

I PROJECT SUMMARY

Title: Diffusion X inélastique et spectroscopie d'électrons en haute énergie

Inelastic x-ray scattering and high-energy electron spectroscopy

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Main beamline characteristics

Source	Energy range	Optics	Spectral resolution (E/ΔE) and flux in the sample spot (HxV)	End stations
U26 type in-vacuum undulator	3 – 12 keV	<ul style="list-style-type: none"> - Collimating mirror - Fixed-exit double crystal monochromator Si (111), - High-resolution 4-bounce monochromator Si(220) or Si(331) - Toroidal focusing mirror - KB mirror 	<p style="text-align: center;">Medium resolution</p> <ul style="list-style-type: none"> - E/ΔE=10⁴ @ 10 keV - F = 1.5 10¹² ph/s @ 8 keV standard focalization spot size :150x50 μm² - F = 0.4 10¹¹ ph/s @ 8 keV KB-focalization spot size : 2x2 μm² <p style="text-align: center;">High resolution</p> <ul style="list-style-type: none"> - E/ΔE=2.10⁵ @ 10 keV 	<p style="text-align: center;">Muti-purpose IXS spectrometer</p> <ul style="list-style-type: none"> - x-ray absorption in partial fluorescence yield mode - resonant inelastic x-ray scattering - non-resonant inelastic x-ray scattering <p style="text-align: center;">High-energy / high resolution electron analyzer</p> <ul style="list-style-type: none"> -XPS, resonant Auger

The main purpose of this project is the construction of an advanced beamline, fully dedicated to the study of the electronic excitations, with an emphasis on two complementary and innovative techniques : Inelastic x-ray scattering and high-energy x-ray photoemission. Such a unique combination of powerful spectroscopic methods on a dedicated beamline would offer new insights into the properties of complex materials. Installed at SOLEIL, the beamline will be easily accessible to the French, and more generally, to the European user community.

Available techniques

IXS setup: Resonant Inelastic X-ray Scattering (RIXS) – X-ray Raman Scattering [= non-resonant IXS] (XRS) – Resonant X-ray Emission (RXES) – Fluorescence – X-ray Absorption in Total or Partial Fluorescence Yield (TFY / PFY-XAS) – EXAFS. All methods are compatible with micro-beam.

- IXS has progressively arisen as one of the major spectroscopic tools with the advent of bright x-ray sources of 3rd generation. As a second-order all photon technique, IXS is a versatile and powerful method to study electronic properties in a wide variety of systems, and under various sample environments. At SOLEIL, IXS will largely benefit from the dedication of the beamline to this technique, in concomitance with the design of a performing multi-analyzer IXS spectrometer. This would help to make up the increasing lag of the French and European IXS communities with respect to communities in the US and in Japan by offering competitive resolution, flux, easier access and continuity.

XPS setup: High-Energy Photoemission (HE-XPS) – Resonant Auger

- XPS is an extremely widespread technique, well implemented in the scientific community as one of the foremost probe of the electronic properties in solids. XPS is already part of different projects at SOLEIL, and its wide scientific relevance in the present context is evident. However, high-energy XPS is far less common in terms of instrumentation and will constitute a unique opportunity at SOLEIL. Increase electron kinetic energy will imply larger probing depth, hence less surface sensitivity, but also the possibility of profiling buried interfaces. Latest results obtained by high-energy XPS all point to dramatic changes in the electronic properties, *e.g.* valent state, Fermi surface, etc. compared to surface states. Photoemission experiments in the 4 to 12 keV range also open the door to resonant XPS and Auger electron spectroscopy experiments involving a deep core hole. Core hole participation makes these spectroscopies element and orbital selective which in turn allows one to distinguish and enhance specific electronic excitations and ultrafast dynamics. High-resolution / high energy XPS will be a challenging extension of this technique, aimed to be installed on the beamline eventually.

Scientific case

Following the recommendations of the SAC, we present a program focused on the points outlined below:

Strongly correlated electrons [RIXS, RXES, HE-XPS]

Correlated electron systems are interesting not only for the fundamental challenge that they provide but also because they give rise to a rich variety of interesting and unexplained phenomena involving both electronic and spin degrees of freedom. These systems have been systematically investigated by spectroscopic methods like photoemission, inverse photoemission and x-ray absorption, leading to a basic understanding. As a bulk sensitive charge and \mathbf{k} -conservative process, RIXS appears, besides HE-XPS, as a powerful method to investigate further their electronic properties such as low lying excited states and their dispersion, or mixed-valent states.

