Applications of core-level spectroscopy

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Outline of talk

- Bonding information
- EXELFS
- Core hole
- Magnetism, dichroism, temperature
- Multiplet calculations
Combining experiment and modelling

Collection of experimental data → Calculation of simulated spectra

Understanding of the problem

Planning further investigations

Density Functional Theory

- Good for periodic systems
- Good for regions close to edge onset
- Can be computationally intense
- All-electron and pseudopotential methods
- Examples: WIEN2k, CASTEP
Green’s Function Methods

- Multiple scattering codes
- Good for aperiodic systems
- Good for vacancies and impurities
- Example: FEFF8

Bonding – carbon materials

![Graph of Diamond vs. Graphite](http://people.ccmr.cornell.edu/~davidm/WEELS/index.htm)
Bonding – graphite

\[ I(E) = |M_{0,1}|^2 N_1(E) \]

Dipole approximation applied to graphite

WIEN2k

Bonding – graphite

In and out of plane contributions to p-dos

WIEN2k
Bonding – $C_{60}$ and $C_{70}$

**Calculation**

$\text{SM Lee}$

(Broadening = 0.14 eV)

**Experiment**
Bonding – \(\text{C}_{60}\) and \(\text{C}_{70}\)

\(\text{C}_{70}\)

\[\text{a b c d e}\]

S.M. Lee et al.

Bonding – \(\text{C}_{60}\) and \(\text{C}_{70}\)

\(\text{C}_{70}\)

\[\text{a b c d e}\]

Micron 37 (2006) 449
Bonding – C\textsubscript{60} and C\textsubscript{70}

- fcc C\textsubscript{60} crystal
- cubic C\textsubscript{60} crystal

Origin of the difference:
- Lattice parameter
- Bond lengths
- Rotational order

Bonding – nitrogen

\[ \text{N}_2 \text{ gas} \]

Trasobares et al.

Jaouen et al. Microsc Microanal
Microstruc 6 (1995) 127

Bonding – nitrogen

Seepujak et al.
Bonding – boron

Boron Nitride

Extended fine structure

Radial distribution function

Hug et al.
Ultra 59 (1995) 121
Extended fine structure

Aluminium metal

Al K-edge
EXELFS and ELNES

Core hole – NbB₂

Ma et al. Ultra (2008) 320
Core hole – NbB$_2$

Ma et al. Ultra (2008) 320

Core hole

- Slater transition state

Paxton et al.
J Phys Condens Matter
12 (2000) 729
Core hole

- Core hole not always straightforward!
- Always include?
- Always use large supercells
- Need to think very carefully about parameters to get a balance between an interpretable calculation and computer time / memory use

Magnetic order

\[
\text{MgCr}_2\text{O}_4
\]

Eustace et al.
Microsc Microanal 13 (2007) 1276 CD

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Magnetic circular dichroism

Schattschneider et al.

http://www.chiraltem.physics.at/Chi-What-is-ChiralITEM.htm
**Temperature**

FEFF8 calculation including Debye-Waller factors

Moreno et al.
Micron 38 (2007) 1

**Valence state**

Oakzaki et al.

Sm atom inside a fullerene cage

$\text{Sm}^{2+} \rightarrow \text{Sm}^{3+}$
Multiplet calculations

- For edges such as the L_{2,3} there can be strong overlap between the core and valence wavefunctions.

- Final states are found by vector coupling final and initial states.

Ni calculation with varying charge transfer

Frank de Groot
Summary

- Combining core level spectroscopy experiments and information can be a powerful way of learning more about a material

Things to think about when simulating spectra
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- What information do you want?
  - Low-loss / core-loss
  - ELNES / EXELFS
  - Bonding / valence state

- What sort of experiments are possible?
  - Energy resolution
  - Standards
Things to think about when simulating spectra

- What sort of structure do you have?
  - Periodic / amorphous
  - Several possible

- What sort of elements do you have?
  - Magnetism
  - K / L / M edge
  - f-electrons
Things to think about when simulating spectra

- What information do you want?
- What experiments are possible?
- What sort of structure do you have?
- What sort of elements do you have?

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