence exciton.

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Optical Absorption and Luminescence of $C_{60}F_{2x}$ Compounds.

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The series of C_{60} and fluorine based compounds were investigated. The $C_{60}F_{48}$, $C_{60}F_{36}$, $C_{60}F_{24}$, and $C_{60}F_{18}$ films were taken, so the degree of fluorination in series was gradually varied in the wide range. We have investigated the reduction of initial C_{60} electronic structure under the influence of growing number of attached fluorines. Consequently we clarify the electronic structure of C_{60} with truncated upper electronic states[1]. From the other hand, these new C_{60} -based compounds could have new and interesting properties.

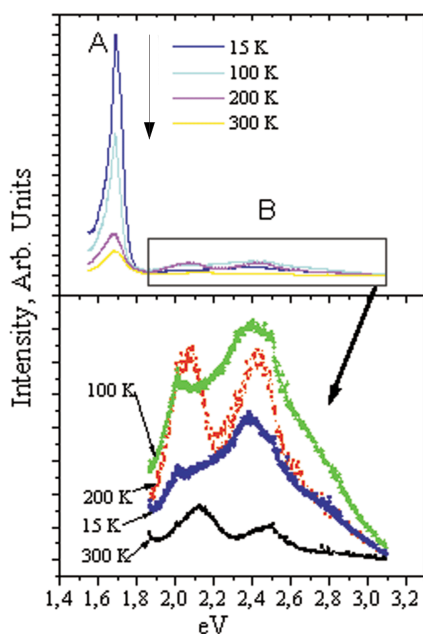


Figure 1. Luminescence spectra of $C_{60}F_{18}$ at different temperatures

The structures of $C_{60}F_{48}$, $C_{60}F_{36}$ and $C_{60}F_{18}$ molecules are known. The most interesting structure appears in the case of $C_{60}F_{18}$. The fluorines are attached to the one side of the molecule, and the point symmetry is reduced strongly from I_h of C_{60} to the C_{3v} . This asymmetry causes the strong dipole moment of the molecule – more than 10 D[2].

The reduction of low-energy p-electron subsystem reveals itself in the lowering of optical absorption in the visible region and the gradual shift of luminescence as a whole to the higher energies. The absorption of $C_{60}F_{24}$ and $C_{60}F_{18}$ films resembles one of C_{60} strongly, thus showing the similarity of electronic structures of C_{60} and these compounds. This resemblance disappears in the absorption spectra of $C_{60}F_{48}$ and $C_{60}F_{36}$. The absorption of these compounds looks like the one of C_6H_6 , because the p-bonds is isolated.

The luminescence of $C_{60}F_{18}$ film has unexpected two-part structure (see Figure 1), with the first part close to the C_{60} luminescence spectra, and the second one lying approximately in the same region with $C_{60}F_{36}$. We attribute this splitting of luminescence spectra to the two different channels for the relaxation of electronic excitation. The first one is connected with fluorinated part of $C_{60}F_{18}$ molecule, the second one – with the free of fluorine atoms part.

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The surface band structure of Li/Be(10 $\bar{1}$ 0).

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The two dimensional band structure of Li/Be(0001) and H/Be(0001) show distinct differences [1,2] compared to the clean close packed surface. At the $\bar{\Gamma}$ point the Be surface state shifts down in energy by more than one eV and at the \bar{M} point only one instead of two surface states are visible.

A detailed investigation of the surface band structure of the Be(10 $\bar{1}$ 0) surface was recently carried out [3]. The refined calculations predicted more surface states than previous calculations and the experimental results verified the existence of all but one. Four surface states were predicted in the band gap at the \bar{L} point but only three were possible to resolve experimentally.

In the present investigation changes induced in the surface band structure of Be(10 $\bar{1}$ 0) upon Li adsorption were studied using angle resolved photoemission. Li films were deposited with the sample at room temperature. The surface band structure of Li/Be(10 $\bar{1}$ 0) was mapped over the Surface Brillouin Zone. Shifts and changes in Fermi level crossings have been observed. These results will be presented and discussed.

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Angle-Resolved Photoemission Study of the Si(111)3×1-Ag Surface.

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We report the investigation of the Si(111)3×1-Ag surface by means of angle-resolved photoemission (ARUPS) using synchrotron radiation. A 2° misoriented Shiraki-etched Si(111) wafer was used in order to obtain a predominantly single-domain 3×1 phase. Sufficiently large regions with a homogeneous 3×1-Ag reconstruction was obtained by desorption of Ag from the Si(111)√3×√3-Ag surface. The surface structures were confirmed by low-energy electron diffraction (LEED) and core-level spectroscopy. Special care was taken to avoid mixed √3×√3/3×1/7×7 phases.

ARUPS measurements were performed using 17 and 21.2 eV photon energy. Spectra were recorded in both the $\bar{\Gamma} - \bar{M}$ and the $\bar{\Gamma} - \bar{A}$ directions of the 3×1 surface Brillouin zone (SBZ), corresponding to the [11 $\bar{2}$] and the [10 $\bar{1}$] crystallographic directions. Due to the single-domain nature of the 3×1 phase, the ambiguities in interpreting data from a multi-domain surface were avoided.

At least two dispersive surface-related states were identified in both directions. At the \bar{M} point of the 1×1 SBZ, their energies are 1.2 eV and 1.7 eV below the Fermi level. These results are compared to previous ARUPS measurements on Si(111)3×1-Na [1] and Si(111)3×1-Mg [2] surfaces, as well as to recent theoretical calculations [3]. The dispersion of the two main surface bands are in reasonably good qualitative agreement with the calculated surface bandstructure for a so-called honeycomb-chain-channel model for $M/\text{Si}(111)3\times 1$ with Li atoms [3].

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Complete Screening and Quasi-Atomic MVV Auger Lineshapes due to Double Core Ionization

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MVV spectra of Rh, Pd and Ag were measured with and without ionization of their L_3 levels. Extra (MMMVV) structure corresponds to the $M_{45}M_{45} \rightarrow M_{45}VV$ transition following the $L_3M_{45}M_{45}$ transition. We interpret the MMMVV structure for Pd as quasi-atomic in nature from its similarity to the corresponding Ag spectral shape and from its agreement with atomic calculations. The Pd quasi-atomic MMMVV spectrum arises from a two final-state hole bound state in the Pd d -band filled by screening of the core-holes. These findings represent the first unambiguous observation of the influence of complete screening on spectral features [1].

