



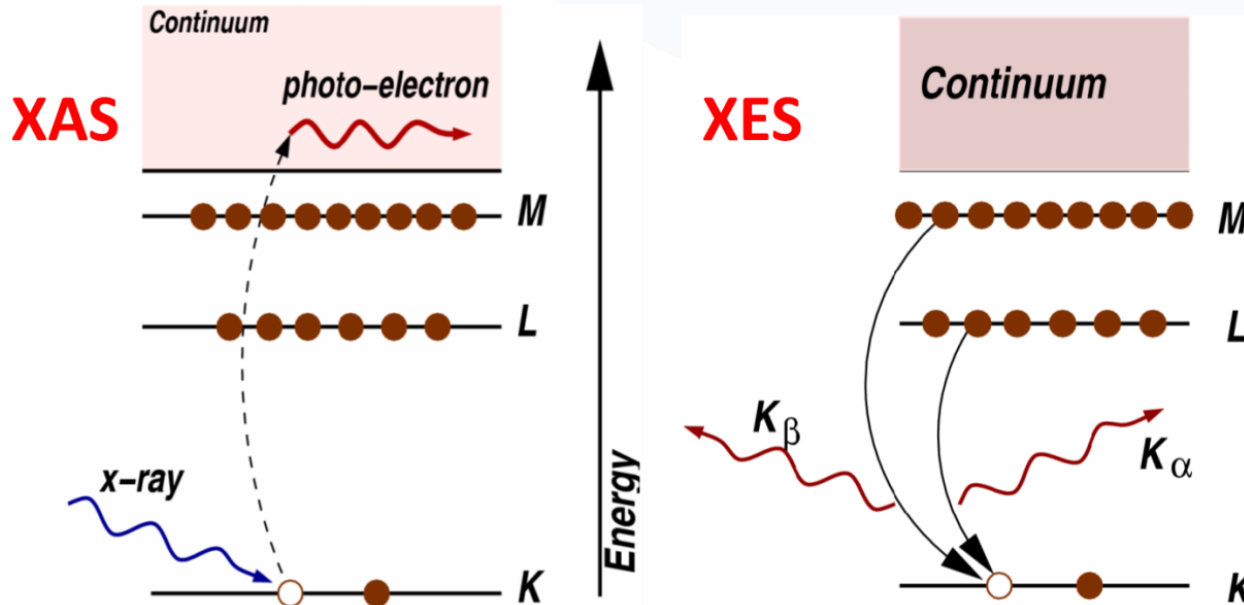
**ALBA-ICMAB
workshop, Alba
synchrotron
February 24th 2020**

Structure and speciation with Hard X-ray spectroscopy in heterogeneous materials (including operando and in-situ)

