

# Resonant Inelastic X-ray Scattering Workshop

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# Improvement of the local order structure by X-Ray emission spectroscopy: application to nickel compounds.

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The K-edge X-ray absorption spectroscopy (XAS) has become a routine tool for the study of 3d transition metals. XAS is widely used to determine short-range (typically 4 Å) geometry parameters of the metal site, metal oxidation state and coordination [1,2]. In particular, the X-ray Absorption Near Edge Structure (XANES) region mainly reflects the delocalized metal p density of unoccupied states. On the other hand, X-ray Emission Spectroscopy (XES) allows to probe the localized state using a hard X-ray technique. Valence-to-core hole transitions (3d and 4p to 1s transitions corresponding to  $K\beta_{2,5}$  and  $K\beta''$  satellite lines) are possibly very sensitive to the chemical bonding of the metal centre to its neighbours (through valence orbitals), and  $K\beta$  emission spectroscopy appears to be a useful tool to derive fine electronic information about the 3d transition metals as it was already shown for Mn [3] or Cr [4] to exhibit the sensitivity of this method.

In this work, we present a study of a series of nickel compounds where the cation is coordinated by oxygen atoms in an octahedral site. So their local structure is very similar and consequently the XANES should not be different. On the contrary, XES of these compounds are completely different. For all the samples, XES and XANES spectra have been collected using a spherically bent Johann type crystal in the Rowland geometry [5,6]. Experiments were performed at BM30B-FAME beamline at ESRF (Grenoble, France).

We are interested in the fundamental understanding of the differences observed in the experimental spectra. Simulation of XES spectra aims to extract quantitative information such as the effective charge of the cation, the density of state and the hybridization of orbitals. Ab initio calculations highlighted that differences are mainly due to the effective charges not the geometry.

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# Theory of probing orbitons in $\text{YTiO}_3$ with RIXS

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In  $\text{YTiO}_3$ , a strongly correlated electron system that likely has degenerate orbitals, orbitons are predicted to exist [1]. This collective degree of freedom has so far not been uncontroversially observed. The hallmark of collective excitations is dispersion. To observe the orbiton dispersion, the rapidly developing technique of RIXS is especially well suited. We analyze recent experimental RIXS data on  $\text{YTiO}_3$  in the Ultrashort Core hole Lifetime framework [2]. The Ti ions in this material have a  $3d^1$  configuration, and the electron occupies one of the three degenerate  $t_{2g}$  orbitals. Many of this compound's ground state properties are explained by assuming that the orbitals on these Ti ions talk to each other through a superexchange mechanism [1]. RIXS could couple to the orbital excitations (orbitons) in these kind of materials in two ways: via modulation of the superexchange interactions [3] and via a shakeup process. We compare our theoretical RIXS spectra to experimental ones, giving strong evidence for the existence of orbitons.

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# RIXS in chemistry

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Carbonyl compounds have been investigated since the early years of chemistry. Nevertheless, the electronic structure of the involved metal centers is still poorly understood. The X-edge X-ray absorption spectra of such compounds exhibit interesting features, which are currently under investigation, but still more detailed spectroscopic and theoretical work is required. With RIXS, more detailed information about the desired electronic d-structure should be available, as is presented.

Beside the more fundamental questions in chemistry, which could be answered with RIXS, also catalysis research is a field of application for RIXS. Since the so-called Marsvan-Krevelen mechanisms of heterogeneous catalysis is still a matter of debate, we hope to get further insights by RIXS. Especially, the oxidation state changes from V(4+) to V(5+) can be hardly addressed by vanadium K-edge XAS. Fluorescence emission lines of such compounds exhibit distinct differences, which will be used to address this question.

# Two-magnon excitations in $\text{La}_2\text{CuO}_4$ studied with RIXS at O K-edge and Cu L and K-edges

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High Temperature Superconductors present very interesting magnetic properties together with their well known superconducting ones. Long range antiferromagnetic order in the copper oxide planes starts to vanish with increasing doping to the advantage of the superconducting properties. Up to now spin dynamics on the copper oxide planes have been mostly studied with neutron scattering [1]. A new probe of spin dynamics complementary to the traditional ones is resonant inelastic X-ray scattering (RIXS) which measures directly both energy and momentum of such excitations [2] giving access to multi-spin correlations.

By means of high resolution RIXS, we study the two-magnon excitation in the undoped  $\text{La}_2\text{CuO}_4$  system. By using RIXS at different excitation energies, we sample the two-magnon density of states in different ways. Two-magnon RIXS cross section at Cu L and K edges are similar: a dispersing branch up to  $\sim 450$  meV is measured along the  $(\pi,0)$  and the  $(\pi,\pi)$  direction. O-K edge RIXS spectra show as well a two-magnon peak [3]. It is centred  $\sim 500$  meV in the  $(\pi,0)$  direction, even at zero momentum, thus probing a not dispersing branch of the two-magnon density of states. Theory based on the ultrashort core-hole lifetime expansion [4, 5] including magnon-magnon interaction fits the two-magnon experimental data with a very good agreement.

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# The incorporation of vanadium in cubic minerals

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The features of the K-edge X-ray absorption spectrum of transition metal cations occurring at low concentration in natural and synthetic minerals provide useful information about their crystallographic environment and electronic structure. In particular, the energy and relative intensity of the pre-edge features depend on the valence state and site symmetry of the absorbing atom. The knowledge of the valence spectral features of an impurity in a structure is particularly relevant to study complex samples where the impurity may occur under several valence states. Vanadium is a typical example of multivalent impurities. It occurs under several redox states (+II, +III, +IV and +V) in natural and synthetic compounds, providing useful information about redox conditions during natural processes.

We present a High Energy Resolution Fluorescence Detected X-ray Absorption Spectroscopy (HERFD-XAS) [1] study of natural and synthetic samples of V-bearing cubic minerals: tsavorite, a V<sup>3+</sup>-bearing garnet (Ca<sub>3</sub>Al<sub>2</sub>(SiO<sub>3</sub>)<sub>4</sub>:V<sup>3+</sup>), and titanomagnetite (Fe<sub>3-x</sub>Ti<sub>x</sub>O<sub>4</sub>:V). Compared with conventional X-ray Absorption Near Edge Structure (XANES) measurements in fluorescence mode, HERFD-XAS leads to a significant sharpening of the pre-edge features and can be used to avoid overlapping fluorescence [2]. The spectra were recorded on the ID26 beamline of ESRF, using a high-resolution emission spectrometer.

