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Resonant Inelastic X-ray Scattering at the ESRF: Hard and Soft X-rays

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The technique of Resonant Inelastic X-ray scattering (RIXS) has been exploited at the ESRF since the very early days of the facility in the 1990s. Of particular importance has been the pioneering hard X-ray work on ID16 and that by the Milano group of L. Braicovich and G. Ghiringhelli in collaboration with the ESRF at the soft X-ray beamline (originally on ID12B and then at ID08). The success of these activities has in many cases led to the development of the technique at other facilities. Both the hard and soft X-ray RIXS facilities at the ESRF will be upgraded in the next two years so it is timely to briefly outline what scientific problems can be addressed by the method, what the current status is at the ESRF, and how the experimental capabilities will be enhanced in the near future.

In general terms, RIXS can be considered as an evolution of resonant X-ray emission spectroscopy (XES) where the fluorescence spectra are excited with synchrotron radiation instead of electron bombardment. Whereas in weakly correlated systems the normal fluorescence emission dominates and the spectra can be interpreted in terms of density of valence states projected onto a core hole, in Mott insulators and other strongly correlated solids (mainly 3d transition metal oxides) the X-ray photon resonant absorption and subsequent re-emission form a single event, in all to be considered as an inelastic scattering process. As a consequence the intrinsic width of the spectra is no longer dictated by the ultra-short-lifetime broadening of the core hole and high experimental energy resolution is crucial for obtaining meaningful results. RIXS can then be seen as an element and (often) site-specific energy loss spectroscopy, with points of similarity with electron energy loss spectroscopy, Raman scattering, and inelastic neutron scattering. Thus RIXS can excite spin, electronic and lattice modes, with momentum resolution. In particular, when performed at the 2p→3d absorption resonance of 3d transition metals in the soft X-ray range, it gives direct access to dd excitations, normally forbidden for electric dipole optical spectroscopies. Moreover, the strong (10 to 20 eV) spin-orbit interaction in the 2p-hole intermediate state opens a direct path to spin-flip processes at the origin of spin waves in magnetically ordered systems. RIXS in the hard X-ray range is complementary to RIXS at the corresponding L-edges and offers some interesting opportunities, e.g. for the study of low-energy electronic excitations in transition-metal based compounds: i) being a hard X-ray technique it is not surface sensitive and in particular allows for experiments in complex sample environments, e.g. high pressure cells or interfaces in heterostructures; ii) it has different selection rules to those in the soft X-ray range – in practice, this allows probing different aspects of the physics of a given system, e.g. it is more sensitive to the charge transfer excitations [1] than to d-d transitions that dominate the spectra in the soft X-ray range [2]; or it allows selecting bimagnon excitations in cuprates at the Cu K-edge rather than single magnon excitations at the corresponding Cu L$_3$-edge [3].

Soft X-ray RIXS: Past scientific achievements

Low count rate has always been the real limiting factor for soft X-ray RIXS: the resolution has to be compromised in order to reach a viable signal on the detector. The progress in synchrotron sources and optics and of X-ray position sensitive detectors has gradually allowed the move from XES to RIXS experiments. At the ID12B beam line (later ID08), the energy resolution of the AXES spectrometer [4] and its dedicated compact monochromator [5] evolved from a standard combined linewidth at Cu L$_3$ (930 eV) of 2 eV in the early 1990s to ~0.8 eV (a resolving power of ~1100) around 2003. This was obtained mainly thanks to a directly illuminated X-ray CCD camera that replaced the original microchannel plate detector [6]. A detailed study of the dd excitations in insulating 3d transition metal oxides thus became possible [7-9]. An example is shown in Figure 1 for NiO. A further improvement came from the relocation of the spectrometer after the high-energy-resolution Dragon-type beam line monochromator and the installation of a toroidal refocusing mirror producing a 5mm x 60mm spot at the sample, allowing a slitless operation of AXES with high gain in the overall detection efficiency. An example of dd excitation spectra collected in few hours on La$_{1-x}$Mn$_{1+x}$O$_3$ is shown in Figure 1, right panels. There the Mn L$_3$ RIXS was used to determine the crystallographic site of the divalent fraction of Mn in the Mn-rich sample, where Mn$^{2+}$ turns out to act as a self dopant [10]. In this new set-up the combined resolving power rose to 2000 and eventually to 4000 (present value). This level of performance allowed the very first detection of dispersing magnetic excitations in layered cuprate parent compounds [11]. The contemporary availability of the SAXES spectrometer at the Swiss Light Source [12],
The study of spin wave dispersion and of dd excitations in cuprates is at present very active using AXES at ID08, moving from traditional materials such as the La$_{2-x}$Sr$_x$CuO$_4$ or YBa$_2$Cu$_3$O$_7$ families to cuprate interfaces and superlattices [15].

