EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Long Term Project Report : Interim/Final

Summary Page

Proposal Number: HC886

Updated on 11/10/2016

1. Beamtime Used

Please give a short summary of progress for each scheduling period for which beamtime has been allocated/used :

Scheduling period	Beamline(s) Used	Shifts Used	Summary of results obtained
2014 /II	-	-	RIXS end station at ID32 not yet available
2015 /I	ID32	24	High resolution mapping of spin wave dispersion in 2 AF cuprates. Preliminary data on paramagnon/phonon/CDW interplay in Bi2201.
2015 /II	ID32	18	3D mapping of spin-wave dispersion in 3 AF cuprates. First measurement of electron-phonon coupling in 3 AF cuprates with 35 meV resolution.
2016 /I	ID32	18	Fully polarized study of charge and magnetic excitations in NBCO. First measurement of the superconducting gap opening in Bi2223

2. Resources Provided by User team (financial, personnel, technical...):

- **CCD detector** Roper/Princeton Instruments PIXIS 2048B (2048x2048 pixels, 13.5 micron pixel size, LN2 cooled), value 80 ~kEur.
- **11 month of PhD student**, Greta Dellea, permanently at ESRF during installation and commissioning of ERIXS spectrometer from Sept 2014 to July 2015 included.
- **2 senior scientists**: Giacomo Ghiringhelli leading the design of the ERIXS spectrometer (full optical design, specs for mechanics, sample environment, vacuum); Lucio Braicovich leading the design of the polarimeter (full optical design, mechanical specs). Both have participated to the commissioning of the spectrometer in February, April, May, July, November 2015.
- **Development single photon counting algorithm for improved spatial resolution**: this method has been developed in Milano starting in 2013, refining it with experimental tests based on a traditional x-ray source and on Montecarlo simulations. It has allowed ERIXS reaching the final target resolution (combined instrumental BW ~30 meV at 930 eV with the high resolution grating) within the first 6 month of operations. This algorithm is significant because it does not require a special hardware as it is applied to the usual CCD detectors.

- **Design and commissioning of polarimeter**: the graded multilayer used as flat response polarimeter in ERIXS is a unique feature, allowing fully polarization resolved RIXS experiments with high energy resolution. The design was conceived by L. Braicovich with G. Ghiringhelli of the users team and N.B. Brookes, C. Morawe, F. Cianciosi and F. Yakhou of the ESRF. In the second year of the LTP our work is being focused particularly on the commissioning and first use of the polarimeter.

3. **Technical and Scientific Milestones Achieved** (in relation to the milestones identified in the original proposal)**:**

Year 1

In the proposal we had foreseen the following milestones:

1) Advanced commissioning for very high resolution: optimization of the performances at the Cu L_3 edge, RIXS spectra of undoped cuprates without the polarimeter in the traditional fixed scattering angle mode. Test measurements at Ti, O, Mn, Ni and Cu in simple oxides to detect dd and magnetic excitations with ultra-high resolution.

2) First use of continuous scattering angle scan: on the same cuprate samples elastic scattering from CDW can be studied with unprecedented accuracy.

Thanks to the close and efficient collaboration between the beam line scientific and technical staff and our team we have fully achieved these goals. Already in July 2015 ERIXS with the mid-resolution grating was used for a systematic study of the in-plane dispersion of spin-waves in the antiferromagnetic layered cuprates $CaCuO_2$ and $NdBa_2Cu_3O_{6.1}$, with the unprecedented **energy resolution of 55 mV at the Cu L_3 edge**, i.e. 2.5 times better than at the best competitor facility (ADRESS at SLS-PSI). With the same resolution, the study of the interplay between charge density waves, magnetic excitations and phonons could be started in underdoped and optimally doped Bi2201.

In November 2015 the spin-wave study was completed, adding the dependence on the out-of-plane direction thanks to the continuous scanning of the scattering angle, and a third sample was added (AF Bi2201). The newly installed high resolution grating in ERIXS allowed also the collection of some spectra at 31-35 meV resolution on the same three AF compounds. These spectra have opened the opportunity of studying the electron-phonon interaction in cuprates. Finally we could make the very first measurement of magnetic excitations in $NdNiO_3$ thin films grown in MPI Stuttgart.