Laura Simonelli
CLÆSS beamline responsible

BL22 – CLÆSS

Core Level Absorption & Emission Spectroscopies



COMPLEMENTARY INFORMATION

BL22 – CLÆSS



Core Level Absorption & Emission Spectroscopies



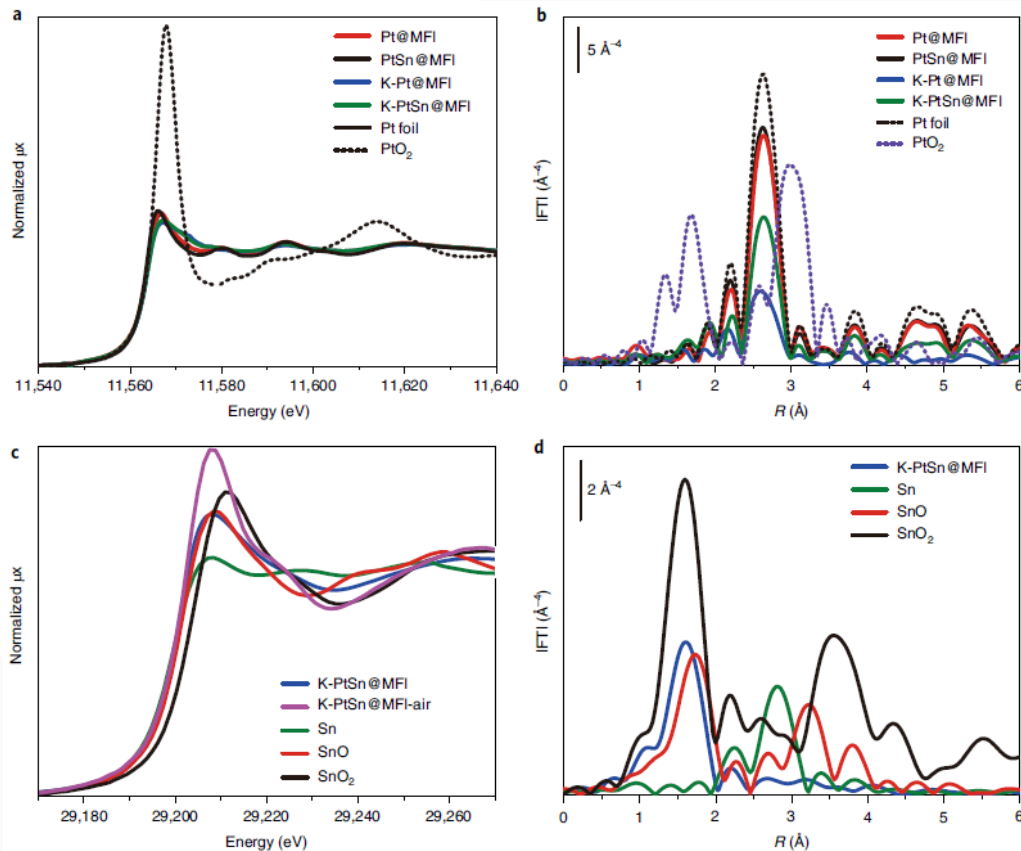
XAS and XES are element sensitive local probe that can be applied to any kind of materials



- Speciation of individual or coexisting phases
- Local structural properties
- Local electronic properties

COMPLEMENTARY INFORMATION

Hard X-rays → in-situ / operando



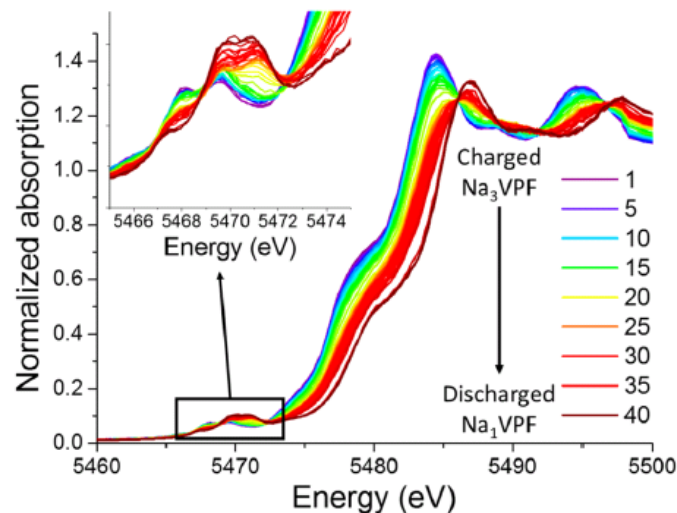
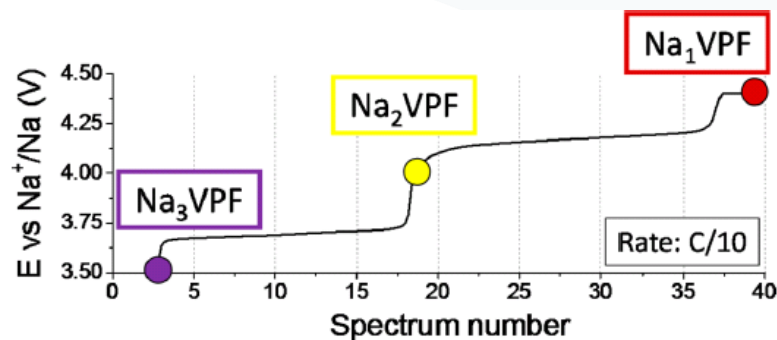
“Regioselective generation and reactivity control of subnanometric platinum clusters in zeolites for high-temperature catalysis”