Hard X-ray RIXS: Past scientific achievements

Hard X-rays RIXS measurements have for long been mainly carried out at the K-edge of transition metal oxides. In these conditions, e.g. at the Cu K-edge main line, photon energy losses in the few eV range are mainly due to “shake-up” processes of the valence 3d electrons taking place in between the creation and the annihilation of the 1s-4p core exciton. RIXS experiments can then capture the physics of charge dynamics through the observation of momentum-dependent excitations. These measurements are difficult though since the inelastically scattered intensity, despite the resonant enhancement, remains low on an absolute scale and, in addition, the elastically scattered intensity is often very large. For these reasons, much work has been devoted to the measurement of charge transfer excitations at a few eV, an energy range that is easily accessible even with the energy resolution of $\approx 1$ eV reached using standard instrumentation. A nice example of these experiments is the study of the evolution with pressure (up to $\approx 100$ GPa) of the charge-transfer excitation in NiO, the prototype charge-transfer insulator [16]: the clear spectral changes could be traced back to the modification of the electronic structure induced by pressure, namely increase in the electronic bandwidth leading to a decrease of the charge transfer gap.

Following recent instrumental developments based on the use of 2D pixel detectors [17, 18], it is now possible to carry out RIXS experiments with energy resolutions in the hundreds of meV range or less paying a minor price in terms of count-rate. This has given the start to higher-resolution hard X-ray RIXS studies. For example, interest has been devoted to the study of the so-called dd or crystal-field excitations, in which only the occupation of the 3d orbitals of a transition-metal ion changes. These excitations, sensitive to the local coordination, provide information on the fine structure of the energy levels of the electrons involved in, e.g., metal-insulator transitions. These dd excitations, whose energies are typically in the eV energy range, have been traditionally studied using optical techniques [19], electron-energy-loss spectroscopy [20], and RIXS in the soft X-ray region [21]. Soft X-ray techniques at the L absorption edge of transition metal ions are, in particular, very well suited for these studies due to their direct dipolar coupling to the 3d electrons. In the case of hard X-ray RIXS studies at the K-edge of transition metal ions instead, the absorption and emission channels can be either dipolar (1s-4p) or quadrupolar (1s-3d) in character, although hybridization of the 3d orbitals with ligand 2p states may bring a dipole character to an otherwise quadrupolar 1s-3d process. In any case, at the K-edge resonance the dd excitations are typically much weaker than at the corresponding L-edge resonance. However, the characteristic features of a hard X-ray probe, i.e. the bulk sensitivity and the possibility to study samples in demanding environments such as...
high-pressure cells, makes K-edge RIXS an appealing technique for these studies. A nice example of this has been provided again for NiO (see Figure 2) [22]: the precise detection of the energy positions of the spectral peaks, which correspond to the splitting of the final 3d levels by the local crystal field and dd interactions, gives direct information on the crystal-field splitting parameters. Follow-up experiments devoted to the measurement of dd excitations in correlated electron materials under high-pressure conditions are now within reach.

**Soft X-ray RIXS: Perspectives**

Energy resolution is the most important parameter for soft X-ray RIXS studies. However, new insight can also come from a better control and measurement of the photon polarization. By knowing how the photon polarization gets modified in the scattering process, one gets information on the symmetry of the resulting excited state left in the solid. In Raman experiments this is a current practice, because polarizing the incident radiation and measuring its polarization state after it has been diffused by the sample is practically very easy. For X-rays, synchrotron radiation sources are always highly polarized, but measuring the polarization can be challenging. For soft X-rays, one has to rely upon multilayered mirrors, whose reflectivity and polarization sensitivity are rather low.