Year 2

In the proposal we had foreseen the following milestones:

3) Fully polarized RIXS experiment: First real measurements made with the polarimeter on superconducting cuprates.

4) Selected experiments with high resolution at edges other than Cu L_3: Based on the results obtained in the first overview of the performances (resolution, count rate) at Ti, O, Mn, Co, Ni, Ce, Tb, Gd edges, 2 or 3 significant experiments on interesting samples will be selected.

The polarimeter has been commissioned very quickly at the Cu L_3 edge, because the pre-alignment was almost perfect and all the needed degrees of freedom were available. As a consequence it has been used by the beam line staff also at the Ce M_5 edge in a very immediate way. We could thus spend a large fraction of the 3rd beam time (6 days in April 2016) in a real experiment using the polarimeter on NBCO samples. Another consequence is that the polarimeter has been made available to all users from the proposal call of September 2016.

Year 3
THIS LTP SPANS OVER 2 YEARS ONLY

4. List of publications directly resulting from beamtime used for this Long Term Project:

YY Peng, G. Dellea, M. Minola, M. Conni, A. Amorese, D. Di Castro, G.M. De Luca, K. Kummer, M. Salluzzo, X. Sun, X. J. Zhou, G. Balestrino, M. Le Tacon, B. Keimer, N.B. Brookes, L. Braicovich, and G. Ghiringhelli, "Influence of apical oxygen on the extent of in-plane exchange interaction in cuprate superconductors" submitted to Nature Physics and **arXiv:1609.05405**.

L. Braicovich, J. van den Brink, G. Dellea, YY. Peng, M. Minola, M. Conni, A. Amorese, D. Di Castro, G.M. De Luca, K. Kummer, M. Salluzzo, N.B. Brookes, and G. Ghiringhelli, "Symmetry effects on k resolved electron-phonon interaction in antiferromagnetic cuprates: a direct insight", in preparation.

YY Peng, G. Ghiringhelli, M. Minola, M. Salluzzo, X. Sun, X. J. Zhou, N.B. Brookes, L. Braicovich, et al, "Disentangling charge and spin excitation spectra in hole doped cuprates", in preparation

REPORT

First RIXS at ID32 and flash-commissioning (April-May 2015)

Our experiment in July 2015 has been the very first RIXS experiment at the new ID32, coming after only few weeks of commissioning realized in April and May by the beam line staff and the Milano group of this LTP. The very first RIXS spectrum has been obtained on 25/4/2015. In the following days the optical performances (monochromator resolution, refocusing on the sample, spectrometer resolution) have been quickly optimized thanks to the excellent work done by the ESRF staff during the beam line pre-commissioning and in the installation and pre-alignment of the ERIXS spectrometer. Therefore the target energy resolution at Cu L_3 (930 eV) and intensity (with the 3 undulators phased together) have been reached already in the second day of this run in July. This is an exceptional achievement for such a complicated instrument. Even more remarkable if one considers that the liquid He sample cold finger had been tested only 3 days earlier and the new 2.5 m long undulator had been installed at the beginning of June. Finally a decisive contribution has come from the implementation of a single photon counting mode in the Princeton CCD detector (property of the Milano group), an algorithm developed and tested in the preceding year in Milano. In this way the 55 meV combined resolution at Cu L_3, reached with the low resolution gratings of both spectrometer and monochromator, has immediately set a new standard in the field of high resolution RIXS, being more than 2 times better than the ADRESS instrumentation at the SLS. And this energy resolution is obtained with comparable count rate! During the April-May commissioning we measured some spectra at room T, as the sample cooling was not available. Therefore we chose very robust samples like the Gd-Ga garnet, NiO and MnO. The intensity was still not optimized, also because the new 2.5 m undulator was not in place yet.