Lichen Liu, Miguel Lopez-Haro, Christian W. Lopes, Chengeng Li, Patricia Concepcion, Laura Simonelli, Jose J. Calvino and Avelino Corma

Nature Materials 18, 866–873 (2019)

Subnanometric clusters size and speciation by XAS

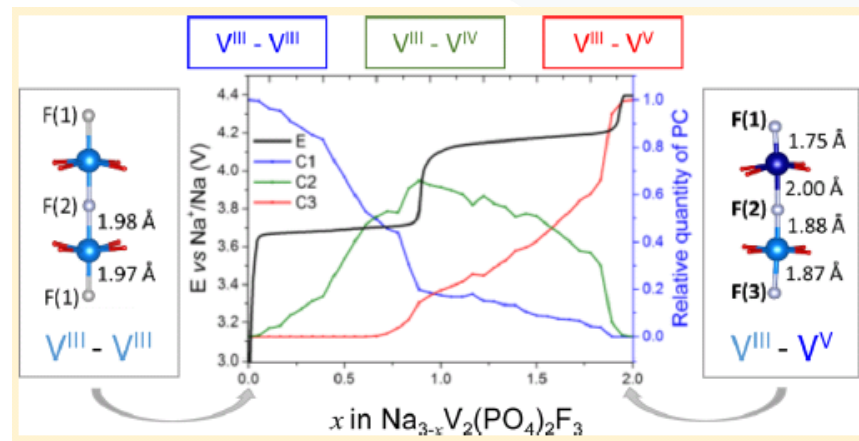
Hard X-rays → in-situ / operando



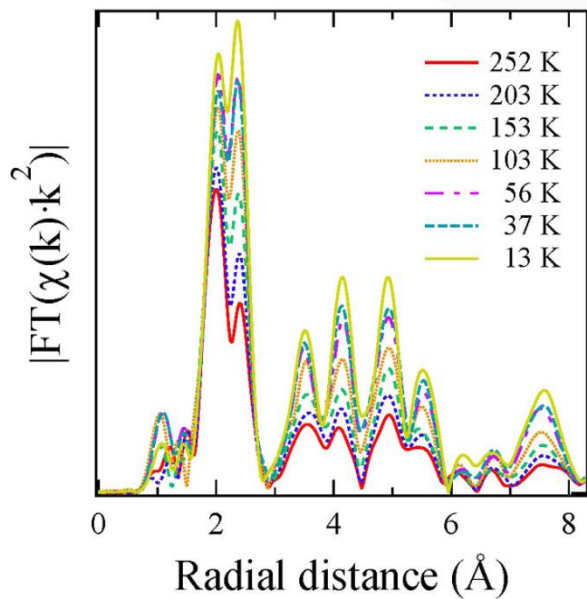
“VIV Disproportionation Upon Sodium Extraction From $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ Observed by Operando X-ray Absorption Spectroscopy and Solid-State NMR”

Thibault Broux, Tahya Bamine, Laura Simonelli, Lorenzo Stievano, François Fauth, Michel Ménétrier, Dany Carlier, Christian Masquelier and Laurence Croguennec, J. Phys. Chem. C 2017, 121, 4103–4111