Our results evidence that vanadium is present only as V<sup>3+</sup> in tsavorite whereas it occurs under +III and +IV in titanomagnetites. The determination of the vanadium redox state in titanomagnetite is important for the understanding of the genesis of the most important vanadium ore in the world (Bushveld Complex, South Africa). Concerning the tsavorite, we also investigated the angular dependence of the pre-edge features to assess the importance of electric quadrupole transitions. Indeed, in a cubic compound, the angular dependence is only related to electric quadrupole transitions [3]. To better ascribe the origin of these transitions, the theoretical X-ray absorption spectrum was determined by monoelectronic calculations, based on the Density Functional Theory. The comparison with the experimental spectra also provides quantitative information about the relaxation of the crystal structure around the impurity [4].

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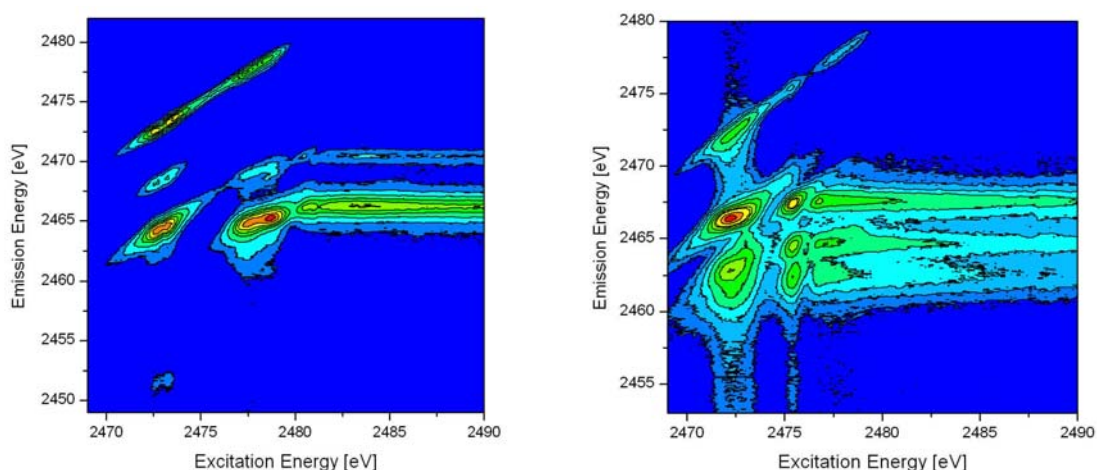


# RIXS spectroscopy of sulphur containing molecules around the 1s threshold

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The 1s2p and 1s3p RIXS maps of H<sub>2</sub>S and SO<sub>2</sub> in the region around sulphur 1s ionization threshold were measured with the high resolution crystal spectrometer built at JSI. The spectrometer was equipped with the Si(111) crystal in Johansson geometry with the Rowland circle radius of 500mm. The diffracted x-rays were detected with back illuminated CCD camera. The 22.5 x 22.5 μm<sup>2</sup> pixel size yielded an overall energy resolution of around 0.4eV. The spectrometer was installed at the ID26 undulator beamline of the ESRF. A closed stainless steel cylindrical target cell separated from the spectrometer vacuum chamber with 12.5 μm thick kapton windows and target pressure 50-80mbar was used. A series of 1s2p and 1s3p emission spectra were collected in the range of excitation energies from 2469 to 2490eV.



**Figure 1:** 1s3p RIXS map of SO<sub>2</sub> (left) and H<sub>2</sub>S (right) around the sulphur K edge. The full scan consists of 85 (106) emission spectra with 0.25 (0.20) eV steps in excitation energy.

The strongest resonances are clearly resolved followed by the edges typical for excitations into continuum. There is a strong signal of elastic scattering due to resonant excitations. Since the detected emission is in polarization plane, the contribution of Rayleigh scattering is negligible. The diagram Kβ emission line exhibits significant deviations from the straight linear dispersion typical for the resonant Raman scattering, which is a consequence of the fast nuclear processes. Even though the core-hole lifetime in this case is only in the order of 1fs, nuclear dynamics can still be observed, similar as it was recently reported for the core excited HCl molecule in [1]. On the other hand, no such effect (or much less pronounced) is observed in the elastic peak, which is following very nicely the linear dispersion curve. More detailed analysis of the measured spectra is in progress.

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# Modification of local motions of protein matrix via the spin state of the non-heme iron in bacterial reaction centers.

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Non-heme Fe is a highly conservative cofactor of photosynthetic reactions centers of type Q but its role remains unclear.

We show that the non-heme iron can be stabilized either in a high and in a low spin ferrous state in the isolated *Rhodobacter sphaeroides* reaction centers whereas it was found mainly in a low spin ferrous state in the *Rhodospirillum rubrum* reaction centers. The temperature dependence studies of the iron mean square displacement using Mössbauer spectroscopy show that the high spin ferrous non-heme iron has more flexible surrounding ( $\theta_D \sim 165$  K) than the low spin ferrous one ( $207 \pm 17$  K). We suggest that the spin state of the non-heme iron may regulate the strength of coupling between the two quinone acceptors and indeed we observe that it influences the stabilization of charge separation and the rate of charge recombination between the quinone acceptors and the special pair of bacteriochlorophylls. The center of the main thermoluminescence component in the spectra obtained for the *Rs. rubrum* reaction centers is shifted by about 12°C towards lower temperatures relatively to that one for the *Rb. sphaeroides* RCs what means that the total free energy of the charge separation is lower in the case of *Rs. rubrum*. In addition, this effect is well correlated with the decrease of the half times of charge recombination between the  $Q_A$  and  $Q_B$  quinone and the special pair. The nuclear inelastic scattering measurements of the collective motions in these reaction centers show that the density of vibrational states originating from the non-heme iron bonds to the protein matrix has well separated modes in the *Rb. sphaeroides* BRCs at low (around 4-17 meV) and higher (around 17-25 meV) energies whereas in *Rs. rubrum* BRCs the vibrations have more uniform distribution with much lower contribution of vibrations at around 6 meV.

These results show that the activation of electron transfer between the two quinone molecules on the acceptor side of the bacterial reaction centers via the motion of the protein matrix is related to the spin state of the non-heme iron.

# Upgrade beamline for soft X-ray resonant inelastic scattering and X-ray magnetic dichroism

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The new beamline will provide new facilities for the user community using soft x-rays at the ESRF to study the electronic and magnetic properties of materials. The aim is to strengthen our competitiveness in this field by focusing on studies utilising dichroism and resonant inelastic x-ray scattering techniques. By building on 15 years of experience, we will provide a state-of-the art facility for absorption spectroscopy (with sophisticated sample environments and tuneable x-ray beam sizes from microns to 100's microns). In addition, an instrument with unprecedented high energy resolution for resonant inelastic x-ray scattering will be built, again incorporating sophisticated sample environments. The facility for x-ray absorption will meet the demands of the very large and expanding user community using magnetic dichroism techniques. In addition, soft x-ray inelastic x-ray scattering has the potential to bring a new complementary tool for scientists who traditionally have used other methods like optical techniques, inelastic neutrons, electron energy loss etc.

