

W1 X-Ray Absorption Spectroscopy for the Crystallographer Hyderabad, 21 August 2017

# **XAS for Materials Science**

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- Introduction
- XAS milestone: atomic scale structure in solid solutions
- Multiferroics
- Nanomaterials
- Data analysis beyond single scattering
- Energy materials: operando studies





#### • Introduction

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# Material

From Wikipedia, the free encyclopedia (Redirected from Materials)

# **Material** is a broad term for a <u>chemical substance</u> or <u>mixture</u> of substances that constitute a <u>thing</u>.



# Materials science

From Wikipedia, the free encyclopedia

- The <u>interdisciplinary</u> field of **materials science**, also commonly termed **materials science and engineering**, involves the discovery and design of new materials, with an emphasis on <u>solids</u>.
- Materials science is a syncretic discipline hybridizing metallurgy, ceramics, solid-state physics, and chemistry. It is the first example of a new academic discipline emerging by fusion rather than fission.
- Materials scientists emphasize understanding how the history of a material (its *processing*) influences its structure, and thus the material's properties and performance. The understanding of processing-structure-properties relationships is called the <u>materials paradigm</u>.





## XAS and Materials science





# Advantages of XAS for Materials Science

- Atomic selectivity: only the structure around the atomic species chosen via the excited absorption edge is determined.
- **Applicability to ordered or disordered matter**: the fine structure originates from photoelectron scattering within at most 1 nm from the absorbing atom so that long range ordered crystals, highly structurally disordered clusters or intermediate aggregation states can be studied within the same interpretative framework.
- A very high distance resolution (even 0.001Å in the first coordination shell), obtainable from high quality EXAFS data.
- Sensitivity to the local site symmetry and three dimensional atomic arrangement (e.g. whether the selected atom is in a tetrahedral, octahedral or other symmetry site), obtainable from analysis of XANES and /or "pre-edge" spectral features.
- Sensitivity to oxidation state and valence, available in many cases from the energy position of the absorption edge and / or a study of the lineshape of "pre-edge" features.
- Sensitivity to electronic structure, available through an interpretation of the XANES lineshape in terms of the site and symmetry projected local density of unoccupied electronic states.
- Applicability to the study of very dilute atomic species (e.g. dopants and impurities) and extremely thin surface layers, possible thanks to specific experimental detection modes and set-ups.
- **High resolution in measurement of the relative atomic displacements**, which can be used to probe vibrational properties or local disorder effects.
- **Possibility of probing structure along given directions** thanks to the linear polarization of the x-ray beam and the vectorial character of the dipole matrix element.
- Micron or sub-micron lateral spatial resolution, available on specially designed beamlines.
- **Time resolutions** ranging from 100's of ps (storage ring sources) to 10's of fs (new free electron lasers), available on specialized beamlines.
- Last, but not least, a rich and interesting underlying physics

#### F. Boscherini, from Synchrotron Radiation Basics, Methods and Applications, Springer 2015

#### XAS for the Crystallographer

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#### Vegard's law

Linear relation between the crystal lattice parameters of an alloy and the concentration of the constituent elements



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#### Atomic-Scale Structure of Random Solid Solutions: Extended X-Ray-Absorption Fine-Structure Study of Ga<sub>1-x</sub> In<sub>x</sub> As

J. C. Mikkelsen, Jr., and J. B. Boyce Xerox Palo Alto Research Centers, Palo Alto, California 94304 (Received 23 August 1982)

In random solid solutions of  $Ga_{1-x}In_xAs$ , the Ga-As and In-As near-neighbor distances change by only 0.04 Å as x varies from 0.01 to 0.99, despite the fact that this alloy accurately follows Vegard's law, with a change in average near-neighbor spacing of 0.17 Å. This result contradicts the underlying assumption of the virtual-crystal approximation. Nonetheless, the cation sublattice approaches a virtual crystal with a broadened single distribution of second-neighbor distances, whereas the anion sublattice exhibits a bimodal anion-anion second-neighbor distribution.