Speciation along charge by PCA

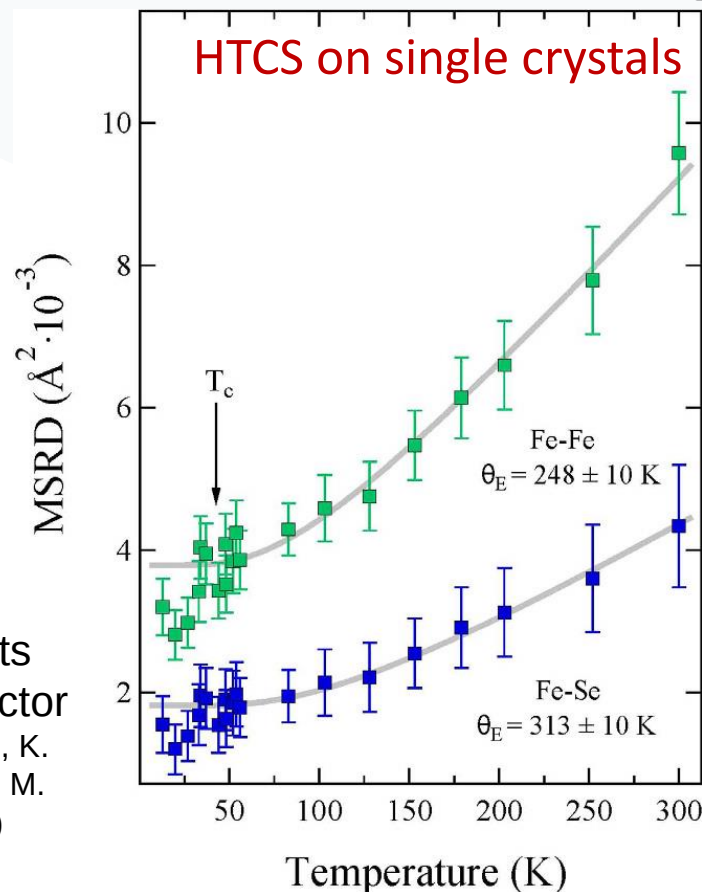


EXAFS(T) $\rightarrow$ dynamics



Temperature dependent local atomic displacements in ammonia intercalated iron selenide superconductor

E. Paris, L. Simonelli, T. Wakita, C. Marini, J.-H. Lee, W. Olszewski, K. Terashima, T. Kakuto, N. Nishimoto, T. Kimura, K. Kudo, T. Kambe, M. Nohara, T. Yokoya & N. L. Saini, Scientific Reports 6, 27646 (2016)