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ENERGY DEPENDENT SPIN-ORBIT BRANCHING RATIO IN SOFT-X-RAY PHOTOELECTRON SPECTROSCOPY FROM Pt(111)

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The spin-orbit branching ratio (B.R.), that is the intensity ratio of the lines of a spin orbit doublet, is one of the quantities that can be easily measured in photoemission experiments. Its statistical value is simply determined by the multiplicity of the initial states. In photoemission from solids or adsorbates the situation changes since electron diffraction has to be accounted and the observation is restricted to the half space above the sample. Indeed, structural information may be obtained from B.R. measurements.

We have investigated the spin-orbit branching-ratio in the photoemission from the 4f state of Pt(111). In particular, we determined the energy dependence of the B.R. for different observation angles using an rotatable electron analyzer mounted on a single-axis-goniometer. The measurements were carried out using linearly polarized synchrotron radiation from LNLS (Brazil). The results show that the B.R. deviates significantly from the statistical value. We will discuss the observed oscillations of the B.R. (see Fig. 1) in terms of photoelectron diffraction. For normal emission case, we have observed resonance-like behavior, as seen at about 320 eV in Fig. 1. Most probably this is due to the Pt-4d excitation.

(Funded by CAPES, CNPq, FAPERGS, LNLS from Brazil, and DAAD from Germany).

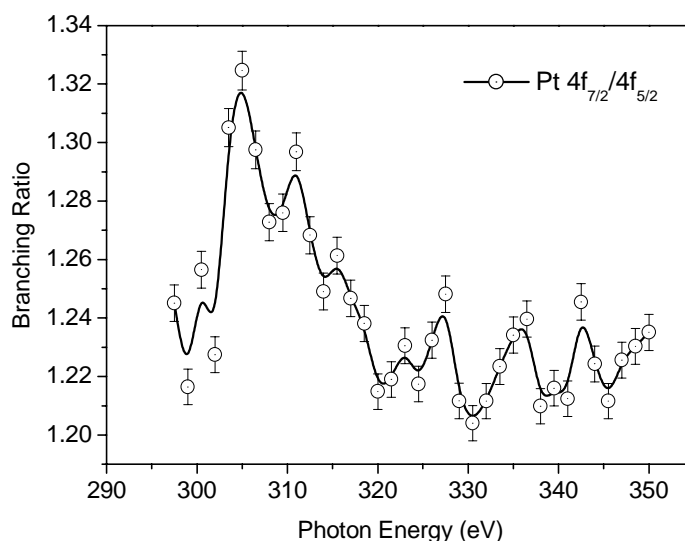


Figure 1: Photon energy dependent Pt 4f B.R. from Pt(111) at normal emission.

RESONANT UPS STUDIES ON RARE EARTH DOPED a-Si:H

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The effects of adding rare earth (R.E.) on silicon is a very active area. In particular, the photoluminescence of Er^{3+} at $1.54 \mu\text{m}$ is quite important due to its potential applications to photonics [1]. This luminescence is due to the transition from the first excited to the fundamental state of the incomplete 4f electronic level. One interesting point concerning Er-doped silicon is the electronic structure of the Er^{3+} impurities. It is still not clear if the 4f levels can be treated as frozen core levels or if their overlap with *s* and *p* states of their neighbors must be considered explicitly. For doped crystalline Si, the 4f levels have been supposed anywhere between 20 eV below the valence band and within the energy gap.

In this paper we report on the first ultraviolet photoemission spectroscopy (UPS) measurements on R.E.-doped a-Si:H. Samples doped with different R.E. contents were prepared by co-sputtering from a Si target partially covered with metallic Er platelets. Also, we prepared samples by ion beam implantation on c-Si (Float Zone (FZ) and Czochralski (Cz)). In order to enhance the R.E. states relative to the Si and H states, the excitation energy was varied around the R.E. $4d \rightarrow 4f$ excitation threshold with a synchrotron light source (LNLS-Brazil). As the photon energy approaches the resonance one peak appears, which corresponds to the R.E.4f state. Figure 1 shows one example for the a-Si:H<Er> sample. We attribute the peak at 10.0 ± 0.5 eV binding energy to the Er 4f level. These are the only occupied states that can be related to the presence of Er, indicating that these levels are not valence states and consequently can be treated as frozen core levels. (Support from CAPES, CNPq, FAPERGS and LNLS are gratefully acknowledged).

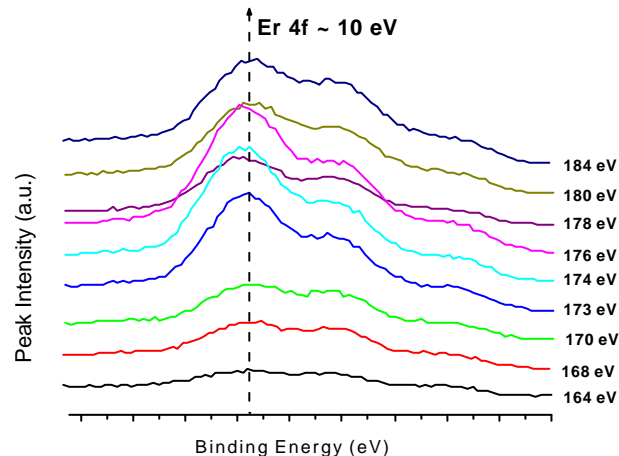


Figure 1: Valence band of the a-Si:H<Er> as we cross the Er $4d \rightarrow 4f$ threshold.