PACS numbers: 61.55.Hg, 78.70.Dm

## Ga<sub>1-x</sub>In<sub>x</sub>As follows Vegard's law

According to the VCA:

- d<sub>Ga-As</sub>=d<sub>In-As</sub>
- Δd = 0.17 for x varying from 0.01 to 0.99



#### For a given composition

- d<sub>In-As</sub> in the solid solution is closer to d<sub>In-As</sub> in InAs than to the value of the VCA
- $d_{Ga-As}$  in the solid solution is closer to  $d_{Ga-As}$  in GaAs than to the value of the VCA

#### Bond lengths stay close to sum of covalent radii Violation of VCA First evidence of strong local structural disorder







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- Simulteneous electric and magnetic order
- Ferroelectricity and ferromagnetism require two opposite mechanisms:
  - d<sup>0</sup> configuration (FE)
  - d<sup>n</sup> configuration (FM)
- Bismuth ferrite ceramic: 'holy grail' as it is magnetic and ferroelectric at RT ( $T_c \sim 1103 \text{ K}, T_N \sim 643 \text{ K}$ )
- Potential applications: magneto-electric random access memory
- Doping improves the magnetic behaviour



# Undoped BiFeO<sub>3</sub> as a f(T)

# Study across the magnetic transition at the Fe K-edge



•All the parameters show an anomaly at  $T_N$ , The magnetic transition is associated to a local structural modification around Fe (foreseen as the magnetism is associated to the partially filled d states of Fe3+)

 With increasing temperature the Fe-O distribution becomes more gaussian, well before the ferroelectric transition





# Eu<sup>3+</sup> doped BiFeO<sub>3</sub> with varying Eu<sup>3+</sup> content

#### Combined XRD, Mossbauer, XAFS study



- XANES unchanged with increasing Eu doping
- Pre-edge splitting
  - Separation of the t<sub>2g</sub> and e<sub>2g</sub>
  - Symmetrization of the Fe-O distribution

The improvement of the magnetic properties is due to a structural deformation

D. Kothari et al., JPCM 22, 356001 (2010)

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### **Identification on NPs**

#### FeCo alloy NPs embedded on mesoporous silica



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#### Experiment

- Measurements at Spring-8
- HAuCl<sub>4</sub> in toluene with dodecanthiol
- DMF solution of NaBH<sub>4</sub>
- 100 ms time resolution
- After the addition of the reducing agent, reaction monitored for 180 seconds
- 1800 spectra recorded after the start of the reaction. 10 spectra averaged

N. Ohyama et al. (2011) ChemPhysChem 12, 127-131



Evolution before the reducing agent

Normalized absorption / a.u. a) b) C) d) e) f) g) 11880 11900 11920 11940 11960 11980 Energy / eV



Table 1. The fractions of  $Au^{3+}$  and  $Au^{+}$  in the solution with various DT/Au ratios before NaBH<sub>4</sub> reduction. The fractions were evaluated by fitting of the XANES spectra of various DT/Au with linear combination of those of DT/Au = 0 and 16.

DT/Au	0.1	0.4	1	2	4
Au <sup>3+</sup> [%]	90.3	79.0	50.3	0	0
Au <sup>+</sup> [%]	9.7	21.0	49.7	100	100
<i>R</i> factor	0.006	0.004	0.005	0.009	0.007

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N. Ohyama et al. (2011) ChemPhysChem 12, 127-131











#### N. Ohyama et al. (2011) ChemPhysChem 12, 127-131

XAS for the Crystallographer



# Magnetite biomineralization in bacteria

#### M. L. Fdez Gubieda et al., ACS Nano 7 3297 (2013)

- Many organisms (magnetotactic bacteria) produces magnetic nanoparticles
- Magnetospirillum gryphiswaldense produces magnetite nanoparticles (biomineralization) surrounded by a lipidic membrane (magnetosomes)



- Chaines used as compass needles to orient in the geomagnetic field
- Good biocompatibility and therefore interesting in biomedical applications
- Understanding of the biomineralization process to design new materials



# Magnetite biomineralization in bacteria

M. L. Fdez Gubieda et al., ACS Nano 7 3297 (2013)

#### XANES

- To identify the oxidation state and local geometry of the absorbing atom
- To identify and quantify the different Fe phases
- 2 eV shift towards lower energies
- LC of ferrihydrite (Fe<sup>3+</sup>) and magnetite (Fe<sup>3+</sup> and Fe<sup>2+</sup>)
- ferrihydrite constant and then in the end of the biomineralization process undetectable







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# Cu<sup>2+</sup>-loaded Cu hexacyanoferrate

M. Giorgetti et al., PCCP **14**, 5527 (2012), M. Giorgetti et al., J. Phys.: Conf. Series 430, 012049 (2013)

# $A_x M_y [Fe(CN)_6] \cdot zH_2O$

"soluble"\* structure (F-43m)