Ferro- and antiferroelectric properties on 20nm thin films

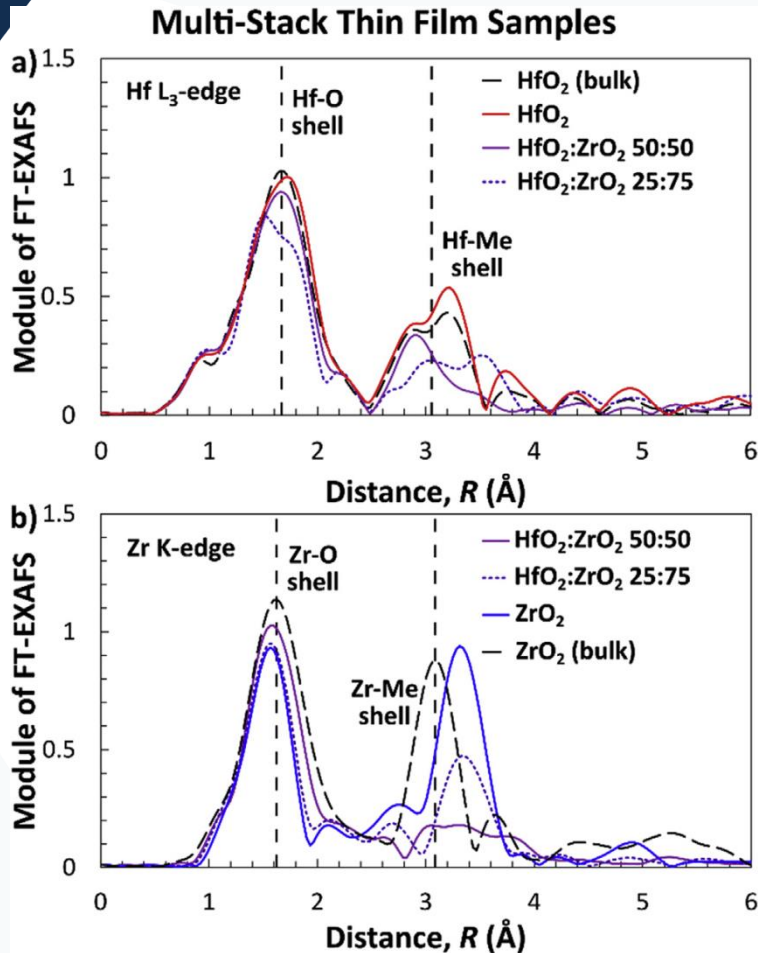


EXAFS → second coordination shell to discriminate different polymorphs.

Local structural investigation of hafnia-zirconia polymorphs in powders and thin films by X-ray absorption spectroscopy

Tony Schenk, Andris Anspoks, Inga Jonane, Reinis Ignatans, Brienne S. Johnson, Jacob L. Jones, Massimo Tallarida, Carlo Marini, Laura Simonelli, Philipp H€onicke, Claudia Richter, Thomas Mikolajick, Uwe Schroeder

Acta Materialia 180 (2019) 158e169



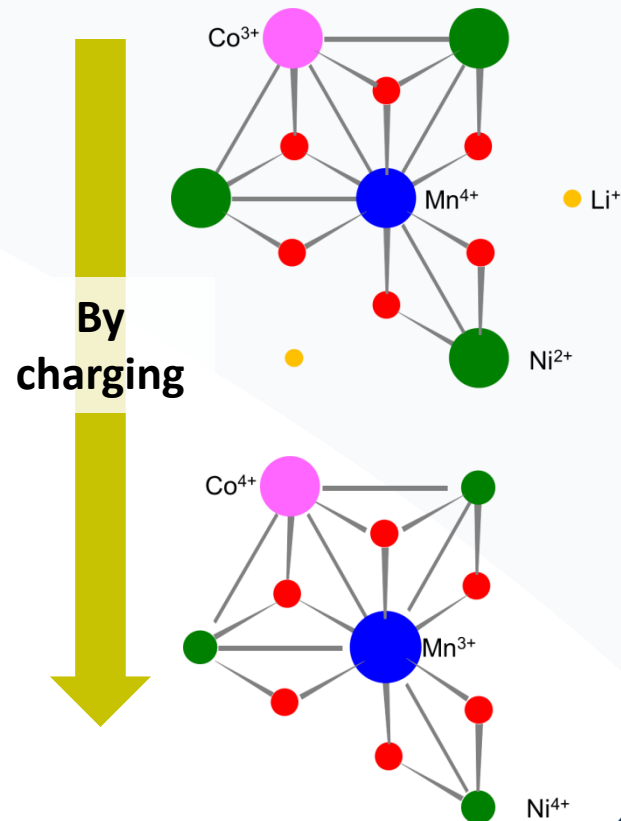
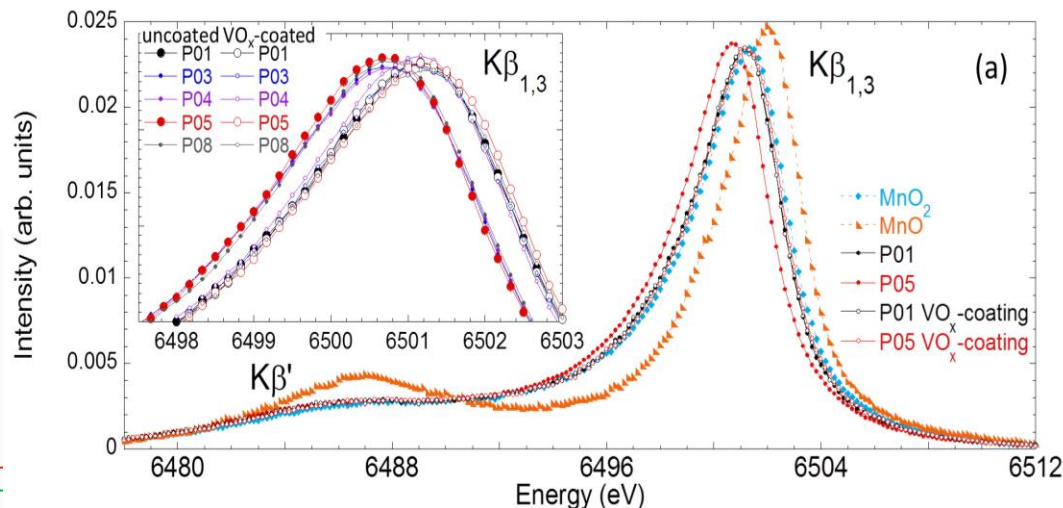
XES complementary to XAS