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Local electronic structure of doping atoms in $MA_2Ca_{n-1}Cu_nO_{2n+3}$ high- T_c superconductors with [M-12(n-1)n] type structures

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Results of X-ray fluorescence measurements of $MA_2Ca_{n-1}Cu_nO_{2n+3}$ compounds with [M-12(n-1)n] type structure ($C_{0.8}N_{0.2}Sr_2CuO_{5.3}$, $[Cu_{0.25}(C,N)_{0.75}]Sr_2CaCu_2O_y$, $Cu_{0.5}V_{0.5}Sr_2CaCu_2O_{7.5}$, $Cu_{0.5}V_{0.5}Sr_2Ca_2Cu_3O_{9.4}$, $Cu_{0.5}V_{0.5}Sr_2(Ca_{3.6}Sr_{0.4})Cu_5O_{13.5}$ and $Cu_{0.5}V_{0.5}Sr_2(Ca_{4.7}Sr_{0.3})Cu_6O_{15.3}$) are presented. The fluorescence soft X-ray emission measurements are performed with synchrotron radiation at the undulator beamline 8.0 at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory. The carbon, nitrogen, oxygen $K\alpha$ ($2p \rightarrow 1s$ transition) and vanadium $L_{2,3}$ XES ($3d4s \rightarrow 2p_{3/2,1/2}$ transition) were taken, employing the University of Tennessee at Knoxville's soft X-ray fluorescence (SXF) endstation [1]. The XES were obtained in the non-resonance regime with diffraction grating (600 lines/mm, $R=10$ m) and energy resolution of 0.3-0.4 eV for carbon, nitrogen and oxygen spectra and about of 0.8 eV for the vanadium spectra. The experiments show that C-atoms form a distorted CO_3 oxyacid group with a partial substitution of copper and nitrogen atoms in the M-sites. It is concluded that the CO_3^{2-} group in $(C,N)Sr_2Ca_{n-1}Cu_nO_y$ and $(Cu,C,N)Sr_2Ca_{n-1}Cu_nO_y$ is substituted by the NO_2^- which induces the creation of hole carriers in these compounds. We have found that V-atoms in the given compounds, form $(VO_4)^{3-}$ tetrahedrons and have a pentavalent state. A spectral estimation of the oxygen concentration shows that the oxygen content under high-pressure/high temperature synthesis conditions is not changed considerably from the start to the final product.

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Vacuum Ultraviolet Absorption Spectra of Solid Hydrogen Halides

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Absorption spectra of solid HCl, HBr and HI films deposited on LiF single crystals cooled around 100 K and those annealed have been obtained in the 4-11.5 eV region. The experimental results are shown in Fig. 1. For each hydrogen halide, the first peak A around the absorption edge in the solid corresponds to the dissociative band in the isolated molecule. Therefore the peak A is due to the local excitation in a molecule and regarded as a Frenkel exciton peak. The peak of as-deposited films became clearer after annealing. This is an irreversible process, which suggests the structural transition from an amorphous phase to a crystalline (fcc) phase. The first peak A is single in HCl but splits into two (A_1 , A_2) in HBr and HI, which are attributed to the spin-orbit splitting of the p-orbitals of Br and I, respectively. The peak A_3 in solid HI seems to correspond to the transition from the p-orbitals to d-orbitals in I. The features are quite similar to those of sodium halides. The broad structures B and C above the peaks A do not resemble the structures of their isolated molecules in the same energy region, which consist of many lines. Therefore in solid hydrogen halides, the higher excited states are not localized but spread, so that the many-line structures are smeared out and become bands. The hydrogen halides can be regarded as rare gases in the united atom scheme, so that the spectra of the solid hydrogen halides have been also discussed with the band calculations of solid rare gases.

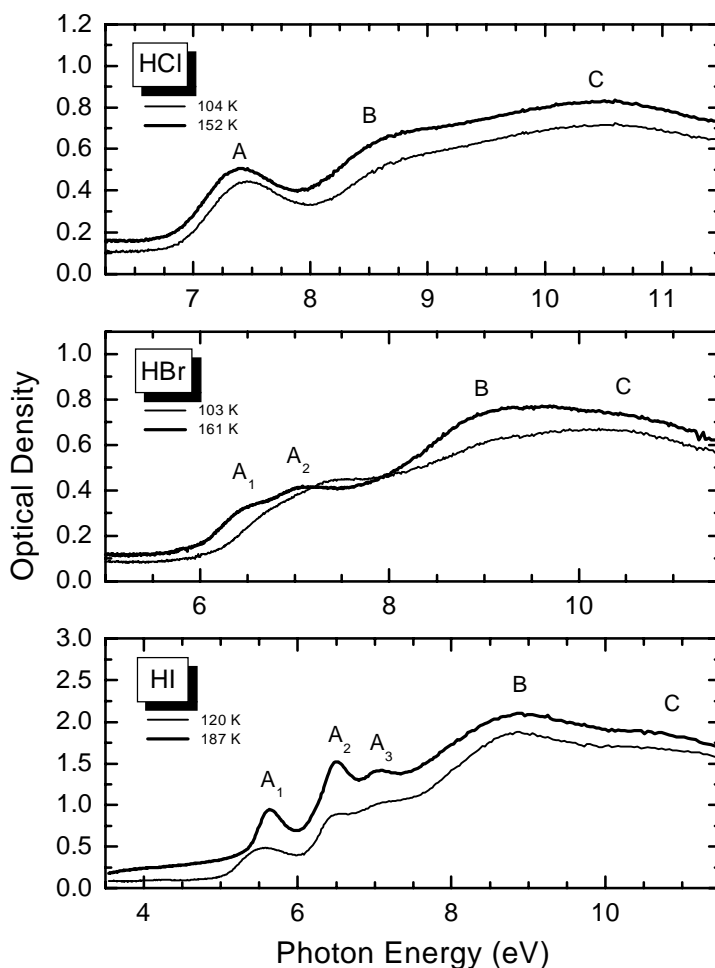


Figure 1: Absorption spectra of solid HCl, HBr and HI.

A Photoemission and Inverse-Photoemission Study of CoSb₃

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The valence-band and conduction-band electronic structure of CoSb₃ crystal with a skutterudite-type structure, which attracts considerable interests as one of thermoelectric materials recently [1], has been investigated by means of ultraviolet photoemission and inverse-photoemission spectroscopies (UPS and IPES). The UPS spectra were measured using a He discharge lamp ($h\nu=21.2$ and 40.8 eV), while the IPES spectrum was obtained by monitoring the emitted photons centered at 9.4 eV with a home-made bandpass photon-detector. Crystals were grown using an induction furnace followed by thermal annealing at 750 °C for 134 hours. Characterization of the crystals were performed by both X-ray powder diffraction and electron-probe micro-analysis, revealing the samples to be a single phase with the skutterudite structure. Clean surfaces were obtained by scraping with a diamond file.

