Applications of core-level spectroscopy

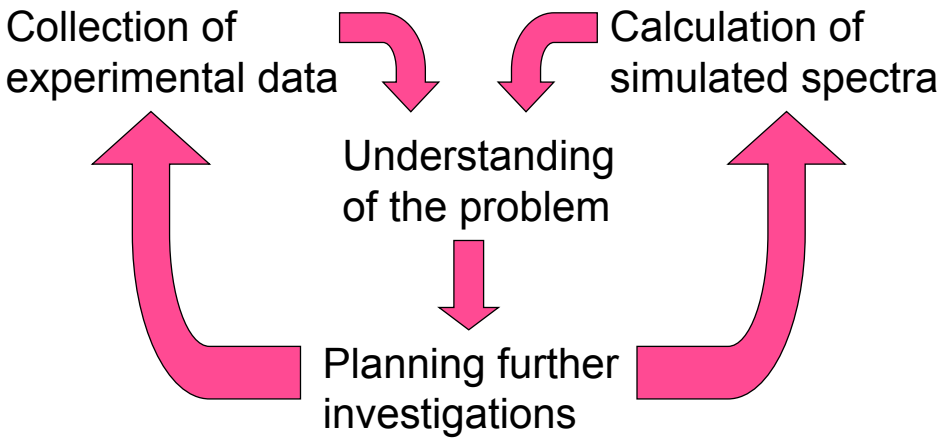
Rebecca Nicholls

OxfordMaterials

Outline of talk

- Bonding information
- EXELFS
- Core hole
- Magnetism, dichroism, temperature
- Multiplet calculations