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**Figure 2:** Measured RIXS spectra of single-crystal NiO with different sample orientations. The direction of the linear polarization vector $\varepsilon$ of the incident beam with respect to the crystallographic orientation of the sample is reported on top of the figure. The spectra were measured at the beamline ID16 of the ESRF using an energy resolution of 250 meV at the Ni K-edge (8331 eV) [22].

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Recently, a demonstration experiment was performed using the AXES spectrometer at ID08 in collaboration with C. Morawe and is described in [23]. As a reflecting element, a multilayer (B₄C/W) was used. It was grown at the ESRF and mounted ~30 cm before the CCD detector. The beam was deflected by ~40 degrees in a plane perpendicular to the grating dispersing direction as sketched in Figure 3 [23]; in this way the multilayer does not degrade the resolution of AXES (E/ΔE ≈ 3500), but we can exploit the different reflectivity for the π and the σ polarization components (respectively parallel and perpendicular to the reflection plane of the multilayer mirror). The reflectivity ratio Rπ/Rσ had been previously measured at the same beamline. The set-up allows the insertion of the multilayer and the lateral displacement of the detector without breaking the vacuum; thus it is easy to switch between the traditional configuration and the polarimetric one. This is particularly important since the data analysis is based on a proper combination of four spectra, with two incident linear polarizations (horizontal and vertical in the laboratory space), and with and without the polarimeter.

There is a vast range of scientific problems that can be addressed by soft X-ray RIXS and many studies can already be done with the instrumentation available today. However, RIXS is still in a growing phase, supported by theoretical progress and experimental efforts for higher-energy resolution. A better resolution would open the field to magnetic excitations in less strongly magnetically ordered systems, at present still out of reach because of the insufficient energy resolution.

**Hard X-ray RIXS: Scientific perspectives**

Direct RIXS experiments in the soft X-ray range have proven to be a powerful technique for the study of electronic and magnetic properties of correlated electron systems [24], and of high-Tc superconductors in particular [13, 14, 25]. The design of dedicated spectrometers and the improvements in energy resolution down to ~100 meV have been crucial in the development of magnetic RIXS [4, 12]. It is clearly of interest to extend these capabilities to the hard X-ray range, e.g. to the L-edge of 5d transition metal compounds for the study of their electronic and magnetic properties. In fact, renewed attention has been recently paid to 5d transition metal compounds and oxides in particular, as it was realized that they may host a large variety of intriguing phenomena, comparable to those displayed by strongly correlated 3d transition metal materials [26, 27]. Due to the more delocalized nature of 5d with respect to 3d states, electron correlation is expected to be small in these systems; therefore, one would naively predict such systems to have a metallic character. However, the spin-orbit interaction which characterizes 5d transition metal compounds is in the order of the Coulomb repulsion among valence electrons: as a result of the competition between spin-orbit coupling (ζ) and correlation effects (U), a variety of interesting phenomena has been observed, such as Mott insulating states [26, 27]. An interesting example of 5d transition metal oxides is provided by IrO₂ (5d⁵ system, owing to the Ir⁴⁺ oxidation state), a compound used as an electrode material for the production of components in advanced memory technologies. First measurements in IrO₂ powder by hard X-ray RIXS at the Ir L₃-edge (11216.5 eV) are shown in Figure 4: as commonly found at the L-edge of 3d transition metal oxides using soft X-ray RIXS, strong dd excitations appear at low energy (<3 eV), while a broad excitation likely due to pd transitions appears at higher energy.

**Figure 3:** Optical scheme of the AXES spectrometer, where a multilayer mirror can be inserted in the exit arm of the spherical grating, just before the CCD detector. When the polarimetric mirror is inserted the beam deviates by approximately 40 degrees and the detector is rotated around the mirror accordingly.

**Figure 4:** Measured RIXS spectrum of IrO₂ powder. The data were collected at the beamline ID16 of the ESRF using an energy resolution of 850 meV at the Ir L₃-edge (11215 eV).
(8 eV). This kind of data can provide useful constraints to further develop models for the electronic structure of this material.