Transition metal oxides: cuprates, cobaltates: Transition metal oxides have been at the core of strongly correlated electron concept. Their complex electronic properties are relevant for many fields of interest such as superconductivity or colossal magnetoresistance, and by far not fully understood. In early RIXS studies, low energy excitations in transition metal oxides have been attributed to crystal-field dd , or charge transfer excitations, or more exotic final states involving excitonic effects across the correlation gap. A unique assignment of the observed features is awaited and needs both better data (resolution, statistics) and more theoretical work. High resolution is a requisite here to resolve the lowest energy states and details of the excitations dispersion. We have recently started off the production of bent-analyzers well adapted to these kinds of measurements. Promising results already obtained with the first analyzers show that the ultimate aim of 100 meV at 10 keV should be achieved in a near future. This shall open up new possibilities in the study of highly correlated materials.

Heavy Fermions / Mixed valent 4f systems: Assessing the valence of 4f electrons in strongly correlated or heavy fermion materials has been one of the major concerns for spectroscopy over the past decades. Conventional XPS and XAS have been widely used as probes of the electron count specially in rare-earth system, where the localized 4f states shows up as sharp well identified peaks in the corresponding spectra. However, surface sensitivity of XPS and strong final state effects in XAS severely handicap data analysis. We have demonstrated that RIXS in turn provides precise estimate of the f valence: The individuals components of each valent state can be easily isolated thanks to the resonant enhancement, and bulk sensitivity ensures true electron counts – comparison with HE-XPS results will be of great interest at this point. Furthermore, the variation of the f valence with temperature or pressure can be addressed. More generally, RIXS appears well suited to tackle fermiology in its various forms, and may yield complementary information about fluctuating valence state, Kondo effect, etc. in rare-earth systems and actinides.

Geophysics, Chemistry, Material science [RXES, PFY-XAS, EXAFS, XRS]

One of the major interests of all-photon high-energy probes relies in their full compatibility with heavily constrained sample environments. IXS offers the unique opportunity to investigate the electronic properties *in-situ*, in a wide under various conditions of pressure, temperatures, or in a chemical cell.

High pressure physics: We already mentioned the utility of pressure as an external thermodynamic parameter, (cf. 4f electron systems). Applied to geophysical issues, the possibility to carry out IXS experiments in high-pressure cells is of prime interest for our understanding for instance of the dynamics of the Earth interior. In particular, the magnetic properties of minerals under extreme conditions of pressure or temperature can be studied through x-ray emission spectroscopy in the fluorescence regime. More information will be gained by on-resonant measurements.

Mapping the electronic states in chemical complexes: As a second order process, resonant x-ray emission depends on both incident and emitted energies. RXES experiments therefore are best viewed as a 2D-mapping of the electronic properties around a given absorption edge and emission line. This method provides a wealth of information (about site-symmetry, redox state, etc.) compared to conventional x-ray absorption or fluorescence. It was successfully applied *e.g.* to mineralogy and bio-physics, as in a recent experiment in chemical complexes involved in photosynthesis. Fast and reliable 2D acquisition of the RXES spectra, using analyzers with bigger solid-angle, will be a major step forwards a standardization of this technique. We envisage combining this technique with micro-focusing capacity for multi-phase systems or small samples.

Absorption edges of light elements: The XANES and EXAFS spectra of light elements can be directly probed by IXS in the non-resonant mode – here the absorption edges are measured in the energy loss spectra, using primarily hard x-rays. Among others, is the possibility to investigate the O-K, C-K or Si-L edges in intrusive sample environments, such as in a high pressure cell, thanks to high penetration depth of x-ray. The development of a multi-analyzer setup covering a large solid angle will certainly make more routine this technique, still largely unused because of its low cross section. Such a setup is currently under preparation.

New advances in theory [RIXS, RXES, XRS]

Unified ab-initio / multiplet calculations: Theoretical support is a necessity when dealing with complexity in both materials and techniques. Theoretical analysis of spectroscopic data conventionally follows two equally advanced albeit opposite approaches, namely parameterized multiplet framework or *ab-initio* one electron band pictures. In many ways, multiplet calculations

provide the best agreement with spectroscopic results. But the non-univocal choice of parameters questions its relevance *e.g.* for extracting the true fundamental values out of the data. In principle, most of these parameters can be retrieved by *ab-initio* methods - for example, the LDA+U scheme well accounts for ground state properties of metal oxides. Unifying these two approaches is the main aim of a collaboration that we have recently initiated. Progress in that field will certainly benefit the entire user community at SOLEIL.

Electron dynamics: Non-resonant IXS can directly probe the dynamical structure factor over a wide range of energy and momentum. As such, IXS spectra may serve as critical test for theories of electron dynamics. Proper treatments of the core-hole interaction and excitonic effects have been implemented recently. This calls for higher quality data (in terms of energy and \mathbf{q} resolution, and intensity). The dedicated IXS setup as available at SOLEIL will constitute a major step in this direction.