# Inelastic X-ray scattering at HASYLAB

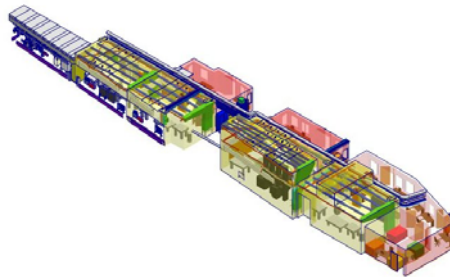
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HASYLAB operates two storage-rings for synchrotron radiation and one soft x-ray free electron laser. The storage ring DORIS is used since 1976 for experiments with synchrotron radiation, and PETRA has been rebuilt recently into a third generation synchrotron radiation facility. Inelastic X-ray scattering experiments have been performed at DORIS since 1984.

Right now, a resonant X-ray emission spectrometer [1] is installed at the wiggler beamline W1 at DORISIII with about 30% use of the beamtime. The spectrometer operates in dispersive scattering geometry by virtually moving the sample into the Rowland circle, i.e. by moving both detector and analyzer. The analyzers are spherically bent with a bending radius of 1m and a diameter of 100mm. Most analyzers have been produced by the anodic bonding technique [2,3]. In addition, some experiments to test new detectors and optical systems are performed on a heavy-load diffractometer.

A new inelastic x-ray scattering experiment for the study of electronic excitations will be installed at the second endstation at the 10m-undulator beamline P01 at PETRAIII. Key-parameter of that experiment are an energy resolution of 500meV (50meV in high-resolution mode), and a focus of 150 $\mu\text{m}$  x 50 $\mu\text{m}$  (1 $\mu\text{m}^2$  in micro-focus mode). The spectrometer will operate in vertical scattering geometry.



**Figure 1:** Beamline P01 at PETRAIII with the optics hutch for the high heat-load monochromator, the second optics hutch for high-resolution monochromators, two experimental hutches for nuclear resonant scattering, and the hutch for the inelastic x-ray scattering spectrometer. At the end of the beamline, a third hutch for micro-focus NRS is installed.

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# Electromagnon excitations in helical magnets

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Electromagnon excitations in helical magnets are studied theoretically following a phenomenological approach. These excitations result from the helical ordering, irrespective of any concomitant ferroelectricity. Both symmetric (exchange) and antisymmetric (Dzyaloshinskii-Moriya) contributions to magnetoelectric coupling are shown to be important when these excitations are probed by means of e.g. neutron scattering experiments [1]. In optical experiments, electromagnon features can be traced back to a resonant magnetoelectric response that, being magnetoelectric in nature, not always can be reduced to an effective electric permittivity [2]. We argue that electromagnons in helical magnets can produce, in addition to the observed peaks in the optical absorption of multiferroics, a (dynamically enhanced) optical rotation and a negative refractive index behavior.

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# Universal momentum dependence of charge-transfer excitations in undoped cuprates from Cu *K*-edge RIXS

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Resonant inelastic X-ray scattering (RIXS), the analog of Raman scattering in the X-ray regime, is a promising new synchrotron-based probe of the momentum dependence of electronic excitations of strongly correlated electron systems. We study the Cu *K*-edge RIXS signal in several undoped high-*T<sub>c</sub>* parent compounds ( $\text{La}_2\text{CuO}_4$ ,  $\text{Nd}_2\text{CuO}_4$ , and  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ ) by constructing dispersion diagrams using a precise normalization procedure that allows the direct comparison of RIXS intensity across the Brillouin zone. This method reveals evidence for the universality in dispersion and intensity patterns of the momentum-dependent charge-transfer excitations, and it enables the separation of the effects of the RIXS cross section from intrinsic properties of the electronic excitations. The universal excitation spectrum of the undoped cuprates is compared to theoretical models, which reveals how electron correlations are crucial to the physics of the  $\text{CuO}_2$  plane.

# High performance photon spectrometer for resonant inelastic scattering studies

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We report on the development of a X-ray spectrometer to operate in the 60-1000 eV energy range. We target versatility with high resolving power (better than 5000) while maintaining an effective angular acceptance of the instrument higher than 100  $\mu$ sr. These requirements are met by a slitless optical scheme which combines mirrors and plane varied-line-spaced diffraction gratings, partially based on previous experience [1]. Our design goals are particularly adapted to challenge low counting rates experiments and therefore addresses topics like diluted systems, deposited molecules or buried interfaces. With the advent of free electron lasers, it opens the perspective of single shot X-ray emission studies with high energy resolution.

The spectrometer is currently being installed at the SOLEIL Microfocus beam line and will be available to the scientific community starting with 2010.

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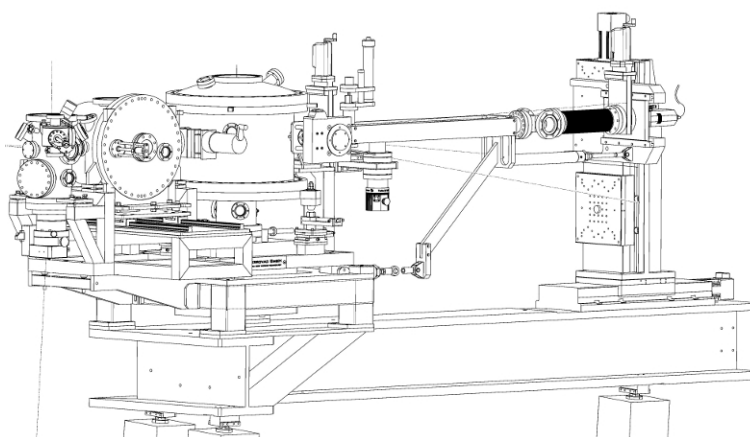


Figure : Overview of the setup.