Combining experiment and modelling



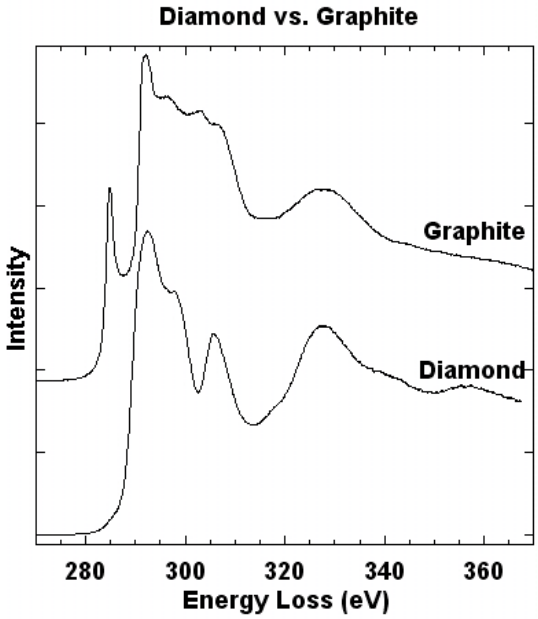
Density Functional Theory

- 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

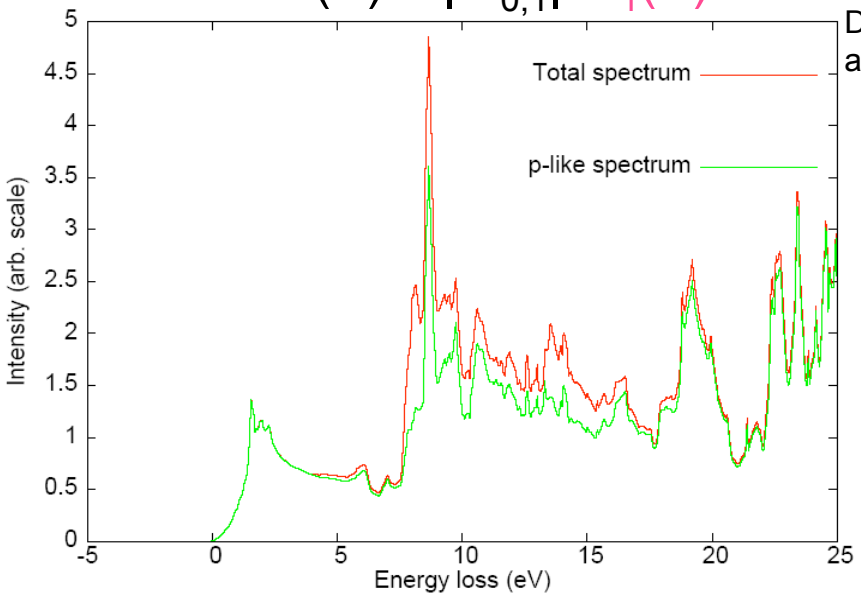


David Muller

http://people.ccmr.cornell.edu/~davidm/WEELS/index.htm

Bonding – graphite

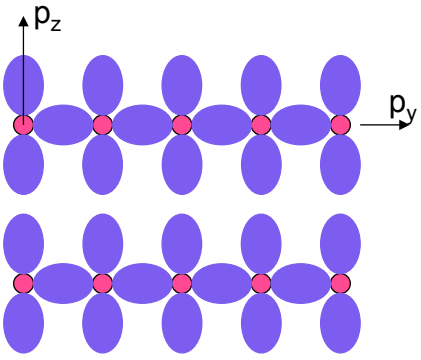
$$I(E) = |M_{0,1}|^2 N_1(E)$$



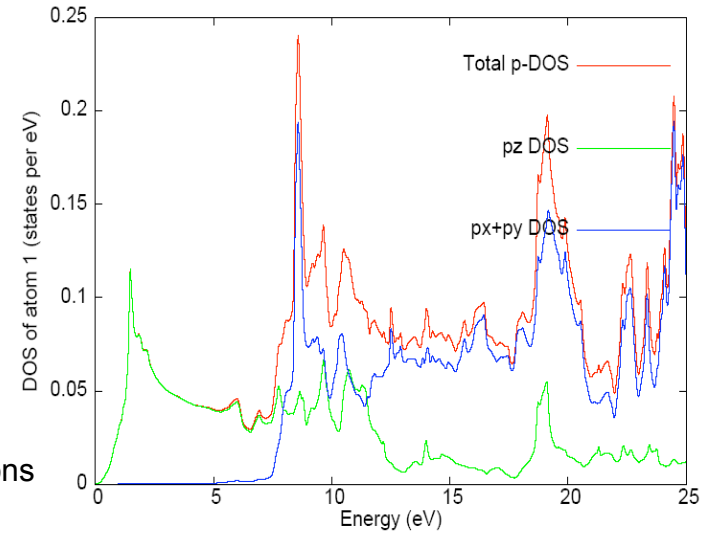
Dipole approximation applied to graphite