"insoluble" \* structure (Pm-3m)



- a ~ 10.2 Å
- alkaly metals occupy intertitial 8c positions
- -CN-Cu-NC-Fe-CN- linear chains
- Fe and Cu in octahedral sites
   6 x Fe-CN-Cu
   6 x Cu-NC-Fe

• Model with [Fe(CN)<sub>6</sub>]<sup>3-</sup> ion vacancies

6 x Fe-CN-Cu 4.5 x Cu-NC-Fe 1.5 x Cu-O



# Cu<sup>2+</sup>-loaded Cu hexacyanoferrate: interest

## Applications

- Electrochromism
- Electrocatalysis
- Ionic and electronic conductivity
- Charge storage
- Photo-induced magnetisation
- Electro-catalytic oxidation of alcohols in alkaline medium

## Aim of the study

- Relationship between structure and properties
- Amount of vacancies linked to the ability of H storage



### Data analysis strategy



Linear chains between Cu and Fe gives rise to a *superfocusing effect* and therefore to a *large EXAFS signal* 



Information on the amount of the vacancies

Signals for the Cu K-edge (CN)				
Two body	$\gamma_1^{(2)}$ Cu-N; (4.5)			
	γ <sub>2</sub> <sup>(2)</sup> Cu-O; (1.5)			
	γ <sub>3</sub> <sup>(2)</sup> Cu-K; (*)			
Three body	$\eta_1^{(3)}$ Cu-N-C; (4.5)			
Four body	$\eta_1^{(4)}$ Cu-N-C-Fe; (4.5)			













## **Fitting results**







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The understanding of the structural and electronic properties of the catalytic active site during the catalytic activity is of prime significance to obtain a rational catalyst design that points towards the improvement of already established reaction and to develop catalyst for new reactions. (a) 0.4 V (under N<sub>2</sub>)

11520

11560

Energy /eV

Voltage	Shell	CN	<i>R</i> /nm	$\Delta E_0/\mathrm{eV}$	$\sigma^2/10^{-5} \text{ nm}^2$
(a) 0.4 V ( $R_f = 1.8\%$ )	Pt–Pt	9.2 ± 1.1	$0.276\pm0.001$	$5\pm1$	$\textbf{7.1} \pm \textbf{0.7}$
(b) 1.0 V ( $R_{\rm f} = 1.7\%$ )	Pt–O Pt–Pt	$\begin{array}{c} 0.8\pm0.3\\ 7.2\pm1.3\end{array}$	$\begin{array}{c} 0.199 \pm 0.002 \\ 0.276 \pm 0.001 \end{array}$	$\begin{array}{c}2\pm5\\5\pm2\end{array}$	$\begin{array}{c} 0.1\pm3.0\\ 7.7\pm0.9\end{array}$
$S_0^2 = 0.94. k$	= 30-12	$20 \text{ nm}^{-1}, R$	= 0.12–0.35 nm.		



11600



8

k /10 nm<sup>-1</sup>

10

 $R/10^{-1}$  nm



# Structural kinetics of Pt/C cathode catalyst

 $0.4 V \rightarrow 1 V (under N_2)$ 



N. Ishiguro et al. (2013) Phys.Chem.Chem.Phys. 15, 18827



# Structural kinetics of Pt/C cathode catalyst



N. Ishiguro et al. (2013) Phys.Chem.Chem.Phys. 15, 18827



# Structural kinetics of Pt/C cathode catalyst



N. Ishiguro et al. (2013) Phys.Chem.Chem.Phys. 15, 18827



# Cells and chamber





Li deinsertion mechanism and Jahn–Teller distortion in LiFe<sub>0.75</sub>Mn<sub>0.25</sub>PO<sub>4</sub>

- The partial sustitution of Fe with transition metals increases the working potential
- Mn hinders the reversible insertion of Li because of a Jahn-Teller distortion at Mn<sup>3+</sup> centres during the charge
- XAS is used:
  - To follow the redox processes involved in the electrochemical lithiation at both centres
  - To follow the modification at their coordination environment
- Chemometric approach for data analysis (PCA and MCR)

A. Iadecola, A. Perea, L. Aldon, G. Aquilanti, L. Stievano J. Phys. D: Appl. Phys. **50** (2017) 144004



Li deinsertion mechanism and Jahn–Teller distortion in LiFe<sub>0.75</sub>Mn<sub>0.25</sub>PO<sub>4</sub>