Role of Manganese in Lithium- and Manganese-Rich Layered Oxides Cathodes

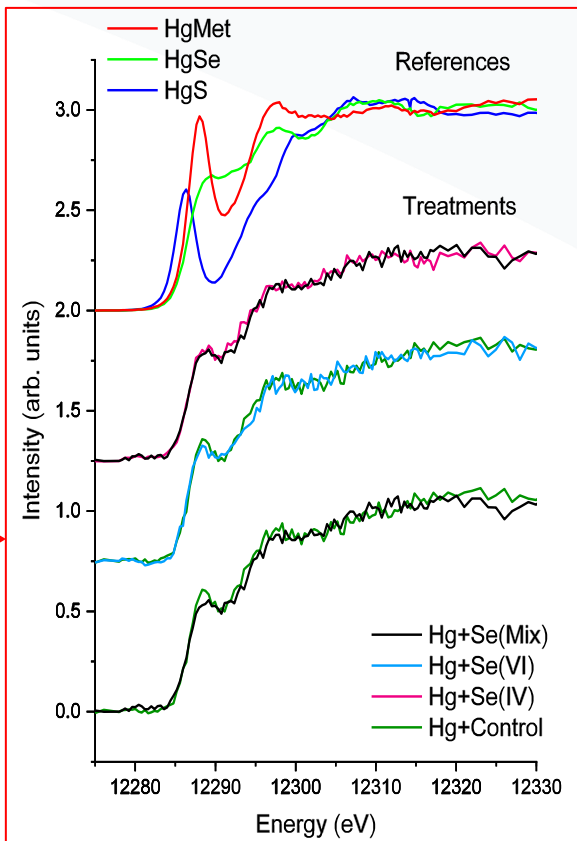
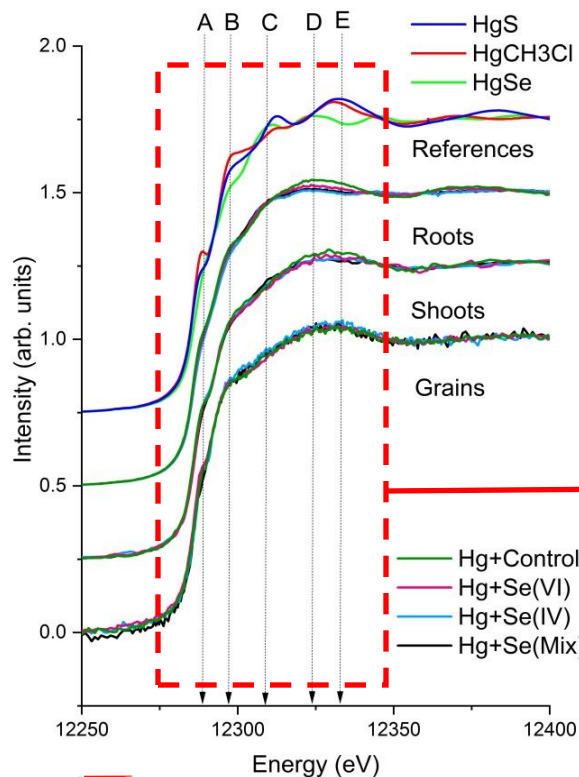
L. Simonelli, A. Sorrentino, C. Marini, N. Ramanan, D. Heinis, W. Olszewski, A. Mullaliu, A. Birrozzi, N. Laszczynski, M. Giorgetti, S. Passerini, D. Tonti