WIEN2k

Bonding – graphite

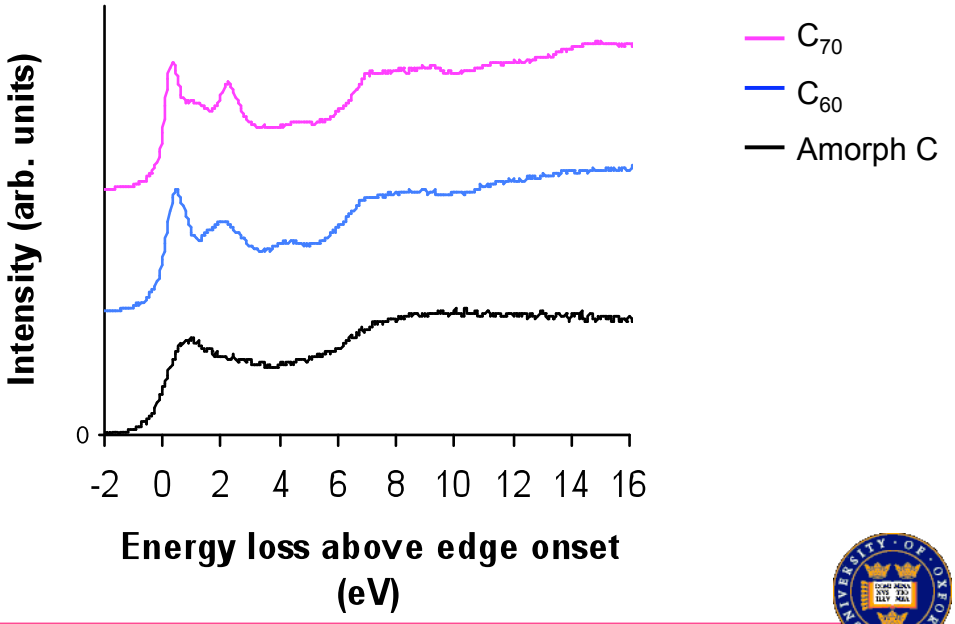


In and out of plane contributions to p-dos

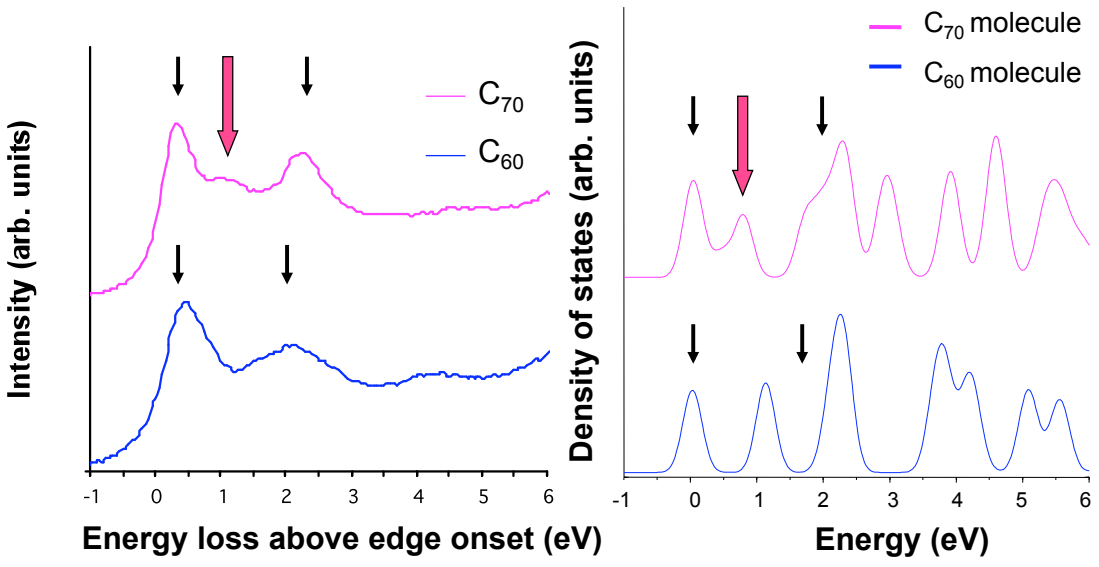


WIEN2k

Bonding – C_{60} and C_{70}

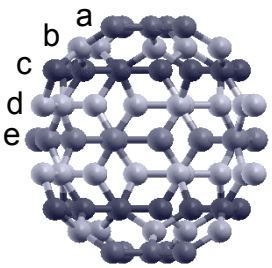


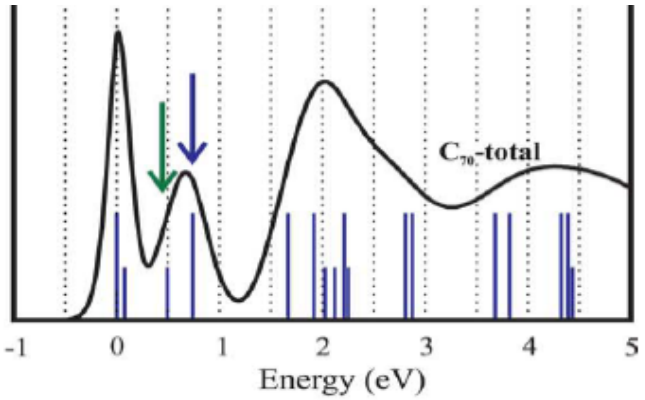
Bonding – C_{60} and C_{70}

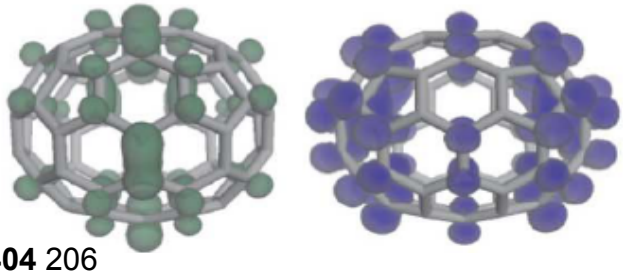


Bonding – C_{60} and C_{70}

C_{70}



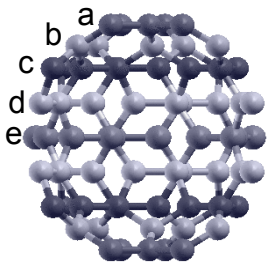


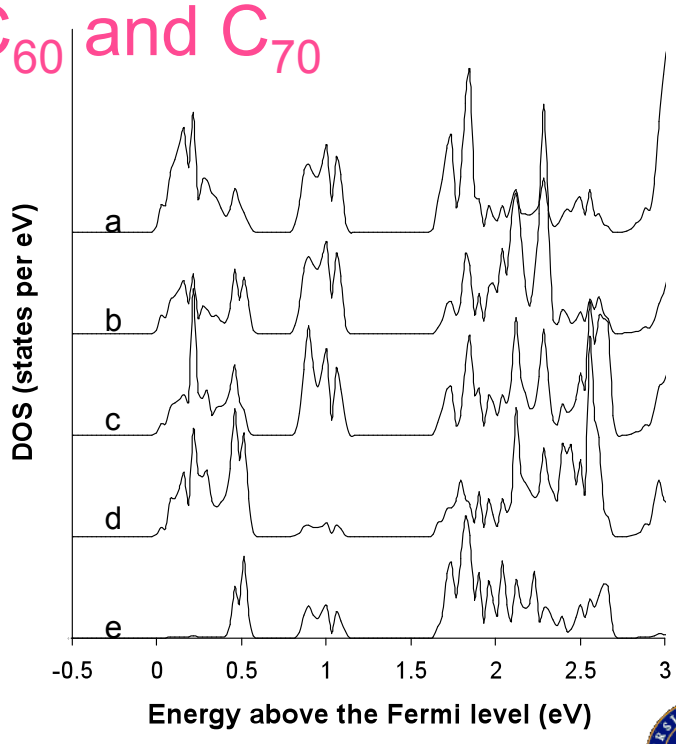


S.M. Lee *et al.*