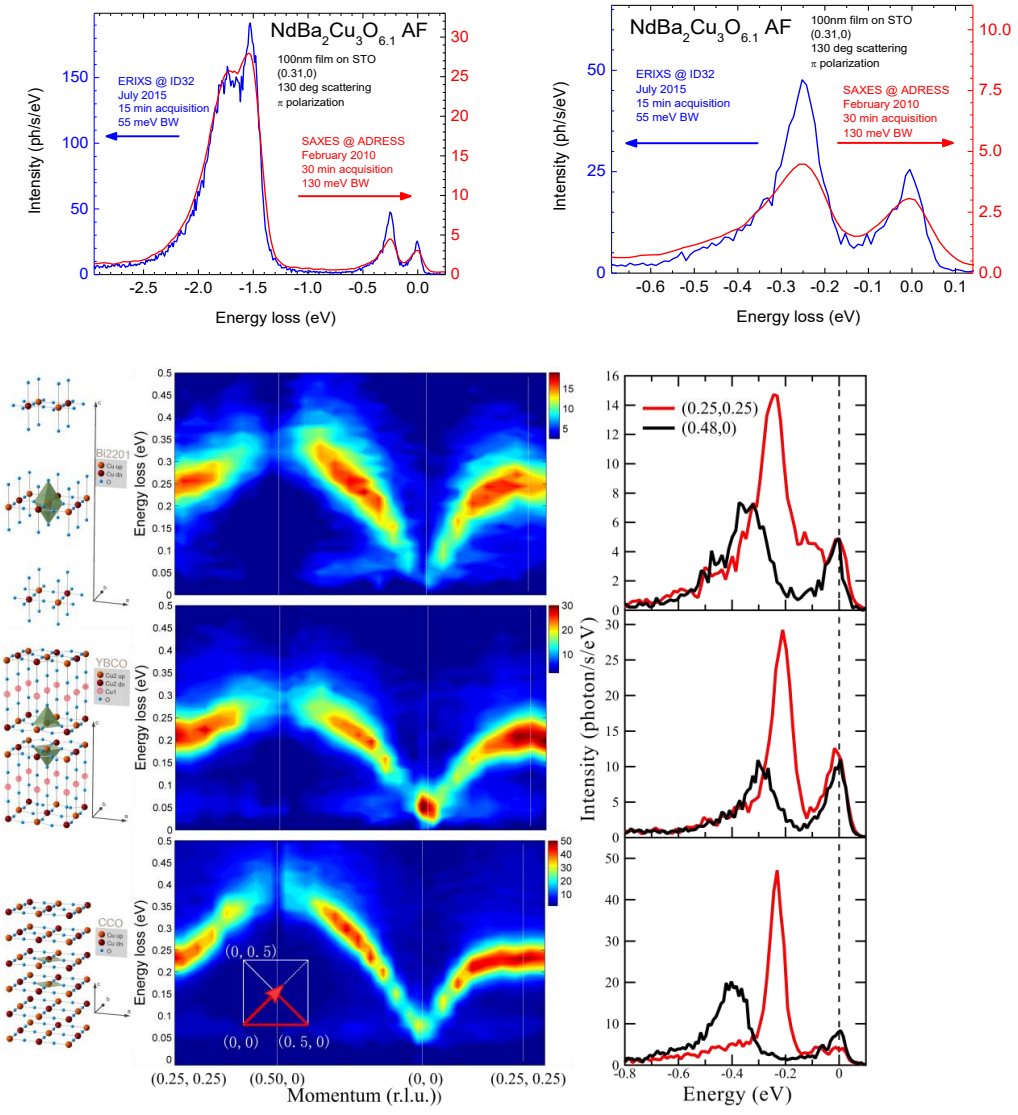
Magnetic excitations in AF cuprates (July and November 2015)

As declared in the proposal, the first milestone was the advanced commissioning of ERIXS to make it reaching the target performances in the mid-resolution - high throughput configuration. We have fully accomplished this task at Cu L_3, whereas in the preceding commissioning significant test measurements had been made at other edges as explained above: Ni L_3, Mn L_3, Ti L_3, Ce M_5, Eu M_5, Gd M_5.