An even more interesting example is provided by Sr$_2$IrO$_4$. Here, a spin-orbit coupling parameter $\zeta \approx 0.5$ eV splits the 5d $t_{2g}$ states in a fully occupied $J_{\text{eff}}=3/2$ ($J_z=\pm 3/2, \pm 1/2$) quartet and a partially occupied $J_{\text{eff}}=1/2$ ($J_z=\pm 1/2$) doublet, the energy separation being in the order of $\zeta$. Although small compared to 3d transition metal compounds, correlation effects ($U \approx 0.5$ eV) effectively split the $J_{\text{eff}}=1/2$ band in a fully occupied $J_{\text{eff}}=1/2$ LHB and an empty $J_{\text{eff}}=1/2$ UHB, thus turning the system into a (spin-orbit induced) Mott insulating state. First measurements of the magnetic excitations in single-crystal Sr$_2$IrO$_4$ by RIXS at the Ir L$_3$ edge just appeared [28], showing that the magnon dispersion is well described by an antiferromagnetic Heisenberg model with an effective spin one-half on a square lattice. This result shows that the low-energy physics of Sr$_2$IrO$_4$ strongly resembles that of undoped cuprates, parent compounds of high-$T_c$ superconductors. It was also suggested that Ir oxides may display high-$T_c$ superconductivity themselves [29]. It is thus clear that the study of the electronic and magnetic excitations of 5d systems is going to represent one of the most relevant research activities for hard X-ray RIXS in the years to come.

**RIXS at the ESRF and the upgrade program**

The ESRF has offered in the past the possibility of state-of-the-art hard and soft X-ray RIXS experimental facilities. With the improvements that the ESRF Upgrade will bring, these possibilities will be enhanced and the users will have access to exceptional instruments for their science in the coming years.

A large expansion in the capabilities of soft X-ray beam lines for RIXS studies has occurred in the last few years. This is the result of pioneering work at many places, not the least at the ESRF, and has resulted in exceptionally high energy resolution. There is a quest to further improve the energy resolution offered in such experiments as well as improving the momentum transfer range and in general optimizing the sample environment for such experiments. At the ESRF this is being tackled by a new upgrade beamline (UPBL07) [30], which will be built on port ID32. The beamline will have two branches with one dedicated to very-high-energy-resolution soft X-ray RIXS studies. It will be commissioned starting in 2014 and be operational for users in the second half of 2014. The beamline will take advantage of the new experimental building, which will allow a 110m-long beamline with sufficient space...
for a 10m scattering arm, continuously covering 100 degrees of scattering angle. The energy range of the beamline is ~0.4–2 keV, covering the oxygen and nitrogen K-edges, the 3d transition metal L_{2,3}-edges, and the rare-earth M_{4,5}-edges. The combined resolving power of the new instrument is aimed at 20–30000 at 900 eV, i.e. 30–50meV. The spectrometer, called ERIXS, will be based on a spherical grating with varied line spacing similar to AXES and SAXES. In addition, a long parabolic mirror will collect and collimate the radiation scattered by the sample, so that the larger sample-to-detector distance will not be detrimental to count rate. In this way, the new apparatus should produce RIXS spectra with 2.5 times better resolution than SAXES at the SLS, but at a similar count rate. Moreover, polarization analysis will be implemented from the beginning.

For what concerns hard X-ray RIXS, the scientific case here, exemplified by the examples reported earlier, has motivated the ESRF to begin the upgrade project UPBL06 within the context of the ESRF upgrade, build a new station optimized for such experiments. This is now part of the upgrade project UPBL06 and UPBL07 for the soft- and hard X-rays beamline ID32 and ID20, respectively. A special thanks goes to C. Henriquet, K. Martel, and R. Verbeni for what concerns the UPBL06 project, and F. Yakhou, the UPBL07 project manager.

The spectrometer, shown in Figure 5, is based on a large 2-circles goniometer allowing the scattering plane to be placed either horizontally or vertically. This will allow some flexibility in the alignment of the sample with respect to the polarization of the incident beam: understanding the polarization dependence of scattering at resonance can indeed be crucial. The spectrometer arm, 1 or 2 m in length depending on the required energy resolution, houses five analyzer crystals for energy analysis. The beamline will offer its users a broad set of Ge and Si analyzer crystals covering almost all the K-edges of 3d elements and some L-edges of 4f and 5d elements.

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Figure 5: The RIXS spectrometer for the ID20 beamline at the ESRF in its configuration for horizontal scattering plane operation. In this drawing the analyzer crystals are located at 1 m from the sample.