Figure 1 shows UPS spectra measured at $h\nu=21.2$ and 40.8 eV and IPES spectrum of CoSb₃. Energy is defined with respect to the Fermi level. In the valence bands, the structures at -1.1 , -2.5 and -5.8 eV are observed. The main peak at -1.1 eV becomes slightly prominent in the UPS spectrum at $h\nu=40.8$ eV, in comparison with that at $h\nu=21.2$ eV. Taking into account the photo-ionization cross sections of the Co 3d and Sb 5p states, and the crystal field splitting of the Co 3d states due to the Sb-square rings around a Co ion site (t_{2g} states are lower in energy than e_g states and the Co ion is in low spin states), the main peak at -1.1 eV is attributed to be the fully occupied Co t_{2g} states, while the structures at -1.1 and -2.5 eV to the hybridization bands between Co 3d and Sb 5p states. Relative intensity does not change so much between the UPS spectra at 21.2 and 40.8 eV, which means that the degree of the hybridization is considerably strong. The whole feature of the experimental spectra is qualitatively consistent with the band-structure calculation [3]. On the other hand, in the conduction bands, a broad feature is observed from the Fermi level to around 4 eV and a dip is slightly found at ~ 1 eV. The structures near the Fermi level and around 3.5 eV are considered to be the Co e_g states and hybridization bands between the Co 3d and Sb 5p states, respectively. The results of the Co 3d partial density of states obtained with the synchrotron radiation resonant photoemission and resonant inverse-photoemission measurements will also be presented in detail at the conference.

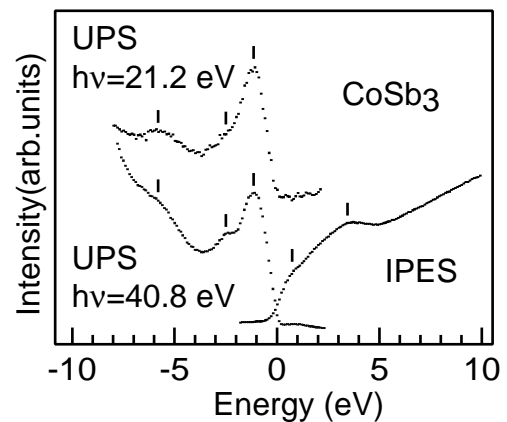


Figure 1: UPS and IPES spectra of CoSb₃.

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M_{4,5} X-RAY RESONANT RAMAN SCATTERING FROM Gd WITH FINAL 4p HOLE: CALCULATIONS AND EXPERIMENT

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We consider the x-ray resonant Raman scattering (RRS) in Gd at the M_{4,5} threshold with a final state containing a 4p hole. As it is known, the concept itself of core hole in a well defined ϕ orbital is not adequate since the final state must be described as a superposition of the two configurations having one 4p hole and two 4d holes respectively (final state configuration interaction). Thus the ground state configuration $4f^n$ ($n=7$ in Gd) gives origin to a final spectrum interpreted as the effect of the sequence $(3d^{10}4f^n) \rightarrow (3d^9 4f^{n+1}) \rightarrow [(3d^{10}4f^{n+1}4p^5) - (3d^{10}4f^{n+2}4p^6 4d^8)]$ with the interacting final state configurations within the square brackets as discussed recently in RRS from Gd [1]. A detailed theoretical account has been done in the prototypical case of La [2]. Up to now La has been the only case where RRS calculations were available mainly due to the substantial computational effort needed for heavier rare earths. The aim of the present communication is to present the first M_{4,5}-RRS calculations on Gd and to compare them with the experiment. To date the calculations feasible with an acceptable effort are based on a finite system (i.e. a single Gd ion). Moreover it is not possible to include the simulation of the non-dispersive part of the spectrum, typical of an extended system, and the Coster-Kronig (CK) decay channel, converting the intermediate state M₄ hole into a M₅ hole. Even in consideration of these rather drastic approximations the comparison with the experiment happens to be particularly interesting:

(i) with M₅ excitation the model reproduces very well the experimental results, including the features appearing at lower $h\nu_{\text{out}}$ and due to final states containing the antibonding mixture of the configurations. The calculations can nicely reproduce also the dispersing part when exciting between M₅ and M₄.

(ii) with M₄ excitation the measurements show a substantial increase of the energy extension of the spectra. This is well reproduced by the calculation. The model reproduces well the spectral region at higher outgoing $h\nu_{\text{out}}$ containing the bonding combination of the above configurations.

(iii) with M₄ excitation it is possible to decompose, within the error bars, the measured spectrum as the sum of the calculated M₄ spectrum and of the spectrum measured at M₅. Thus the measured M₅ spectrum reproduces rather well the CK converted spectrum. This is not trivial because the outer shell configuration created in the CK process is different from that created in the direct M₅ excitation.

In conclusion, the presented results, holding on a demanding computational case, show that RRS with final states containing a ϕ hole is becoming a feasible and useful spectroscopy.

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CATION AND ANION ELECTRONIC EXCITATIONS IN MgO AND BaF₂ CRYSTALS UNDER EXCITATION BY PHOTONS UP TO 75 eV

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Recently significant attention has been paid to the investigation of the relaxation, multiplication, self-trapping and the decay of intrinsic electronic excitations in alkali halides and wide-gap oxides using synchrotron radiation under normal incidence conditions (energy range below 40 eV). Applying luminescent methods we have succeeded in showing that the creation of secondary anion excitons (with the formation energy E_c) or electron-hole pairs by hot photoelectrons (PEs) takes place in alkali halides after the absorption of VUV photons [1]. Such processes occur above the threshold energy $E_g + E_c$ or $E_{gc} + E_c$ due to the PEs formed at the ionization of anions and cations, respectively (E_g is the energy gap and E_{gc} is the ionization energy of cations). However, the 2p-3s and 2p-3d cation excitons in MgO (50-65 eV [2]) and secondary cation excitations ($\geq 2E_{gc}$) in BaF₂ are located in the energy range above 35 eV and are significantly less studied.