# Application of the Hilbert++ program to the calculation of x-ray absorption and resonant x-ray diffraction spectra

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The program Hilbert++ [1] allows calculating spectra from different spectroscopies. The program starts from a model Hamiltonian written in second quantization formalism and applies Lanczos tridiagonalization to the Hilbert space spanned by the electronic degrees of freedom of the resonant ion and of its near neighbors. The calculations of the spectra are based on atomic multiplet calculations in a crystal field. Cowan's atomic multiplet program provides ab initio Hartree-Fock values of the radial Coulomb Slater integrals, direct and exchange contributions and the spin-orbit interactions for an isolated ion. In order to take into account the screening effects present in the real system with respect to the atomic picture, we scale down all the Slater integrals to 75% of their atomic values. For Double-decker [DD] phthalocyaninato [Pc] terbium complexes [(Pc)<sub>2</sub>Tb<sup>III</sup>] deposited on graphite we calculate XAS and XMCD spectra at the M<sub>4,5</sub> Tb edges aiming to compare the anionic and neutral species and to investigate the role of the interaction with the substrate on the molecule properties. These complexes show a long magnetization relaxation time at relatively high temperatures making them interesting as a magnet at single-molecular level. By using structural information of the Tb-DD molecules and different sets of parameters for crystal field and hybridization we calculated XAS and XMCD spectra. The results obtained allow establishing the ground state magnetic properties and degree of charge transfer in the Tb<sup>3+</sup> ion. For rare-earth diborocarbides (RB<sub>2</sub>C<sub>2</sub>), we calculate the energy dependence of the resonant soft x-ray Bragg diffraction intensity at the Dy M<sub>4,5</sub> edges. The experimental results [3,4] in the antiferroquadrupolar and antiferromagnetic phases of DyB<sub>2</sub>C<sub>2</sub> are explained by introducing an intra-atomic quadrupolar interaction between the 3d core and 4f valence shell. The results obtained agree with the experimentally determined behavior of the resonant x-ray scattering intensity around the M<sub>5</sub> edge in the antiferromagnetic phase.

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# Metal-metal excitations in the chromium X-ray absorption K-pre-edge of chromium(III)-iron(III) oxyhydroxides

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Pre-edge spectral features below the main X-ray absorption K-edge of transition metals show a pronounced chemical sensitivity and are promising sources of structural information [1]. Analyzing these transitions opens up new opportunities for the study of chromium substitution and for the study of poorly ordered solids of environmental relevance. The aim of our research was to determine the factors affecting the chromium K-pre-edge features in trivalent chromium-bearing oxides and oxyhydroxides. The selected phases varied in the degree of octahedral polymerization and the degree of iron-for-chromium substitution in the crystal structure. We investigated the pre-edge fine structure by means of high energy-resolution fluorescence detection X-ray absorption spectroscopy (HERFD-XAS) and by 1s2p resonant X-ray emission spectroscopy (RXES). Multiplet theory [2] and multiple scattering theory [3] were used to analyze the experimental data. We show that the chromium K-pre-edge contains localized and non-localized transitions. Contributions arising from metal-metal transitions [4] are sensitive to the nearest metal type and to the linkage mode between neighboring metal octahedra.

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# A hard X-ray photon-in photon-out study of the electronic structure in Mn(III) complexes

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The formal oxidation state of Mn can vary between II and VII. This wide range of oxidation states makes Mn a versatile ion taking a fundamental role in many fields of natural sciences. Mn is, for example, found at the center of photosynthetic water oxidation and gives rise to colossal magnetoresistance in manganites. An oxidation from Mn(II) to Mn(III) is particularly important because the half filled  $3d^5$  shell is opened with dramatic changes in the electron-electron interactions and the local symmetry. This can be directly observed in the Mn K absorption pre-edge. The absence of multiplets enables to derive the crystal field splitting from the pre-edge in Mn(II) systems with local octahedral symmetry. However, strong electron-electron interactions and Jahn-Teller distortions in Mn(III) systems result in a complicated splitting of the valence shell energy levels and thus a complex spectral shape of the pre-edge.[1, 2]

We present polarization and spin dependent X-ray absorption studies on Mn(III) single crystals and compare spectra from solid state systems with coordination complexes. We find considerable quadrupole contributions to the absorption pre-edge. We argue that intra-atomic electron-electron interactions predominantly shape the pre-edge and not interactions between neighboring Mn atoms. This is in contradiction to previous studies.[3, 4] The difficulties when attempting a theoretical interpretation of the pre-edge are addressed. We furthermore demonstrate how polarization dependent X-ray emission and absorption studies allow separating electronic from structural changes.

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# Valence band RIXS spectroscopy of phthalocyanine complexes - probing excitations in the optical range

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Phthalocyanines are a fascinating class of molecules which can be used in a vast array of applications including organic electronics, pigments, and cancer treatments[1,2]. They consist of an organic macrocycle with a metal atom in the centre. The metal atom, and possible side or axial groups can be easily changed to tune the molecular properties. Thus understanding the electronic structure of these molecules is vital to fully exploit their properties.

New and powerful spectroscopy techniques are currently being developed to probe the electronic structure of a variety of samples. Beamline ID26 at the ESRF can record resonant inelastic X-ray scattering (RIXS) spectra at the metal K-edge over the K-beta satellite emission lines to selectively access electronic transitions in the valence band region. In this study we used valence band RIXS to study transitions in Ti and Co phthalocyanine systems.

The Ti molecules studied (TiPcO, TiPcCl<sub>2</sub> and PMCP-TiCl<sub>3</sub>) are of interest in photovoltaic and organic electronics applications. The geometries and axial ligands of the two phthalocyanine compounds permit different electronic transitions to take place, which are recorded in the valence to core RIXS plane. PMCP-TiCl<sub>3</sub> shows an additional peak in the optical excitation range compared with the phthalocyanines. CoPc was also measured, both as a powder and as an encapsulated species inside carbon nanotubes [3,4]. CoPc alone shows an optical range excitation in the valence band RIXS plane which is suppressed upon encapsulation. The origins of these optical peaks is under discussion and is compared with UV-visible measurements.

Using valence band RIXS to study molecular complexes is a new and exciting method which will provide valuable insight into the electronic properties of molecular materials.

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# RIXS phenomenology in insulating quasi-zero dimensional $\text{CuB}_2\text{O}_4$

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We present a K-edge RIXS study of  $\text{CuB}_2\text{O}_4$ , which consists of unlinked  $\text{CuO}_4$  plaquettes. The spectra of this relatively simple electronic system are clean, exhibiting a few strong features which are well-separated and relatively sharp. While some aspects of the data can be understood in terms of a finite number of electronic degrees of freedom, we find this insufficient to exhaust the observed phenomenology. The limitations of electron-only calculations are discussed and the phenomena are set into context of the wider scope of RIXS in cuprates.

## **I20 The Versatile X-ray Absorption Spectroscopy Beamline at Diamond Light Source**

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The Versatile Spectroscopy beamline at Diamond Light Source, I20, is currently under construction and aims to begin operation in late 2009 and early 2010. The beamline will cover applications across the broadest spectrum of scientific disciplines, from physics, chemistry and biology through material, environmental and geological science. Three very distinctive modes of operation will be offered at this beamline: scanning X-ray Absorption spectroscopy (XAS), XAS in dispersive mode, and X-ray emission spectroscopy (XES). To achieve this, the beamline has been designed to deliver both monochromatic and polychromatic x-rays using a pair of canted wigglers to two independent experimental end-stations. The novel design of the beamline allows both branches to operate simultaneously.