J. Phys. Chem. Lett. 2019, 10, 12, 3359-3368

TM size depending on both oxidation and spin state



HR XANES



Mercury speciation in Selenium enriched wheat plants grown in Hg contaminated environment

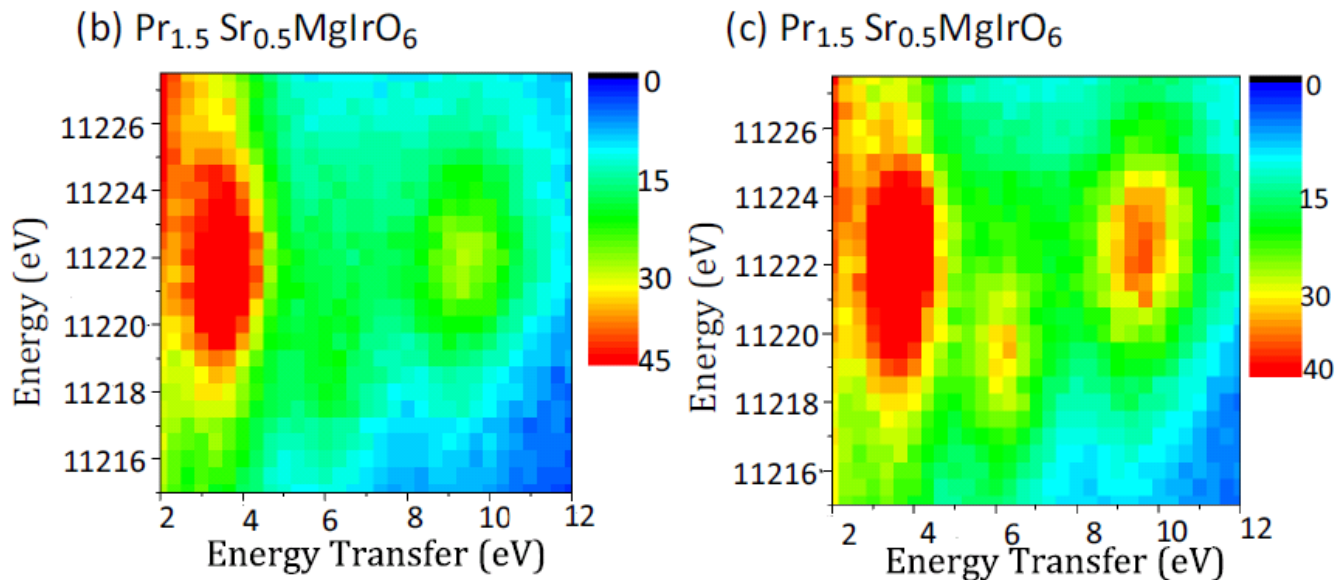
N. Manivannan, R. Boada, M. A. Subirana, C. Marini, M. Llugany, M. Valiente, L. Simonelli

In preparation

HR XANES accessible also in diluted systems (few hundreds of ppm)

Local electronic structure

L_3 -edge RIXS easily accessible



Evolution of electronic and magnetic properties in a series of iridate double perovskites
 $\text{Pr}_{2-x}\text{Sr}_x\text{MgIrO}_6$ ($x=0, 0.5, 1.0$)

A. Bandyopadhyay, I. Carlomagno, L. Simonelli, M. Moretti Sala, A. Efimenko, C. Meneghini, and S. Ray

PRB 100, 064416 (2019)