The luminescence properties of MgO and BaF₂ crystals at temperatures from 8 to 300 K were investigated under excitation by photons up to 75 eV at the BW3 beam-line of HASYLAB, DESY. The time-resolved excitation spectra were recorded for the free exciton (FE) emission (7.69 eV) in MgO as well as for the large- and small-radius bound exciton emissions peaking at 7.65 eV and 6.8 eV in Ca²⁺ doped MgO, studied earlier under electron excitation [3]. The decay time of FEs in pure MgO practically coincides with the instrumental time response (FWHM ~300 ps). In MgO at 8 K, the decay of cation excitons is accompanied by the formation of anion excitons. The excitation spectra for the fast radiative recombination of valence electrons (2p F⁻) with cation holes (5p Ba²⁺), known as cross-luminescence ($\tau=0.9$ ns, emission at 4-7 eV), and the slow self-trapped exciton emission peaking at ~ 4 eV in BaF₂ crystals were studied as well. In BaF₂, a sharp increase of the intensity of cross-luminescence (5.63 eV) takes place in the region 38-43 eV, where the formation of secondary holes by hot PEs in the 5p shell of Ba²⁺ ions is expected. Secondary cation excitons are formed as a result of the multiplication of cation excitations as well. However, the decay of both secondary and primary cation excitons (formation regions 37-39 eV and 17-18 eV, respectively) does not cause the appearance of the cross-luminescence. The relaxation and decay processes of primary and secondary cation excitations in MgO and BaF₂ will be discussed.

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Photoabsorption and Resonant Photoelectron Spectroscopy of a Rare-earth Borocarbide LaB_2C_2

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Rare-earth borocarbides RB_2C_2 (R: rare-earth (RE) metals) are intercalation compounds in which RE metal cations are intercalated in the planar BC sheets with fused 4- and 8-membered rings. These compounds are interesting electronic and magnetic properties. For example, RB_2C_2 are metallic conductor, and some of them show superconducting behavior ($T_c=2.4$ K for LuB_2C_2) [1]. Therefore it is important to know their electronic structure in order to clarify the mechanism of these properties. Resonant photoelectron spectroscopy is a powerful tool to investigate the electronic structure of materials, because the partial density of states at the core-excited atom are enhanced in resonant photoelectron spectra [2]. In this study, the La 3d photoabsorption and resonant valence photoelectron spectra of lanthanum borocarbide (LaB_2C_2) were measured to investigate the electronic structure of LaB_2C_2 .

Photoabsorption and resonant photoelectron spectra were measured at the soft X-ray beamline BL1A of the UVSOR facility of the Institute for Molecular Science. A piece of polycrystalline LaB_2C_2 was scraped by a diamond file in the preparation chamber before the measurements. The base pressure of measurement and preparation chambers was $\sim 3 \times 10^{-10}$ Torr.

The off- ($h\nu=826.4$ eV) and on- (850.6 eV) resonant and photoelectron spectra of LaB_2C_2 in the valence region are shown in Fig. 1. Abscissa represents the binding energy relative to the Fermi level (E_F). La 3d photoabsorption spectrum of LaB_2C_2 is also indicated in the inset. A La 5p band (~ 20 eV) and some bands near to the E_F (0-7 eV) are significantly enhanced in the on-resonant spectrum. The latter resonant enhancement suggests some occupied density of states near to E_F are localized on La atom. This does not support the complete donation of the three valence electrons of La to the BC sheet, and means that some valence electrons are still on La.

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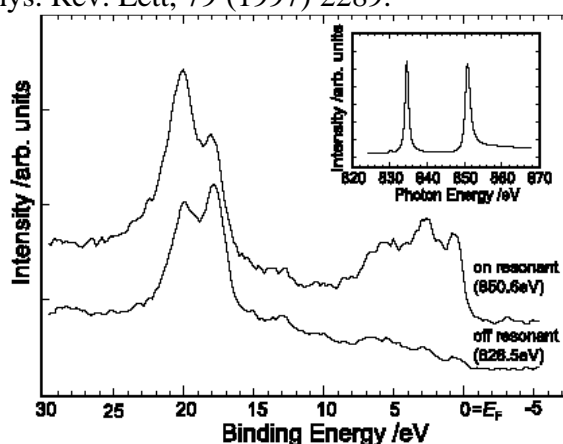


Fig. 1. La 3d photoabsorption and resonant photoelectron spectra of LaB_2C_2 .

RESONANT SOFT X-RAY EMISSION SPECTROSCOPY OF BINARY AND TERNARY VANADIUM OXIDES

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3d transition metal oxides display a broad variety of electronic, magnetic and structural materials properties. The binary vanadium oxides V_2O_3 [1] and VO_2 [1, 2] exhibit insulator-to-metal transitions at 160 K and 340 K, respectively. NaV_2O_5 is regarded to be the second example for an inorganic spin-Peierls (SP) [3] compound, showing many materials properties consistent with a SP-transition at 34 K. LiV_2O_4 is a conducting nonmagnetic metal down to the lowest temperatures and is known to be the first heavy fermion (HF) d-electron material.

In the present work the electronic structure of these vanadium oxides has been studied by means of soft x-ray absorption spectroscopy (SXAS) and resonant soft x-ray emission spectroscopy (RSXES). The soft x-ray emission was recorded with a high-resolution Rowland-mount grazing-incidence grating spectrometer [6] with a two-dimensional detector.

RSXES spectra were recorded for a series of excitation energies on resonances of the V L- and O K-absorption band. The V L- and O K-emission bands of the RSXES spectra possess considerable overlap. By resonant excitation we can tune the energy to the absorption thresholds thereby eliminating this overlap. Hereby we obtain the V 3d and O 2p projected density-of-states (DOS) of the valence band. Resonant inelastic x-ray scattering (RIXS) is found to be weak in V_2O_3 , which we explain as being due to its metallic character at room temperature (RT). In contrast, VO_2 , which is semiconducting at RT, shows considerable RIXS features at the O K-emission band. Distinct RIXS structures are also visible in RSXES spectra of the insulator NaV_2O_5 . Our observation, that RIXS is stronger for insulators and semiconductors than for metals can be taken advantage of for studying insulator-to-metal transitions in vanadium compounds.