The total instrumental band-width of 55 meV at 931 eV (resolving power = 17000) has been obtained with 15 micron exit and entrance slit on the monochromator, 4 micron spot size on the sample, the 800 lines mm^{-1} grating of the monochromator, the 1400 lines mm^{-1} grating of the spectrometer, and the single photon detection mode in the Princeton 2048×2048 13.5 micron pixel detector, cooled at -110°C by liquid nitrogen. The samples were cooled at ~35 K, and were mounted on the 6 axis in-vacuum Huber diffractometer/manipulator. The instrumental BW was measured as FWHM of the non-resonant diffuse scattering from a piece of polycrystalline graphite tape.

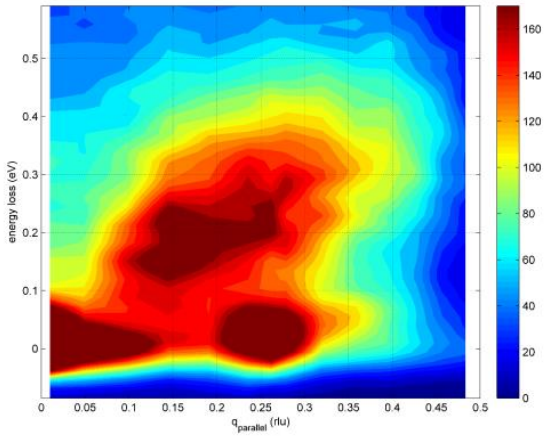
We started from antiferromagnetic layered cuprates, whose RIXS spectra are characterized by sharp *dd* excitations and resolution limited spin-wave excitations whose dispersion in momentum space ranges from zero to 350 meV. The $NdBa_2Cu_3O_{6.1}$ (NBCO) is the parent compound of an YBCO-like high Tc superconductor. The superior quality of the spectra is immediately visible in the example of the figures in the next page that compares ERIXS results in red with the state of the art spectra measured at with SAXES at the ADDRESS beam line of the SLS: the magnon at 0.25 eV is sharper and next to the

elastic peak the phonon peak becomes immediately visible around 60 meV. Moreover the intensity is clearly higher in ERIXS than in SAXES, as expected from the design. The resolution has allowed the first observation by RIXS of the magnon gapped branch near Γ of this bilayer compound, where a non-negligible interlayer magnetic coupling is present. The fitting of the data according to the model used in PRB 54 6905 (1996) leads to an estimate of the in-plane $J_{//}$ = 125 meV and interlayer $J_{\perp}$ = 7 meV super-exchange constants. Similar measurements have been carried on the infinite layer $CaCuO_2$, where a fully 3D AF order develops, as demonstrated by the fact that we could measure a dispersion of the magnetic excitations not only in the CuO_2 planes, but also perpendicularly to them. The latter measurements were made possible for the first time, as they exploited the possibility of changing in a continuous way the scattering angle. We could also measure, for the first time, the dispersion of the magnon excitations along diagonal direction and the AF Brillouin zone boundary simultaneously thanks to the azimuthal rotation available on the manipulator. Finally we measured the spin-wave dispersion also on the very underdoped (p = 0.03) single-layer Bi2201. This impressive set of data is totally original and could have been obtained neither by RIXS elsewhere nor by inelastic neutron scattering. A summary of the data is shown in the figure below.



Preliminary measurements on superconducting cuprates (July 2015)

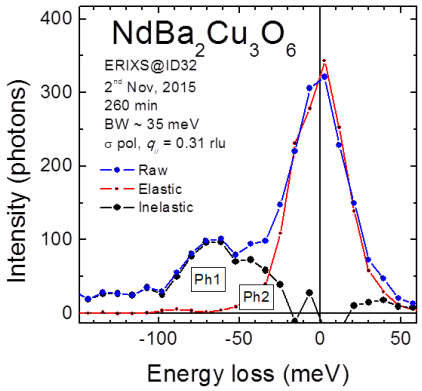
We used part of the beam time to take partial sets of data on underdoped and optimally doped YBCO and single layer Bi2201. These results provide information on the counting time, spectral quality and reproducibility that will serve for future runs of this LTP and other standard proposals on specific scientific cases on doped cuprates. That type of experiments requires systematic measurements, where parameters such as temperature and doping are varied in order to gain valuable information on the physics of high-T_c superconductors. In fact the magnetic excitation features of doped cuprates are **not** resolution limited and only phonons sharpen up visibly when improving energy resolution. Therefore the superiority of ERIXS over the competing instruments in this field is in the simultaneous availability of very high energy resolution, of precise and complete sample manipulation and of continuously variable scattering angle. In the figure below we show some false-color maps of Bi2201 (cleaved in vacuum), measured with π polarization at 35 K. The goniometer guarantees that the beam does not move on the sample surface when the angle of incidence is scanned to change the in-plane momentum transfer: the resulting dispersion maps are of higher quality and the charge density wave peaks can be detected very directly around 0.26 r.l.u. in underdoped Bi2201.