Chem. Phys. Lett. (2005) **404** 206

Bonding – C_{60} and C_{70}

C_{70}

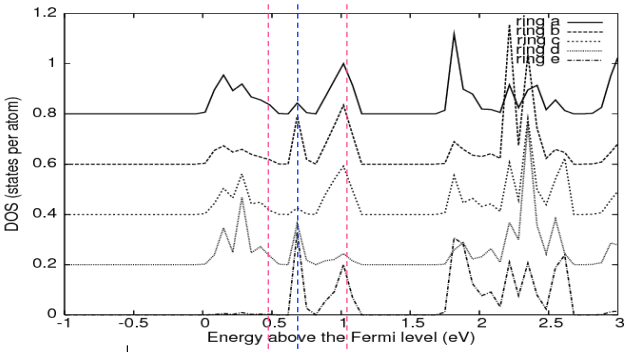




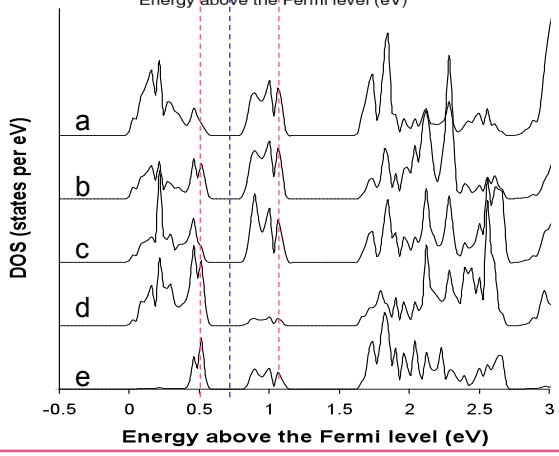
Micron **37** (2006) 449

Bonding

C_{70}



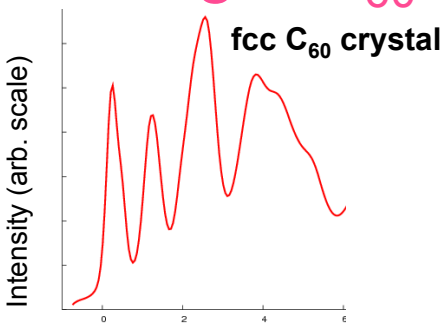
relaxed

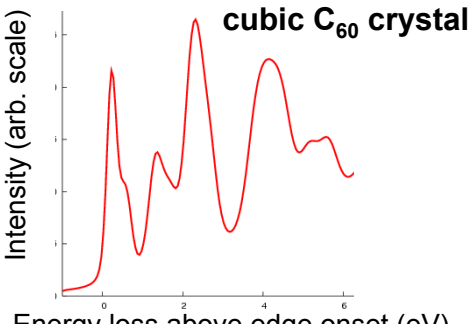


unrelaxed

J of Phys Conf Ser:
126 (2008) 01238

Bonding – C_{60} and C_{70}



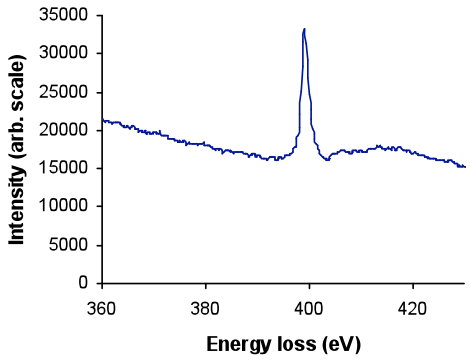


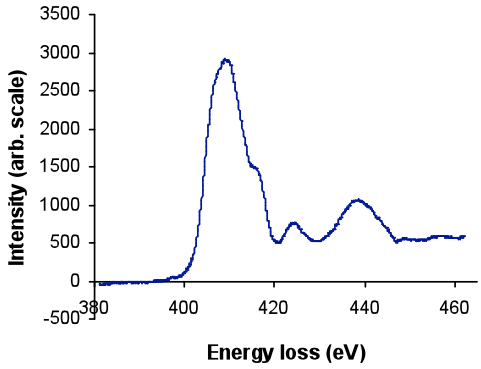
Origin of the difference

- Lattice parameter