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Quantum-well-state development in monolayer-like Au,Ag films on W(110)

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A significant number of experiments devoted to the study of Quantum Well (QW) states in thin metallic films can be well described from the viewpoint of confinement of electron waves in the spacing between substrate and vacuum. As result of this, formation of standing waves takes place, which display themselves in photoemission spectra as periodic oscillations of the spectral intensity near the upper edge of the valence band. The aim of the present work is to investigate QW states, which are formed in ultrathin Au and Ag films grown on top of the W(110) surface, beginning from submonolayer coverages and up to thicknesses where the well-developed classical type QW states are formed leading to oscillations of the spectral intensity successively shifted towards the Fermi level upon Au,Ag deposition. As a result of our investigation a series of spectra has been obtained with sharp features corresponding to both QW states of sp and d character. To further investigate the nature of the experimental features, the dispersion of the QW states has been measured and analysed in dependence on the emission angle relative to the surface normal. The assignment of the observed QW state behavior to sp- and d-character was carried out with results of the tight-binding- approximation and an evaluation made on the basis of the phase accumulation model.

Evolution of the band structure of epitaxial Pb on $\sqrt{3} \times \sqrt{3}$ Au/Si(111)

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The development of the three dimensional band structure from the two-dimensional structure of Pb as a function of film thickness has been studied by Spectroscopic Photoemission Microscopy. The layers were grown epitaxially on $\sqrt{3} \times \sqrt{3}$ Au/Si(111) in the layer by layer mode.

At sub-monolayer coverage (0.55 – 1 ML) no dispersion with k perpendicular is observed for the Pb states or the Au 5d derived states, as expected for two-dimensional systems. Only dispersion as a function of parallel momentum is observed, and changes of relative intensity. However already at 2 ML, dispersion-like effects can be observed with shifts in binding energy of the observed maxima as a function of photon energy for normal emission. This is more appropriately interpreted in a molecular orbital type picture as combinations of atomic orbitals, rather than a band picture. At 5.5 ML, marked dispersion is observed in the Pb 6p bands and the behaviour in photoemission is that of a developed band structure.

As Pb is deposited, the Pb 5d peak shifts by about 0.4 eV to lower binding energy while the Au 5d peak shows a corresponding shift to higher binding energy.

The dispersion behaviour can also be presented in the form of cuts in k space, fig. 1, to give a more intuitive illustration of the band behaviour. Furthermore photoelectron diffraction patterns, fig. 2, are indicative of the structural changes that occur on growth.

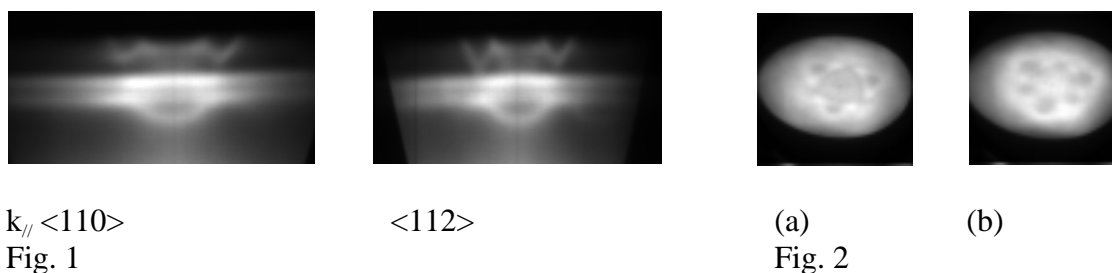


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Fig. 1. Cuts through k space perpendicular to the surface and along the $<110>$ and $<112>$ azimuths, showing one-dimensional dispersion. Coverage: 1 ML of Pb on $\sqrt{3} \times \sqrt{3}$ Au/Si(111). The strong horizontal bands are due to the Au 5d states. The weaker bands above are Pb 6p derived.

Fig. 2. A photoelectron diffraction pattern of 2 ML of Pb on $\sqrt{3} \times \sqrt{3}$ Au/Si(111). Photon energy 52 eV, core level (a) Pb 5d_{3/2}, (b) Pb 5d_{5/2}.

STRUCTURAL AND ELECTRONIC PROPERTIES OF $\sqrt{7}\times\sqrt{3}$ In/Si(111)

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We present angle-resolved photoemission measurements for $\sqrt{7}\times\sqrt{3}$ In/Si(111), a metallic monolayer [1] whose bandstructure suggests a nearly ideal trivalent two-dimensional electron gas. We prepared surfaces using vicinal substrates which were both single-domain and free of other, coexisting reconstructions. X-ray photoelectron diffraction confirms 4-fold coordination in the In layer. The dominant reciprocal space features (in both diffraction and bandstructure) resemble those of a distorted square lattice with secondary features relating to the $\sqrt{7}\times\sqrt{3}$ symmetry. The material appears to be stabilized by gap formation at the $\sqrt{7}\times\sqrt{3}$ Brillouin zone boundary in the [11-2] direction.. [1] A dramatic sharpening of the bands at low temperature suggests a remarkably large electron-phonon coupling interaction.

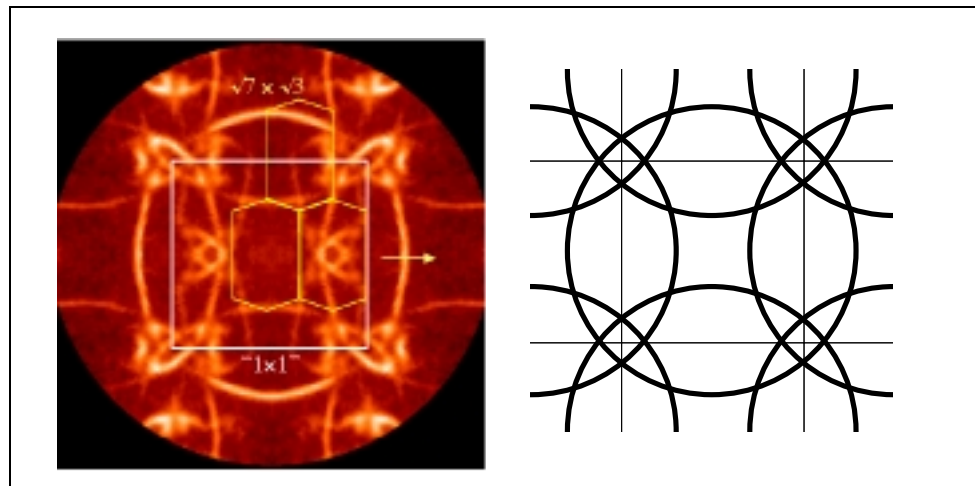


Figure 1: (left) Fermi surface of $\sqrt{7}\times\sqrt{3}$ In/Si(111). The dominant circular features suggest a trivalent metal on a square lattice. (right)

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Excitation of Luminescence in $C_{60}F_{2X}$ Compounds.