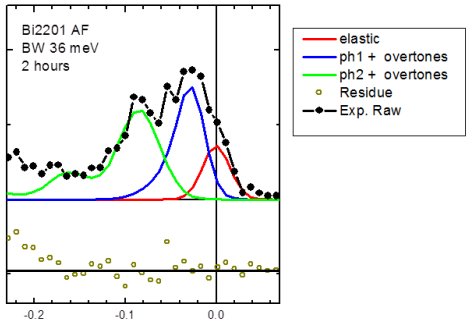


Very high resolution Cu L_3 RIXS and phonons (November 2015)

The 2400 lines/mm grating for highest resolution measurements was installed in ERIXS in October and in November it could be used, immediately reaching the target performances. At the bginning of November L. Braicovich and G. Ghiringhelli contributed to the commissioning of the new grating so that it could be ready for the LTP run one week later. In the same days we started also the commissioning of the polarimeter: the first results are very encouraging, but more work is needed to reach full operations. In the LTP run from 10 to 17 th November, at the cost of a factor 10 in count rate, it was thus possible to measure RIXS at the Cu L_3 edge down to 31 meV BW, a new world record. We exploited this new opportunity to study the intensity of phonon peaks in the CCO, NBCO and Bi2201 AF compounds already mentioned above. The data allowed us disentangling different modes in NBCO, where the large buckling of the CuO_2 planes enables the observation of out-of-plane modes in addition to the most common (in RIXS) breathing modes. Together with the intensity evolution of the phonon peak measured at medium resolution, this allows a direct mapping of the electron-phonon interaction in cuprates, a key information for the determination of the actual role of phonons in superconducting pair coupling. In the figure below we show some examples of these

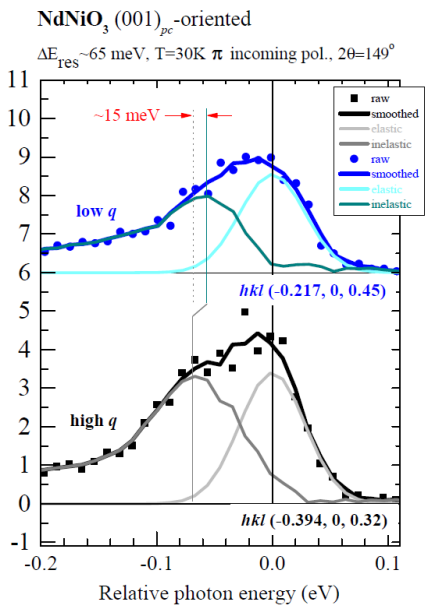
data. A manuscript on these results is in preparation in collaboration with J van den Brink for the theory..