Here, we present an overview of the beamline design, highlighting the unique capabilities of I20. For the monochromatic end station special attention has been paid to the design of the optic components to deliver a very stable x-ray beam at the sample position to allow high spectral quality data to be collected in the energy range of 4 to 34 keV. This branch of I20 is based on a scanning spectrometer operating from a four bounce monochromator. This device guarantees that the x-ray beam delivered to the sample has an energy resolution solely determined by the Darwin width of the installed monochromator crystal cuts, Si(111) or Si(311). One of the important elements in this end station is a secondary spectrometer, allowing high-energy emission studies to be conducted. The secondary spectrometer is planned to be made available to the user community in late 2010. The aim of the other branch line is to deliver 6keV to 26keV polychromatic x-rays with a broad energy bandpass (>10%). This broad bandpass will allow the collection of extended XAFS spectra in a single shot and should make the beamline particularly suitable to follow processes that occur on sub-second timescales down to milliseconds and microseconds.

# Doping induced electron redistribution and strong covalency in $\text{La}_{1-x}\text{Sr}_{1+x}\text{MnO}_4$

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The effect of doping on the electronic structure at the Mn sites in the  $\text{La}_{1-x}\text{Sr}_{1+x}\text{MnO}_4$  series ( $x=0, 0.3$  and  $0.5$ ) has been studied by means of non-resonant hard X-ray emission spectroscopy (XES) [1]. We have observed a linear dichroism in the Mn  $K\beta$  main lines ( $3p$  to  $1s$  transitions), largest for  $x=0$  and diminishing with increasing  $x$  up to  $0.5$ . The Mn  $K\beta$  main lines in the poly-crystalline samples change considerably less upon increasing the hole doping (substitution of La by Sr) than it would be expected based on the change of formal valence [2]. This allows to conclude that the charge and spin density at the Mn sites are only little affected by doping. Therefore, holes injected in the  $\text{La}_{1-x}\text{Sr}_{1+x}\text{MnO}_4$  series mainly result in a decrease of charge density on the oxygen atoms, i.e. oxygen takes an important part in the charge balancing as other works have also suggested [3]. These findings are supported by many-body cluster calculations.

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# Current status of SPring-8 Taiwan beamline RIXS station

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SPring-8 BL12XU(Taiwan beamline) is designed primarily for high-resolution non-resonant(IXS) and resonant(RIXS) inelastic x-ray scattering experiments to explore frontier research in material science. This beamline has been opened to users since February 2003. Since then several contributions on RIXS experiment have been done using our beamline.[1][2]

In this workshop we are going to present recent results and future plan of our RIXS station.

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# Resonant inelastic x-ray scattering in single-crystal superconducting PrFeAsO<sub>0.7</sub>

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A prerequisite to elucidate the mechanism underlying superconductivity in the iron oxypnictides is an in-depth knowledge of the low-lying electronic excitations. In an attempt to unveil those low-energy excitations, we have performed a resonant inelastic x-ray scattering (RIXS) measurement at the Fe *K* edge in a single crystal of the underdoped superconductor compound PrFeAsO<sub>0.7</sub> ( $T_c=42$  K).

The dependence of the RIXS spectra upon the incident energy  $E_1$ , measured with the momentum transfer  $Q = (0\ 0\ 6.5)$  which corresponds to  $(0,0)$ , is observed to be nearly featureless. This is at stark contrast with the usual RIXS signal obtained on the Cu high-temperature superconductors, and can be accounted for by the itinerant nature of the Fe *3d* electrons in the FeAs materials. In the  $E_1=7124$  and  $7125$  eV spectra, we discern a feature centered around 4 eV which undergoes a slight resonant enhancement. The energy of this feature is reminiscent of the metal-ligand charge transfer in the cuprates, therefore we are tempted to ascribe it to the charge transfer between Fe *3d* and As *4p*. No dispersion was found in the  $E_1=7125$  eV spectrum measured at  $Q = (0.5\ 0\ 6.5)$ , which corresponds to  $(\pi,0)$ , suggesting that this excitation is non dispersive. We plan to compare this work with theory, aiming at contributing to the understanding of the role of the charge transfer in the superconductivity of iron arsenides.



# Core Level Emission Analyzer and Reflectometer (CLEAR) at ALBA-CLÆSS beamline

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A new x-ray emission spectrometer being developed at the Core Level Absorption & Emission Spectroscopies (CLÆSS) beamline of ALBA synchrotron is presented. Its main features are:

- Fluorescence is collected in back scattering direction. Thus a) no additional side window is required in an in-situ cell or a cryostat, which means a simplified cell design with more uniform heating (cooling) and b) there is no depth-related fluorescence source broadening as at the usual  $45^\circ$  incidence, which means a better energy resolution.
- The geometry allows energy dispersive images in two scales: some eV (due to diced crystal) and some hundreds eV (due to in-Rowland circle position of the sample). Thus no  $\theta$ - $2\theta$  scans are required. The static acquisition alleviates requirements for mechanical accuracy.
- 3 Johansson-like diced Si crystals: (111), (220) and (400) splitted into two halves with  $(1.2\text{--}1.5\text{ mm})^2$  facets. The crystals cover the energies 2–28 keV ( $\theta = 35\text{--}80^\circ$ ) with energy resolution better than the width of the corresponding  $K\alpha$  lines.
- Dynamical sagittal crystal bending, which depends on Bragg angle and in-circle coordinate, allows small sagittal image size. Thus a 1D, not 2D, detector is required.
- The movable tank allows for insertion of large sample infrastructures (magnet, cryostates), enables completely windowless operation and also allows using the spectrometer as reflectometer and polarimeter.

The main characteristics of the spectrometer as energy resolution, count rates etc. are demonstrated on the basis of extensive ray-tracing. Various aspects of the fabrication and metrology tests of Johansson-like diced crystals are discussed. Possible candidates for 1D or 2D detectors are compared. The organizational issues are considered as well. The Conceptual Design Report of the spectrometer can be found on the beamline web page.