Absorption energy range

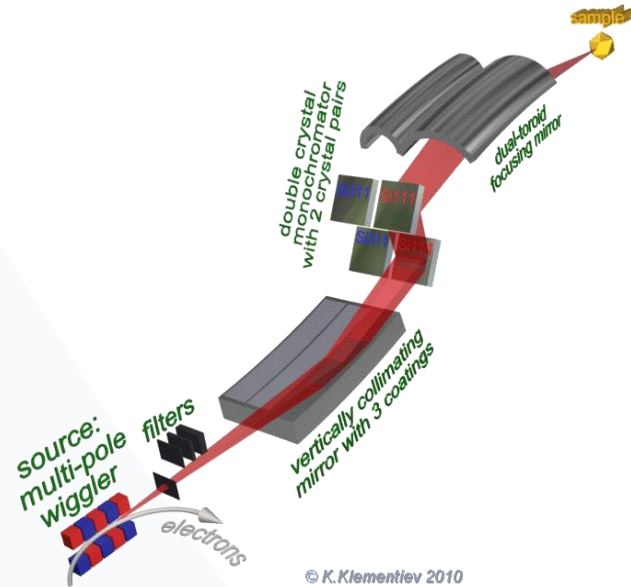
(2.4 – 63 KeV)

Emission energy range

(6.2 – 22 KeV)

Beam size

From 200x100 mm² (HxV) to 8x1 mm (HxV)



hydrogen 1 H 1.0079	beryllium 4 Be 9.0122
lithium 3 Li 6.941	magnesium 12 Mg 24.305
sodium 11 Na 22.990	calcium 20 Ca 40.078
potassium 19 K 39.098	strontium 38 Sr 87.62
rubidium 37 Rb 85.468	barium 56 Ba 137.33
cesium 55 Cs 132.91	francium 87 Fr [223]

k-edges
L-edges

boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]

scandium 21 Sc 44.956	titanium 22 Ti 47.887	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
ytrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	bohrium 105 Bh [262]	seaborgium 106 Sg [266]	meitnerium 107 Mt [268]	hassium 108 Hs [269]	dubnium 109 Db [268]	roentgenium 110 Rg [271]	copernicium 111 Cn [277]	nihonium 112 Nh [277]	flerkovium 114 Fl [289]					

* Lanthanide series

* Actinide series

lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

Scan speed

XAS : 1 (15) min per EXAFS and 30 s (2 min) per XANES scan in transmission (fluorescence) mode.

XES: 15 (45) min per emission line or high resolution XANES. 4-6h per RIXS map.

Sample setups

(XAS in fluorescence and transmission modes and XES)



Dynamic
liquid cells
(RT)

Solid-gas reactor

20-700 °C

up to 10bar

GAS mix unit with 6 lines
gases at 5-50 (10-1000)
ml/min

Mass spectrometer

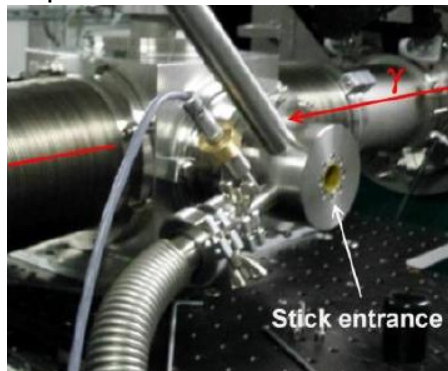


LHe-cryo

5 K – 320 K

Low temperature sample
exchange

Liquid cells



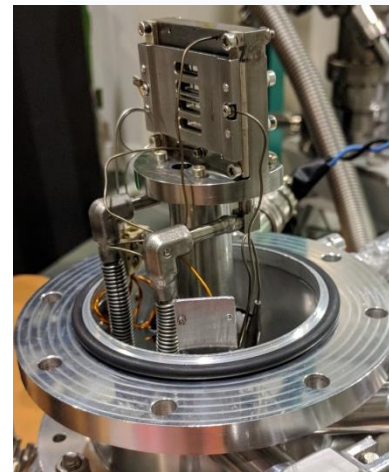
LN₂-cryo/furnace

80-830K

TEY

RT sample exchange

Static liquid cells



THANK YOU FOR YOUR ATTENTION