Community potentially interested

Main associates

- Laboratoire de Chimie Physique – Matière et Rayonnement, Université Paris 6
- Laboratoire de Minéralogie Cristallographie, Université Paris 6 et 7 (futur IMPMC-Paris 6)
- Laboratoire de Cristallographie (Grenoble)

IXS :

Strongly correlated electrons, magnetism, theory

- European Synchrotron Radiation Facility (Grenoble)
- CENG, CEA (Grenoble)
- Laboratoire de Magnétisme Louis Néel (Grenoble)
- Laboratoire de Physique du Solide, Université Paris-Sud, (Orsay)
- Department of Physical Sciences, University of Helsinki (Finland)
- Institute of Solid State Physics, University of Tokyo (Japan)
- Brookhaven National Laboratory, NSLS, (USA)
- Laboratoire Léon Brillouin, Saclay

Biophysics, Geophysics, High pressure

- Physique des Milieux Condensés, Université Paris 6
- Institut de Physique du Globe (Paris)
- Laboratoire de Géomatériaux, Université de Marne la Vallée
- Lawrence Berkeley National Laboratory, University of California-Berkeley (USA)

Materials, chemistry

- Groupe de Dynamique des phases condensées, Université de Montpellier II

- Institut des Matériaux Jean Rouxel, Université de Nantes
- Utrecht University, Netherlands

Micro-spectroscopy

- Laboratoire Pierre Süe, CEA (Saclay)
- Laboratoire de Géologie Marine- IPGP (Paris)
- Laboratoire de Géophysique interne et Tectonophysique (Grenoble)
- Centre Européen de Recherche et d'Enseignement de Géosciences de l'Environnement (Marseille)

XPS, Auger

High energy XPS

- Elettra (Italy)
- Istituto Nazionale per la Fisica della Materia (Italy)
- Ecole Polytechnique Fédérale de Lausanne (Suisse)

And more generally, the French scientific community involved in XPS

Resonant Auger

- IPCMS (Strasbourg)
- Laboratoire Louis Néel (Grenoble)
- Laboratoire de Cristallographie (Grenoble)
- LMCP (Paris)
- LPM (Nancy)
- Laboratoire de Recherche sur la Réactivité des Solides (Dijon)
- Laboratoire de Physique de la Matière Condensée (Toulouse)
- Laboratoire mixte CNRS-St Gobain (Aubervilliers)
- CNRS-LCR Thalès (Orsay)

II Recommendations du Comité scientifique consultatif (6-7/02/03)

Beamline Proposal 24 : proposal presented by Jean Pascal Rueff.

“Inelastic x-ray scattering and high-energy electron spectroscopy ”

A very broad range of experiments is proposed for this beamline, covering Inelastic X-ray Scattering and High Energy Photoemission. An extensive review of all possible experiments has been presented in the document: SAC appreciates that in the oral presentation the proponents have focused on specific domains, unlike what was done in the written proposal. This field is of growing importance internationally, and is very promising. SAC expresses no doubt about the existing competences and skills to operate and manage efficiently this project. However SAC is concerned by the expected performances at high energy (above 8 keV). Indeed high energy installations like ESRF, APS or Spring8 have a brilliance about one order of magnitude larger at these energies; thus the lower brilliance of SOLEIL could be a problem when considering experiments with hours or days acquisition time. However in view of the present limited access time to the existing beamlines installed on high energy machines for such experiments and of the probable increasing demand in the future, SAC considers the choice of constructing this beamline as a SOLEIL management decision.

SAC recommends

- to select some specific areas in the present, broad scientific case for which SOLEIL is competitive, insuring that there is a complementarity with the ESRF scientific program in the same area
- to clarify the expected use of high resolution in the photoemission program

SAC approves the presented proposal and asks for a more focussed research program

III Propositions de la Direction de SOLEIL

La direction de SOLEIL demande l'aval du Conseil pour le lancement de la construction de la ligne « Diffusion X inélastique et spectroscopie d'électrons en haute énergie », pour une ouverture en 2008. Dans la gamme d'énergie proposée, 4 à 12 keV, les possibilités offertes par SOLEIL sur un onduleur sous vide se situent à niveau comparable à celui des meilleures sources mondiales. Cette ligne est dédiée à l'étude des excitations électroniques en développant deux techniques expérimentales de pointe dont les performances sont en plein essor : la diffusion X inélastique et la photoémission haute énergie. La combinaison de ces deux techniques sur une même ligne ouvrira des perspectives très prometteuses pour la caractérisation électronique de matériaux complexes, en particulier ceux à électrons fortement corrélés. La communauté scientifique concernée est en expansion et concerne des thématiques très variées : magnétisme, supraconductivité, domaine de l'électronique de spin, oxydes de métaux de transition et fermions lourds, mais aussi géophysique, chimie et science des matériaux en général. SOLEIL se dote d'un outil de pointe pour répondre à des questions posées tant en physique fondamentale que pour la définition de systèmes optimisés pour des applications ciblées. La ligne de Diffusion X inélastique et spectroscopie d'électrons en haute énergie de SOLEIL, sera le complément indispensable de l'ESRF pour les communautés scientifiques françaises et européennes.