- Bond lengths
- Rotational order

Chem. Phys. Lett.
470 (2009) 116

Bonding – nitrogen





N_2 gas

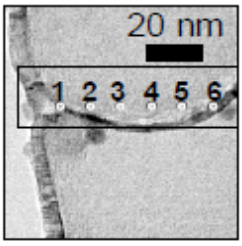
Trasobares *et al.*
Eur Phys J B **22** (2001) 117

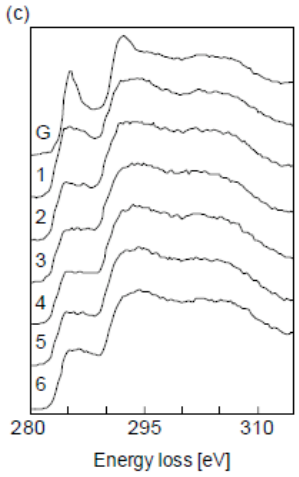
cBN

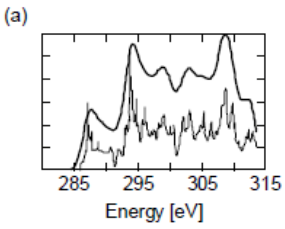
Jaouen *et al*. Microsc Microanal Microstruc **6** (1995) 127

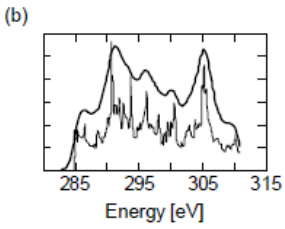
Bonding – nitrogen

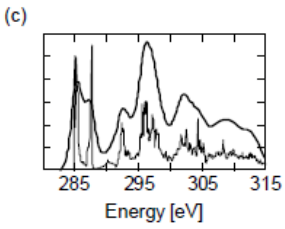
Seepujak *et al.*
J Phys Conf Ser:
26 (2006) 161





