

**Experiment title:**

The origin of magnetism in a supposedly nonmagnetic osmium oxide

Experiment number:

HC-4277

Beamline:	Date of experiment: from:19/01/2021 to:26/01/2021	Date of report: 23/02/2021
Shifts:	Local contact(s): Christoph Sahle	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

Marco Moretti and Giacomo Ghiringhelli, Politecnico di Milano

Cesare Franchini, Samuele Sanna and Federico Boscherini, Università di Bologna

Francesco Borgatti, CNR – Unità di Bologna

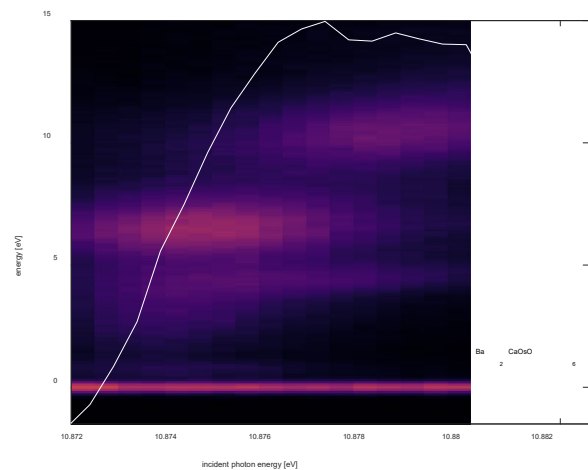
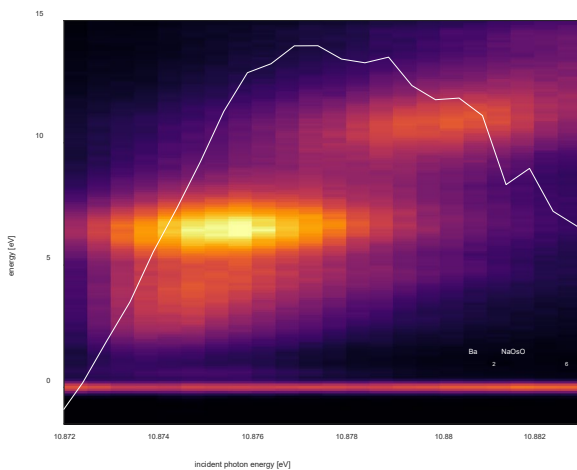
Report:

We measured RIXS spectra of $\text{Ba}_2\text{Na}_{1-x}\text{Ca}_x\text{OsO}_6$ ($x = 0.0, 0.5$ and 1.0) at the Os L3 (~ 10.870 eV) edge with the following setup:

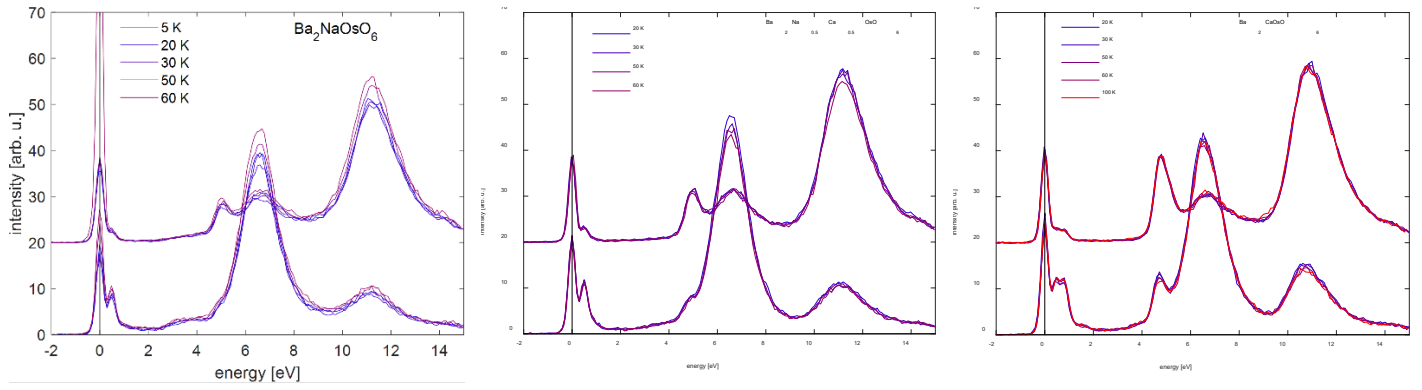
- spectrometer : R = 1 m diced spherical Si(664) analyzer;
- beamline :
 - medium resolution (330 meV) : Si(111) mono + Si(311) channel-cut
 - “high” resolution (120 meV) : Si(111) mono + Si(664) back-scattering

The beam size was increased to 220 (H) x 50 (V) mm² for a better powder average over the various grain orientations (a bad powder average initially resulted in an unrealistic temperature dependence of the RIXS spectra).