- Experiment: XAS at Mn K-edge and at Fe K-edge
- Data analysis
  - PCA: determination of the number of independent components contributing to the whole series of collected spectra during electrochemical cycling
  - MCR-ALS: reconstruction of the spectral components which are necessary for interpreting the whole multiset of operando spectra
  - STANDARD EXAFS ANALYSIS: on the reconstructed spectral components

A. Iadecola, A. Perea, L. Aldon, G. Aquilanti, L. Stievano J. Phys. D: Appl. Phys. **50** (2017) 144004



- Li-ion exchange between the electrodes
- Electrodes materials must favour the intercalation/release of Li-ions during the charge/discharge



- Metal hexacyanoferrates based materials used as cathodes
- Intercalation materials with high void space

M. Giorgetti et al., J. Phys.: Conf. Series (2016) **712**, 012127



## **Operando XAS measurements**



- K<sub>0.44</sub>Fe<sub>1.56</sub>Co(CN)<sub>6</sub>
- C/30 charge discharge
- Fe K-edge data
- Co K-edge data

- Charging: K<sup>+</sup> extraction
- Discharging: Li<sup>+</sup> insertion





### Fe data - 1



 $K_{0.44}Fe_{1.56}Co(CN)_6 \rightarrow 0.44 \text{ K}^+ + Fe_{1.56}Co(CN)_6 + 0.44 \text{ e}^-$ 

 $x \operatorname{Li}^+ + \operatorname{Fe}_{1.56}\operatorname{Co(CN)}_6 + x \operatorname{e}^- \rightarrow \operatorname{Li}_x\operatorname{Fe}_{1.56}\operatorname{Co(CN)}_6$ 



Fe data - 2





- Fe<sup>2+</sup> of the pristine electrode is oxidized during the first charge
- Oxidized Fe species reduce during the discharge
- Process not fully reversible
- Fe electroactive







Cobalt is NOT electroactive (in the investigated electrochemical potentials)



## **EXAFS** analysis







(Simplified) electrochemical reactions between Li and S:

$$S_8 + Li^+ + e^- \rightarrow Li_2S_x$$

$$(2.4 - 2.1 \text{ V})$$

$$Li_2S_x + Li^+ + e^- \rightarrow Li_2S_2 \text{ and/or } Li_2S$$

$$(2.1 - 1.5 \text{ V})$$

The reactions include solid-liquid-solid transformation, causing great complexity







**Experimental details** 

#### Measurements

- XAFS beamline at Elettra
- S K-edge
- Fluorescence mode

### Cathode composite

- MnS-1 (4.5 wt %)
- Printex XE2 (Degussa) carbon black (70.5 wt %)
- sulfur (25 wt %)

Electrolyte

 1M LiTDI in TEGDME:DOL (tetra(ethylene glycol) dimethyl ether:1,3dioxolane)





## **Operando XANES results**



- 1 spectrum/65 min (C/20 rate per electron, i.e.  $\Delta x \approx 0.054$  in Li<sub>x</sub>S)
- Three components: S, PS Li<sub>2</sub>S





Project n. 314515 www.eurolis.eu

R. Dominko et al., J. Phys. Chem. C 2015 119, 19001-19010 giuliana.aquilanti@elettra.eu 50



## Linear combination fitting





Project n. 314515 www.eurolis.eu



# **EXAFS results**



### High voltage plateau

- Same main frequency
- Decrease of the intensity
- Compatible with the decrease of the average number of nearest neighbors of sulfur because of the formation of PS

# Start of the low voltage plateau

- Appearance of an extra frequency
- Attributed to the onset of the occurrence of Li<sub>2</sub>S





## EXAFS results – quantitative analysis





- Sharp decrease of CN at the beginning of the low voltage plateau
- CN constant at the end of the discharge







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# EXAFS results – quantitative analysis



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- $S/Li_2S = 30(5)/70(5)$
- No other signal ruling out any specific interaction of the S species with the composite or the electrolyte



- XAS (XANES + EXAFS) in operando conditions
- The use of zeolite additive retains the polysulfides in the cathode up to a certain extent
- The use of S-free electrolyte allowed us to do a full EXAFS analysis
- The concentration of PS reached a maximum at the end of the high voltage plateau
- From the EXAFS we detect clearly the onset of the formation of Li<sub>2</sub>S
- No other components, apart form S and Li<sub>2</sub>S, have been detected and therefore no interaction between the cathode and the composite have been evidenced