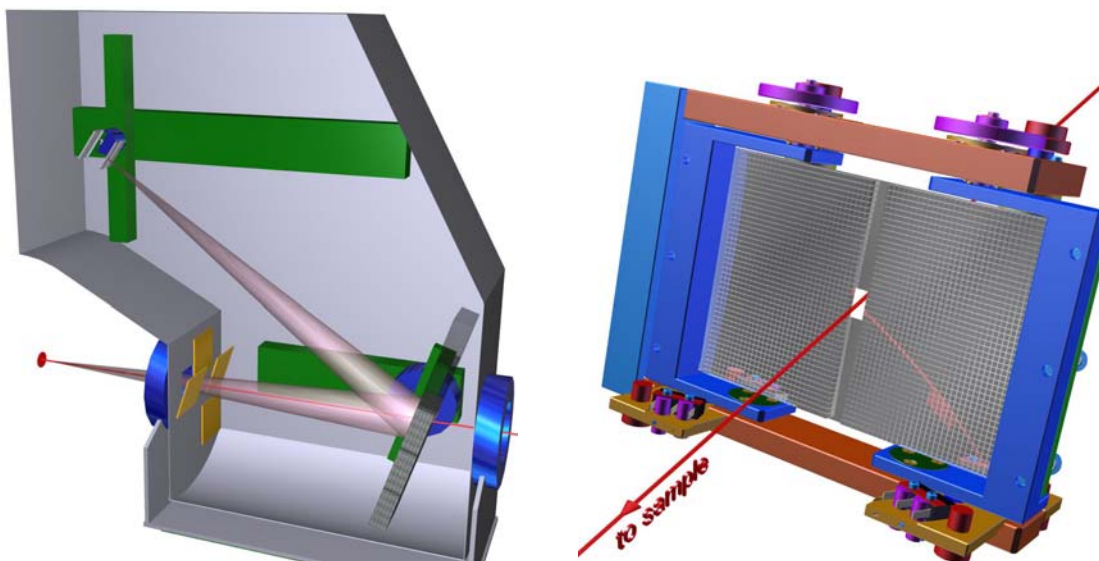


Figure 1: General conceptual view of the spectrometer (left) and the diced crystal with sagittal bender (right).

# Resonant inelastic X-ray scattering of cerium and ytterbium systems

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The importance of generally neglected quadrupole transitions have been shown using resonant inelastic X-ray scattering for the cerium (III), (IV) and ytterbium (II), (III) systems. Observation of generally weak quadrupole  $2p^5 4f^{(n+1)}$  excitations is fully reproducible and supported by atomic multiplet theory. We demonstrate that XANES spectrum measured with a help of x-ray emission spectrometer reveal hidden dipole and quadrupole features which can be used in interpretation of electronic structure of organometallic complexes: cerocene  $Ce(C_8H_8)_2$  and ytterbocene  $Cp^*_2Yb(bipy)$ .

# Proposal for a new beamline for inelastic x-ray scattering studies at the ESRF

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We present the proposal for a new beamline dedicated to inelastic X-ray scattering (IXS) at the ESRF. This project has been prepared within the context of the upgrade of the facility and aims at further developing the IXS programme now carried out at beamline ID16 to study electronic excitations in condensed matter. The scientific case of the beamline rests on the capability of providing a spectroscopic tool with the specific advantages of a hard X-ray probe: bulk information, high-penetrating power, elemental and spin sensitivity. The main idea of the present proposal is to strengthen the advantages of IXS over complementary techniques providing: i) an intense, stable beam focused down to few microns (with an option to go to submicron sizes in the future) leaving at the same time enough free space around the sample for complex sample environments; ii) two spectrometers optimized for high efficiency with medium energy resolution ( $\sim 300$  meV) and for high energy resolution applications ( $< 100$  meV), respectively; iii) an optical scheme to extend the energy range of applicability of the technique from the 6-12 keV interval used today up to  $\sim 20$  keV.

# RIXS and resPES studies on Cu-Phthalocyanine

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We investigate (Cu)- Phthalocyanine (Phthalo) films and report on the XAS and RIXS data recorded at the Cu L edges. We compare these results to data recorded for Cu and CuO samples as well. The RIXS data are taken at the ALS BL8, resonant photoemission is done at Bessy.

For Cu-Phthalo we find well resolved d-d excitations in the RIXS data. The signature of these d-d excitations is also observed in the Cu3d valence band spectra when recorded at resonant excitation. Here we use valence band photoelectron spectroscopy to map and separate the final state configuration interactions that occur upon resonant photo excitation from Cu2p, O1s, and Cu3p core levels of Cu<sup>0</sup>, and Cu<sup>+2</sup>. We display our data in a (photon energy / binding energy) matrix and identify the Cu3d<sup>8</sup>, the Cu3d<sup>9</sup>, and the Cu3d<sup>10</sup> states, respectively, which are counterbalanced by inner-atomic d-d transitions, by charge exchange with Cu4s states, or by charge transfer from O2p ligands.

With these data we learn whether the life time of the photo-excited electron is short enough to interfere with the photo-emission channel or is long enough to decay via a resonant Auger mechanism.

Further, we analyze the profiles around the Cu2p, Cu3p, and O1s thresholds for photo-emission and Auger channels. We find Fano profiles (with q=0) to identify the Cu3d<sup>10</sup> states. The Cu3d<sup>7</sup> state causes a split when excited from the L<sub>II</sub> level. Most stable is the Cu3d<sup>8</sup> state which is identified by its characteristic multiplet structure splitting.

With such information from our combined RIXS and resPES study we gain many details on the final state configuration interaction which otherwise remain unrevealed when conventional XAS techniques are applied.

# Site selective RIXS by fluorescence interferometry

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Resonant Inelastic X-ray Scattering (RIXS) provides certainly valuable element specific and symmetry selective information about momentum-transfer dependent excitation, but the method is not intrinsically site specific, if non-equivalent sites of the same element are involved. This makes the assignment of specific RIXS spectral details to certain constituting parts of a more complex compound under investigation difficult, e.g. the assignment of indirect Cu RIXS spectra to CuO<sub>2</sub> planes or CuO chains in YBCO.

In this study, the utilization of the so-called fluorescence interferometry (FI) (1) is proposed to make RIXS spectra site sensitive.

As first pointed out by Ma and Blume (1), the coherence of the absorption and re-emission process of RIXS has a consequence, which is best demonstrated by applying the basics of the classical Young double-slit experiment to RIXS from a diatomic molecule. Ma and Blume (1) have demonstrated that the re-emission from such a diatomic molecule of two equivalent atoms leads to a Young-like interference pattern, provided (i) the two atoms are interacting thus constituting molecular orbitals, (ii) the energy splitting between bonding and antibonding orbitals can be resolved experimentally, (iii) the two atoms are positioned within the coherence volume of the incident beam.