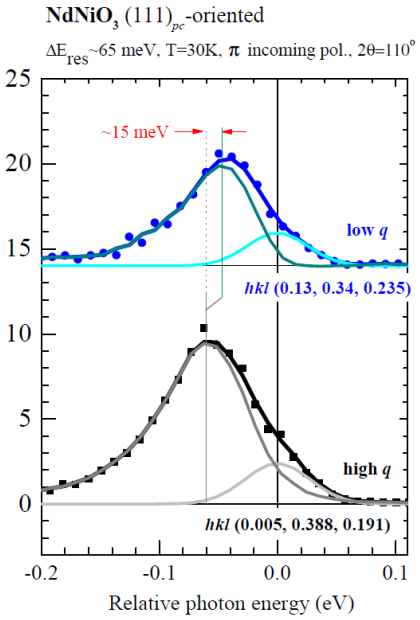




Exploration of magnetic excitations in $NdNiO_3$ (November 2015)

Using the mid- resolution set-up we briefly explored the possibility of measuring spin excitations in rare-earth nickelates (*RE*NiO_3). These compounds show interesting magnetic and electronic properties that can be tailored by strain and spatial confinement when the samples are grown with epitaxial techniques. However the mere observation of spin excitations had never been made before, because neutron scattering cannot deal with such small samples and RIXS had insufficient energy resolution. In a few hours we could unequivocally detect a dispersing magnetic excitation peak around 40-60 meV in thin films of $NdNiO_3$: this will serve to design future experiments on these samples.

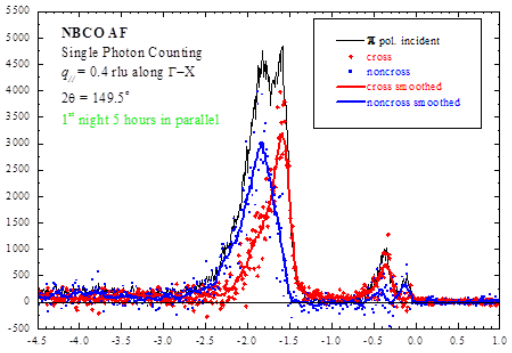


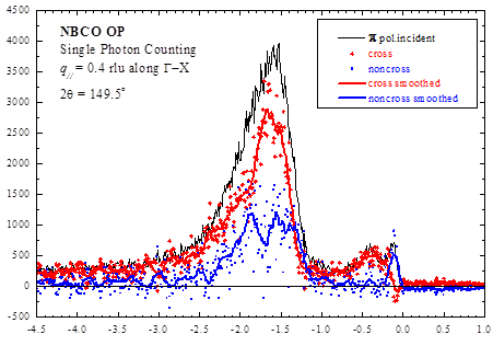


Fully polarized RIXS of doped NBCO (April 2016)

Using the mid- resolution set-up and the polarimeter we measured the Cu L_3 RIXS spectra of undoped, underdoped and optimally doped NBCO, in order to definitively resolve the spin and charge contributions in the mid-IR energy range. We used two in plane **q** vectors along the (10) direction, one close to Brillouin zone boundary (0.4 rlu) where the incident polarization is expected

to act as main selector between crossed and non-crossed scattering events (π_{in} mainly crossed, σ_{in} mainly non-crossed); and another one mid-way to the Γ point, $q_{//}$=0.2 rlu, where the situation is much more mixed. The first ne is useful as a cross check using the AF compound, to see if the polarimeter woks properly. The other cases are all scientifically interesting: they can be used to measure how much the charge excitation continuum in the SC compounds has spin flip character, at different **q** values. Here we provide two examples, showing that the instrumentation works well and that systematic data can be now acquired with it. The data analysis has not been completed yet, but we envisage preparing a publication in the forthcoming months.





First evidence in RIXS of SC gap opening in Bi2223 (April 2016)

Using the mid-resolution set-up and the polarimeter we measured the Cu L_3 RIXS spectra of the tri-layer compound Bi2223, having a SC gap of about 20 meV and a pseudogap twice as large. Lindhard susceptibility calculations had predicted RIXS to be sensitive to the superconducting gap opening, particularly at relatively small **q** values along the (10) direction. Based on these calculations we took spectra at various T across Tc (110 K, nominally) and T* (pseudogap opening T). Indeed the RIXS spectra change in a way similar to what is predicted by calculations (see figure) despite the complication of having two different Tc for the internal and interface CuO2 layers in this material. Moreover the sample was not optimum, as shown by the broad resistivity vs T diagram. Nevertheless this is an exceptional achievement, opening the opportunity of studying the SC gap with x-rays, an option particularly welcome for samples not suited for surface sensitive techniques like STM and ARPES.