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We have studied the excitation spectra of photoluminescence in film samples of $C_{60}F_{18}$, $C_{60}F_{24}$, $C_{60}F_{36}$, $C_{60}F_{48}$ and of pure C_{60} . The excitation was made using powerful (1 kWt) Xe lamp for the region 3-5 eV and synchrotron radiation of KSRS Siberia-1 storage ring for 4-11 eV.

The special interest to these measurements was caused by the C_{60} . Previously [1], [2] it was demonstrated that the strongly delocalized π -orbital of this molecule have a lot of features in this region. Namely, the π -plasmon, π - σ plasmon excitations exist here. These are collectivized electronic states of valence electrons of C_{60} . From the other hand, we have shown [3] that π -part of electronic structure partially conserve its intrinsic structure in C_{60} fluorides, and this is revealed in absorption and luminescence. Therefore the interest was to study the interaction between collective degrees of freedom of C_{60} electron subsystem and the optical emission.

The spectra presented have features in the high-energy region and the smooth increase near band gap. The possible reasons of this behavior are discussed.

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Photon energy dependence of rare earth photoemission multiplets

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In our previous study an unexpected dependence of the multiplet structure on photon energy has been found for the Gd 4d and 5p levels [1]. With the present study we found that the structure of the 4d multiplet depends on photon energy also for europium and terbium. It concerns mainly the feature, which is visible for all rare earth 4d PE (photoemission) spectra at high binding energy (BE), separated from the main lines by about 25 eV. For both Eu and Tb the high BE features are not detectable for photon energies below about 500 eV and their intensity increases with energies above that threshold. A possible explanation relates that feature to the 5p→5d excitation. The 4d satellites which are close to the main peaks (up to about 6 eV) have been related for Gd to the excitations within the 4f unfilled shell. For Eu and Tb their behaviour is different than for Gd and it may be connected to the different structure of the valence band and different 4f-conduction electron interactions.

The Gd 5p multiplet also shows a structure dependent on photon energy. The structure of the multiplet, which is well resolved in the XPS regime (1486 eV), is not visible at photon energies lower than 1000 eV. It concerns mainly the high binding energy features at about 27 eV, which may be attributed to the 5p_{1/2} sublevel. Despite of the better experimental overall energy resolution for the synchrotron studies, the component lines of the multiplet show larger line-widths. This means that the life-time of the photo-excited states depends on photon energy. Photoemission studies in the region of the giant 4d-4f resonance (120-180 eV) indicate a possible explanation of the effect. The relative intensity of two 5p spin-orbit split components changes drastically when energy is tuned through the threshold and above that threshold only one structure-less line in Gd 5p PE is observed for a very broad energy region (200-1000 eV). We suppose that it may be connected to the more effective relaxation of the photoexcited 5p states, especially by the Auger process from the 4f shell.

Surprisingly the PE from the Gd 4p level shows the opposite tendency as concerns the intensity of the second peak of the spin-orbit split level.

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X-RAY PHOTOELECTRON DETERMINATION OF THE Ln5p,4f – ELECTRONIC STATE DENSITY OF LANTHANIDES IN OXIDES

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Earlier the Ln4f electrons before chemical bond formation were traditionally suggested to be promoted to, for instance, the Ln5d atomic orbitals. The calculation results show that the Ln4f atomic shells can participate directly in the formation of molecular orbitals in lanthanide compounds. This important fact needs experimental corroboration. Another important phenomenon we have thoroughly studied recently is effective participation of the filled inner valence Ln5p atomic shells in formation of the outer (OVMO) and inner (IVMO) valence molecular orbitals. The comparability of the experimental and theoretical partial Ln4f and Ln5p electron densities can serve a criterion of correctness of the electronic structure calculation of lanthanide compounds. The present work analyses the fine structure of the low-energy (0 – 50 eV E_b) X-ray photoelectron spectra of lanthanide (La through Lu excepted for Pm) oxides, and compares it with the non-relativistic X_α- Discrete Variation calculation results for the clusters reflecting the close environment of lanthanides in oxides.

The obtained results show that the Ln4fⁿ- electrons of lanthanides in oxides by their spectral parameters have much in common with the M3d- electrons in oxides of the 3d-transition metals, in whose compounds the M3d atomic orbitals take an active part in formation of the molecular orbitals. According to these data, the Ln4f shell in lanthanides is rather outer and can participate in formation of molecular orbitals in compounds. The XPS data at least do not contradict the theoretical suggestion about the significant participation of the Ln4f- electrons in formation of the molecular orbitals in the studied materials. Indeed, the noticeable difference between the experimental and theoretical Ln4f relative line intensities is in agreement with the fact that the atomic wave functions for the Ln4f- electrons can differ from those for the lanthanide ions in compounds. A significant growth of the 4f line intensity (photoemission cross-section) while going from Lu (Z=71) to Hf (Z=72), Ta (Z=73), W (Z=74) and further proves that the Ln4f- electrons in lanthanide oxides are significantly more delocalized than in the further elements.

The spectra in the Ln5p – O2s binding energy region of the studied lanthanide oxides were found to exhibit the complicated structure instead of detached peaks due to the electrons of the Ln5p_{3/2,5/2} and O2s atomic shells. Taking into account the energy differences between the inner (Ln3d) and outer (Ln5p) electronic shells for some metallic lanthanides and their oxides, the Ln5p atomic shells were shown to participate in the formation of the inner valence molecular orbitals. That agrees qualitatively with the calculation results.