These prerequisites for FI are also met, if we consider a RIXS process of a group of identical atoms on equivalent lattice sites, provided their valence and conduction electron bandwidths are larger than the energy resolution of monochromator and analyser. This way, interference of the radiation re-emitted by this group of atoms leads, as shown on the basis of the Kramers-Heisenberg formula (2), to a double differential scattering cross section, which is proportional to the square of the **partial structure factors**  $F(\mathbf{g})$  of the group of atoms on equivalent lattice sites, where the corresponding reciprocal lattice vectors  $\mathbf{g}$  are determined by the momentum transfer vector  $\mathbf{q}$ .

Thus, in order to assign a certain structure in the RIXS spectrum to a definitive group of atoms on equivalent lattice sites, the relative intensity of this structure as a function of  $\mathbf{q}$  (and the matching  $\mathbf{g}$ 's) has to follow the square of the corresponding partial structure factors  $F(\mathbf{g})$ 's.

This way, RIXS spectra can be analysed site selectively with respect to the contributing atoms in complex structures.

This new method is exemplarily demonstrated on indirect RIXS spectra of YBCO with the aim to distinguish between the contribution of CuO<sub>2</sub> planes and CuO chains to the spectra.

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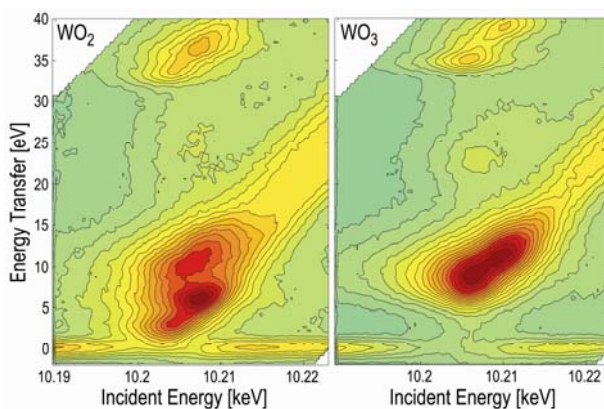
# 2p-5d RIXS of tungsten and rhenium oxides

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The 5d transition metals are important additives in a wide spectrum of industrial applications, due to their excellent mechanical strength and resistance at high temperatures, good surface stability and corrosion resistance. They are common ingredients in catalytic converters as well as opto- and spin electronics devices. The chemical state of the late 5d elements is being routinely probed *in situ* using X-ray absorption spectroscopy, due to high sensitivity of the  $L_{2,3}$  spectral shape to the occupation of  $d$  orbitals. In the case of the early 5d elements the spectral changes are less pronounced, due to smaller relative change in the occupation of empty states upon electron transfer, which makes difficult the quantitative analysis. Here the bulk and element sensitive technique probing density of valence states would be preferred.

The resonant inelastic X-ray scattering spectra become directly sensitive to the valence shell when the final state energy is only of a few electron volts. Therefore the 2p-5d RIXS is a promising technique in this context. Here we present a results of preliminary measurements of a set of 2p-5d RIXS spectra performed on the W and Re oxides (fig.1). Four  $MO_x$  ( $M = \text{Re}, \text{W}$ ,  $x = 2,3$ ) samples of formal  $5d^n$  ( $n = 0-3$ ) occupation were probed, revealing significant differences in the shape and position of spectra.



**Figure 1:** Comparison of the 2p<sub>3/2</sub>-5d<sub>5/2</sub> rixs spectra of WO<sub>2</sub> and WO<sub>3</sub>, reproduced from [1].

With increasing formal charge of the 5d ions the RIXS spectral width in excitation (emission) energy direction is decreasing (increasing), as expected for rising occupation of the 5d band. Moreover the gradual shift in the spectral intensity towards lower energy transfer with rising formal charge is observed, which is attributed to the closing of the band gap and increase of the 5d DOS at the Fermi level. The experimental spectra can be nicely reproduced using multiple-scattering calculations (FEFF 8.4) providing a way for their detailed analysis and leading to potential use of the technique in chemical characterization of a wide class of samples.

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# Temperature dependence of the d-d excitations in the $\text{La}_{5/3}\text{Sr}_{1/3}\text{NiO}_4$ system

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The correlation between high  $T_c$  superconductivity and stripe ordering in cuprates requires the understanding of the charge stripes dynamics.

In particular, the 214 type nickelates and cuprates exhibit charge stripe order when holes are doped into the system. The nickelates, non-superconducting systems isostructural to cuprates, have been studied intensively and a substantial amount of the work has been dedicated to the  $\text{La}_{5/3}\text{Sr}_{1/3}\text{NiO}_4$  due to the fact that the charge ordering for this doping is stable, nearly commensurate, and visible to most of the experimental probes, making it a model system to address low-temperature ordering and stripe correlations in the TMO perovskites [1-5]. In this system the charge ordering process occurs in a very large temperature range, between 100 and 240 K. It can be described as a continuous 2D transition. Additionally the system shows also spin ordering around 190 K, where the system develops a local antiferromagnetic order in a paramagnetic matrix. It has been widely recognized that the orbital degree of freedom plays a key role in the understanding of the physical properties observed in nickelates. In particular, the charge ordering takes place in the 3d orbitals, thus our interest in the investigation of the energetics of the 3d levels. Here we report the temperature dependence of the crystal field, i.e. d-d, excitation spectra in  $\text{La}_{5/3}\text{Sr}_{1/3}\text{NiO}_4$  system by resonant inelastic x-ray scattering (RIXS) at the Ni K main edge.

We detected temperature dependent excitations in the 1-3 eV energy range that could be correlated to the charge ordering phenomena.

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# Probing electron correlation in Lanthanides using resonant inelastic X-ray scattering

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Electron correlation in the atomic spectra is the inherent aspect of the many body problem and the breakdown of independent electron picture. In this work I will discuss correlation effects arising from mixed- and symmetry entangled-discrete states disclosed in lanthanides  $N_{IV;V}$  XAS edges.

Due to strong localization of the  $4f$  valence shell, the tightly bound excited states are symmetry entangled states that involve a degree of correlation.

Very notable for these systems, the highly intense giant resonance introduces a further mixing with the localized quantum entangled states. At these excitation energies, coherent decays of similar amplitudes from mixed states result in strong interference effects which are visualized in the asymmetrical spectral profiles of the total electron absorption yields. Controversially, the fluorescence yield measurements revealed a symmetrical Lorentzian profile.

In order to investigate the subtleties of electron correlation in lanthanides we carried out resonant inelastic X-ray scattering (RIXS) experiments at the  $N_{IV;V}$  -edges of light lanthanide ions (La, Ce, Pr) accompanied with theoretical calculations. We found that symmetry aspects of the dipole transition cause breaking of coherence in some of the decay channels and modify the true spectral profile of the fluorescence yield.