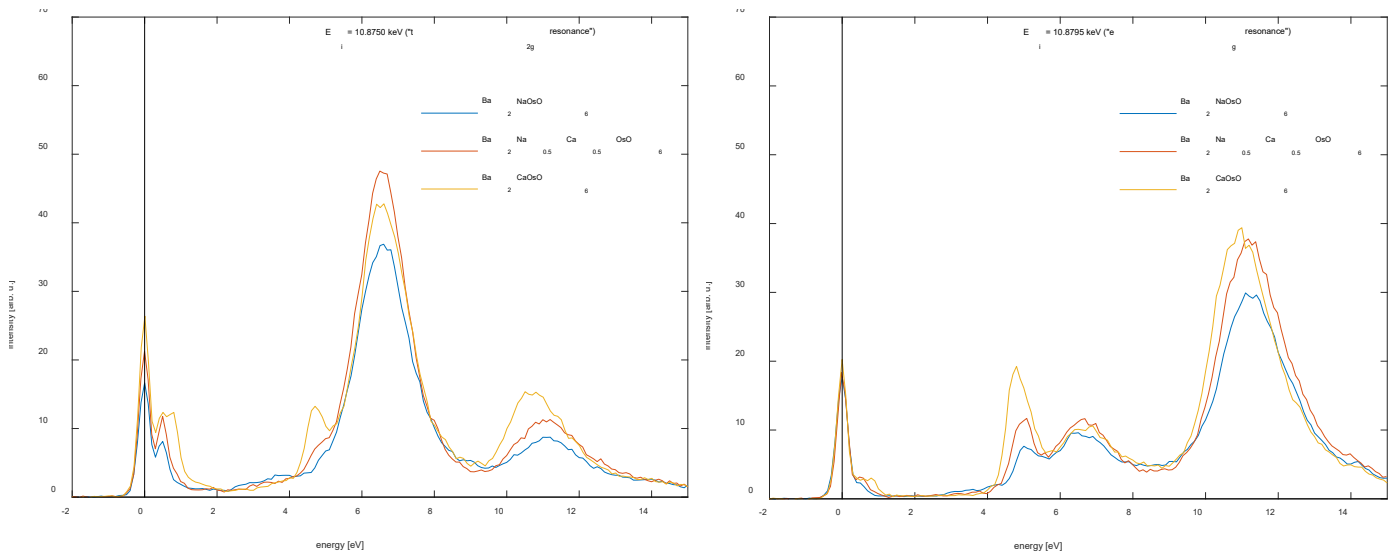
Initially, we measured RIXS maps on the two extreme compositions over a wide energy loss range in order to identify the main features and their resonance behaviour. The RIXS maps show various excitations with Raman (constant energy loss, as opposed to fluorescence) character up to 12 eV energy loss. These are likely d-d (or crystal field) excitations.



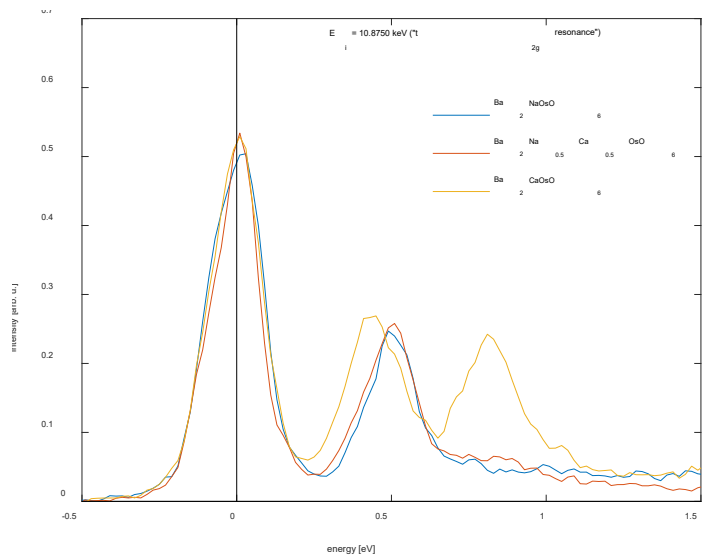
Cuts at two incident photon energies are shown below, together with their temperature (in)dependence:



We note distinct peaks at approximately 5, 7 and 11 eV, whose intensity and exact position is sample-dependent, as shown below. Their temperature dependence, if any, is small. It seems that the 5 and 11 eV features grow with Ca content, and possibly shift to lower energies. A broad feature around 3.5 eV possibly displays the opposite trend. Also, Ba₂CaOsO₆ shows extra intensity at low energy, see below.



Low-energy excitations are also visible below 1 eV. In order to investigate these, we then switched to the “high” resolution setup in the right figure. We note that the spectra of Ba₂NaOsO₆ and BaNa_{0.5}Ca_{0.5}OsO₆, on one side, and BaCaOsO₆, on the other side, are qualitatively different: BaCaOsO₆ shows a double peak structure (also visible in the medium resolution data), absent in the other two compounds.



Ba₂NaCaOsO₆ is nominally 5d¹ with a “trivial” multiplet structure, so:

- the excitation at ~ 0.5 eV might correspond to $j_{\text{eff}}=3/2$ -to- $j_{\text{eff}}=1/2$ transitions. For a single-ion model, the spin-orbit coupling constant can be extracted from $3\lambda/2 = 0.5$ eV, that is $\lambda = 0.33$ eV;
- the presence of a narrow peak suggests that the local symmetry of the Os ion is close to cubic because a lower symmetry (e.g., tetragonal) would lift the degeneracy of the $j_{\text{eff}}=3/2$ states.

Ba₂CaOsO₆ is, instead, nominally 5d² and features a less trivial multiplet structure. It is then reasonable that its RIXS spectrum is qualitatively different from that of Ba₂NaOsO₆, but it surprises that the change does not seem monotonous, but abruptly occurs between 50% and 100% Ca content. Instead, in *J. Phys. Chem. C* 2020, 124, 16577–16585 it is stated that “XANES measurements show a smooth decrease of the oxidation state of Os from 7+ (5d¹) to 6+ (5d²) with increasing Ca concentration”, therefore calling for further investigations.

Unfortunately, we could neither measure the intermediate compositions (25% and 75% doping) nor make a full temperature dependence at “high” resolution because of the lack of time. Indeed, the measurements started with almost two days of delay because of unexpected hardware and software problems. Moreover, initial measurements were affected by experimental artifacts due to a bad “powder average” and we spent some time to optimize the experimental setup in order to mitigate these effects. But since the data in our hands are particularly promising, we will resubmit the proposal and ask for beamtime from completion of the work.