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LOCAL VIBRONIC CHARACTER OF ELECTRON STATES IN SOLID C60

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Results from 1s resonant photoelectron spectroscopy (RPES) investigation of solid C60 will be presented. RPES results in the same final state as valence photoemission, but RPES takes place via an intermediate excited state. To illustrate the impact of this on the vibrational coupling we sketch a simple energy vs. general coordinate diagram in the figure below, including discrete vibrational modes for illustrative purposes. We assume vertical transitions as usual in the Franck-Condon approximation.

We find a marked dispersion in the valence band of all the participator structures, which we interpret as a result of localised electron-phonon coupling throughout the valence bands and an indication that varying the vibrational coupling has a dramatic effect on the electron state.

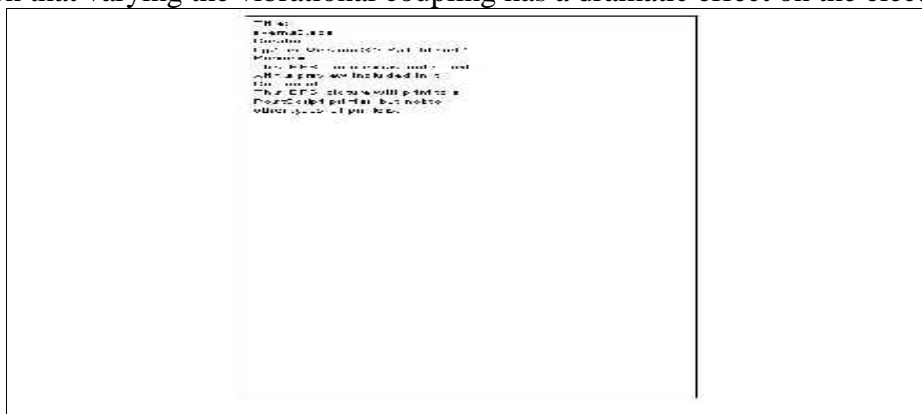


Figure 1: **a)** PES and RPES, showing the connection between the final electronic states. **b)** Energy level schematic of the same processes, showing simplified vibrational potentials for the ground, 1s-excited, and valence-hole states. The dashed line represents the PES transition, and the solid lines the resonant channel studied here. On the right the C 1s XAS of the LUMO is shown with a preliminary analysis of the line shape. The HOMO and LUMO bands indicated there are those corresponding to travelling states, as measured in PES and inverse PES [1,2]. Thus the LUMO resonance lies in the fundamental gap of solid C60, confirming vibrational excitation as the explanation for the observed line shape [1,2].

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TIME RESOLVED PHOTOLUMINESCENCE INNER CORE EXCITATION IN ZnCdSe MQWs

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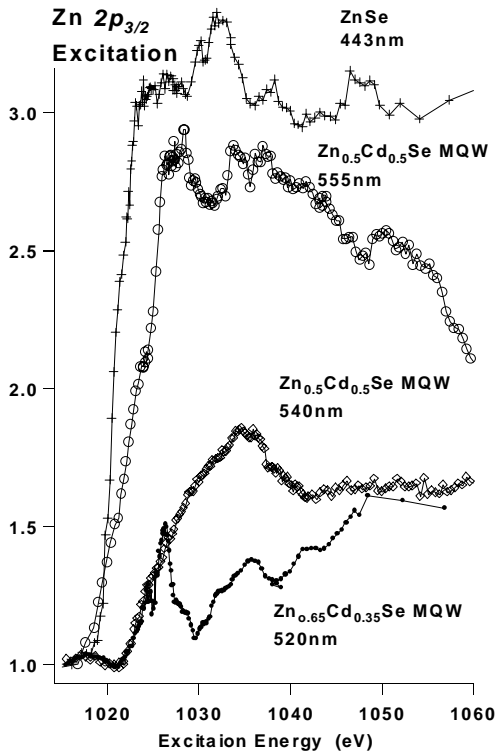
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The core hole generation in quantum confinement structures gives rise to several interesting physical problems such as 1)hetero interface core excitons, 2)competition between core hole potential and quantum confinement potential, and 3)core hole decay dynamics in the confinement structures.



We have applied photoluminescence inner core excitation (PLICE) as a local probe for these problems in several semiconductor quantum structures[1]. The results strongly suggest that the excitation spectra probe the buried quantum structures, however, they still provide no sound evidence that proves the degree of local sensitivity. Inevitable involvement of hot electron-hole pair generation due to Auger decay of core holes, and their diffusion are thought to degrade the local sensitivity in the steady state measurements.

Here we report our recent time resolved (τ) PLICE measurements, which we performed to improve the local sensitivity of the method, in ZnSe single crystalline thin layers and ZnCdSe multi quantum wells (MQW) on GaAs substrates. The experiments were done at BL19B of Photon Factory, KEK. The photoluminescence (PL) fundamental band peaks at around 443nm in ZnSe. In case of MQWs, it peaks in the range of 520nm-555nm, corresponding to the degree of confinement. These bands show a very fast component, of which profile is determined by SR bunch profile, and two delayed components with latent time of 0.3nsec and 1nsec. The excitation spectra of integrated fast PL bands in the Zn 2p excitation regime is shown in the figure. The results clearly indicate that the confinement potential drastically affects the core absorption in the quantum structures, and that τ -PLICE has high local sensitivity for the study of the problems mentioned above.

- [1] K. Kobayashi, T. Ota, K. Maehashi, H. Nakashima, Y. Ishiwata, and S. Shin, *Physica E* 7 (2000),595-599.

CASCADE EFFECTS IN THE SOFT X-RAY EMISSION SPECTRA OF LANTHANUM COMPOUNDS

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We studied cascade effects in the soft x-ray emission spectra (XES) of Lanthanum compounds. The integral La 4d XES intensity is found to be enhanced for LaF₃ when the excitation energy is tuned through the deeper lying La 3d-threshold. The increase of the intensity of the 5p-4d emission when scanning across the 3d-4f photo excitation resonance is shown to be conditioned by the photon emission during the cascading decay of the resonantly excited 3d⁹4f¹ state. The corresponding spectrum has a very complex satellite structure reflecting the multitude of transitions taking place in a variety of multivacancy configurations created by the cascade. It extends over an energy range of about 15 eV. Integral intensity of the 3d⁹4f¹ cascade produced 5p-4d emission is compared with calculations that take self-absorption as well as cascade effects into account.