1



# Femtosecond magnetization dynamics in itinerant and local moment ferromagnets

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The magnetic circular dichroism in Inelastic X-ray Resonant Scattering in perpendicular geometry (circularly polarized X-rays with wave vector normal to the magnetization) at the  $L_{2,3}$  absorption region of magnetic transition metals is exploited to investigate the magnetization dynamics of itinerant and local moment ferromagnets. In ferromagnetic metals, the dichroism in the energy regions between the  $L_3$  and  $L_2$  absorption edges and above  $L_2$  is related to a spin dependent screening of the polarized core hole created during the ultrafast scattering process (timescale around 1 – 2 fs) [1]. A model based on the screening by the conduction electrons [2, 3] has been already successfully exploited to describe the relevant trends of the phenomenon across the 3d transition metals (Fe, Co, Ni) and to gain information on the screening time constant down to fraction of fs.

We will show that the introduction of magnetic impurities in diluted ferromagnets allows to improve the experimental sensitivity of the method. Within the model mentioned above, the present study allows a more stringent evaluation of the screening times in Ni metal and Fe metal host, which result to be some femtosecond and some hundred attosecond, respectively [4].

Furthermore we will present recent results obtained on itinerant magnets and local moment magnets, showing the presence of spin dependent screening at the ultrafast timescale also in strongly localized systems with low carrier density and mobility. This somewhat unexpected behaviour together with few features of the dichroism unseen in the itinerant magnets are not easily interpreted within the above model, and suggests the possibility of different mechanisms at the origin of the dichroism.

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# Theoretical study of Resonant Inelastic X-ray Scattering of NiO

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Recently RIXS measurements at Ni  $L$ -edge with high resolution were performed for the NiO [1,2]. The results showed two different charge transfer (CT) excitation peaks in the CT satellite region of x-ray absorption spectra. It was believed that the origin of these two CT excitation peaks is ascribed to the lower and upper edge of the  $3d^9\bar{L}$  nonbonding in the final state of RIXS[3]. Here we talk about the experimental data and our new theoretical analysis with extended configuration-interaction model including intra-atomic multiplet structure and a new screening channel derived from the Zhang-Rice doublet bound state near Fermi Energy. Very good agreement with experiment is obtained. This model was originally proposed in the analysis of Ni  $2p$  core-level hard x-ray photoemission spectroscopy (HX-PES) [4]. Unlike conventional soft x-ray PES, Ni  $2p$  core-level HX-PES spectrain NiO have shown a low binding energy feature with significantly large intensity in addition to the  $2p^53d^8$  and  $2p^53d^9\bar{L}$  features, where  $\bar{L}$  represents the O  $2p$  ligand hole. The structure, position of the main peak and satellite structures were well explained by this model. The lowest binding energy peak was attributed to screening from the Zhang-Rice bound state.

In the present study, we discuss the relation between the bound state screened peak in core-level HX-PES and charge excitation in Ni  $L$ -edge RIXS in terms of a common model which is valid for both techniques for NiO.

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# Electronic structure of Cu-doped ZnO thin films by x-ray absorption and emission spectroscopy

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The electronic structure of Cu-doped ZnO thin films, synthesized with a nominal composition of  $\text{Zn}_{1-x}\text{Cu}_x\text{O}$  ( $x = 0.03, 0.05, 0.07, 0.10$ ) by using spray pyrolysis method, has been investigated using near edge x-ray absorption fine structure (NEXAFS) measurements at the O K- and the Cu  $L_{3,2}$  -edges and using resonant inelastic x-ray scattering (RIXS) measurements at Cu  $L_{3,2}$  edge. All the prepared  $\text{Zn}_{1-x}\text{Cu}_x\text{O}$  thin films showed ferromagnetic behavior at room temperature, as measured by using an alternating gradient force magnetometer (AGFM). The intensity of the pre-edge spectral feature at the O K -edge increases with the Cu concentration, which clearly reveals that there is strong hybridization of O 2p-Cu 3d orbitals in the ZnO matrix. Spectral features of the Cu  $L_{3,2}$  -edge NEXAFS exhibit multiple absorption peaks followed by a strong x-ray magnetic circular dichroism (XMCD) signal at room temperature. These results clearly demonstrate that Cu is in mixed valence state of  $\text{Cu}^{2+}/\text{Cu}^{+1/+3}$ , substituting at the Zn site. RIXS experiments at Cu  $L_{3,2}$  edge show that the substitution by Cu atoms can explain the magnetic interaction in Cu-doped ZnO.

# First successful RIXS measurements on (GaMn)As

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Introduction of magnetic moments into semiconductors results in a new class of materials called diluted magnetic semiconductors (DMS). Among the DMS systems (GaMn)As have attracted particular interest because they turn out to be ferromagnetic, with relatively high Curie temperature (up to 110K has been reported). The electronic structure of (GaMn)As has been studied extensively in recent years. However, so far no X-ray emission data have been published though such data should be useful for characterization of local 3d states on the Mn sites. In this paper we present the first emission data of this system, and show that clear resonant inelastic X-ray scattering (RIXS) features can be observed. The presence of RIXS features indicates localized character of electronic states, i.e., rather weak hybridization between the Mn 3d and As 4s,p states.

# High resolution X-ray emission spectroscopy (HRXES): an advanced tool for actinide research

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High resolution X-ray emission spectroscopy (HRXES) is becoming increasingly important for our understanding of electronic and coordination structures.

Through combination of such information with development of quantum theoretical tools, we can one day hopefully predict reactivity and physical behavior especially of 5f elements. HRXES can be used to remove lifetime broadening by registering the partial fluorescence yield emitted by the sample (i.e., recording a windowed signal from the energy dispersed fluorescence emission while varying incident photon energy), thereby yielding highly resolved X-ray absorption fine structure (XAFS) spectra, which often display resonant features not observed in conventional XAFS. The spectrometer set-up can also be used for a wide range of other experiments, for example, resonant inelastic X-ray scattering (RIXS), which can be used to obtain bulk electron configuration information, in solids, liquids and gases. Valence-selective XAFS studies, where the local structure of a selected element's valence state present in a mixture of valence states can be obtained, as well as site-selective XAFS studies, where the coordination structure of a metal bound to selected elements can be differentiated from that of all the other ligating atoms.

A HRXES spectrometer is presently being constructed and commissioned. It will ultimately be made available for use at the INE-Beamline for actinide research at the synchrotron source ANKA at FZK. We present the spectrometer compact, modular design, optimized for attaining a wide range of energies<sup>2</sup>. First measurements of actinides complexed with partitioning ligands both in solid state and in solution will be shown. Results from HRXES studies of their lanthanide counter parts, as well as polarized dependent characterization of a single crystal uranyl system, will be presented too.

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