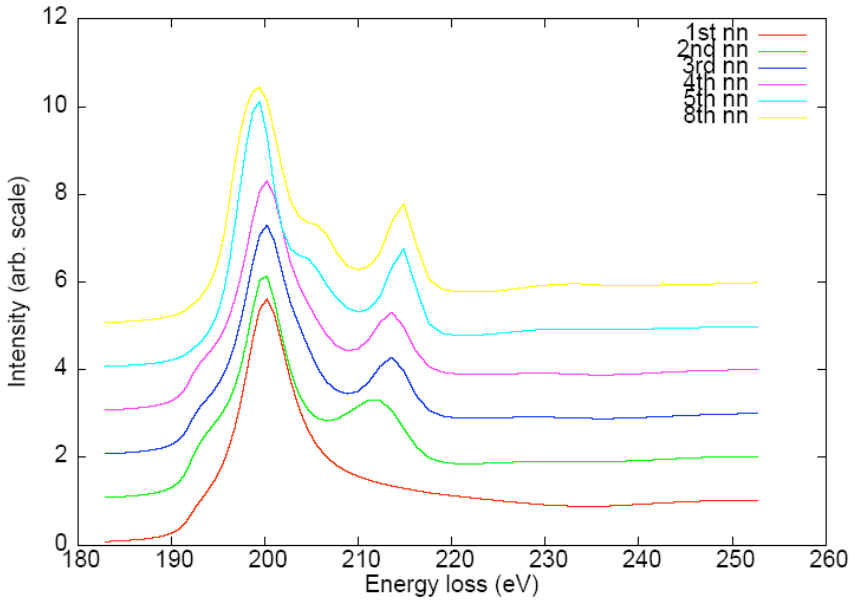






Bonding – boron

Boron Nitride



B K-edge ELNES

Extended fine structure

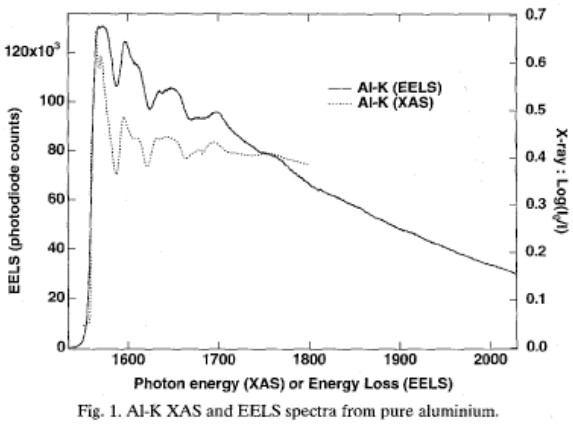
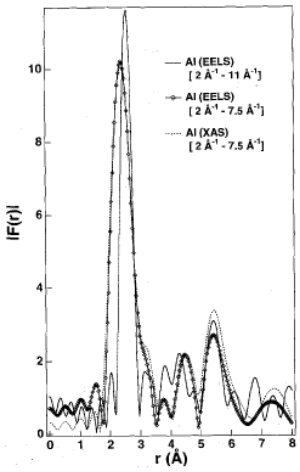


Fig. 1. Al-K XAS and EELS spectra from pure aluminium.

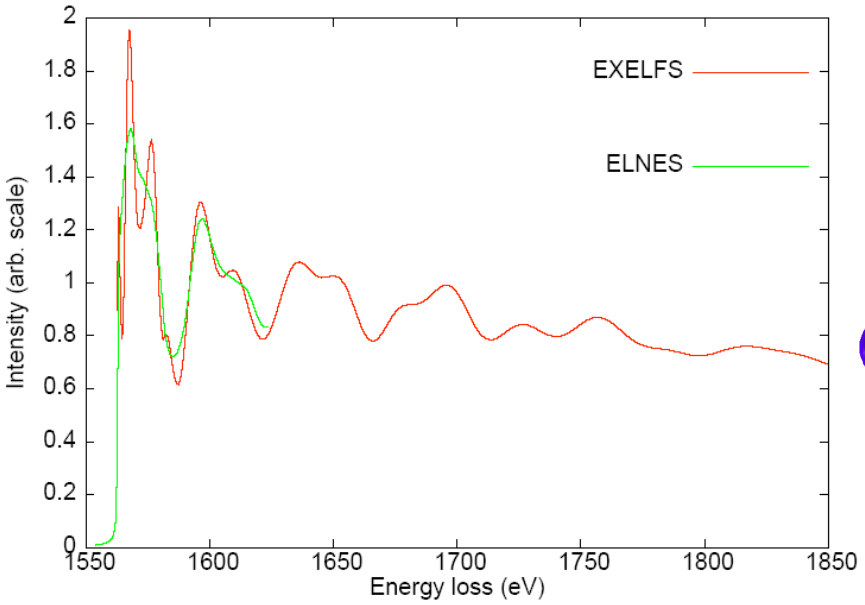


Radial distribution function

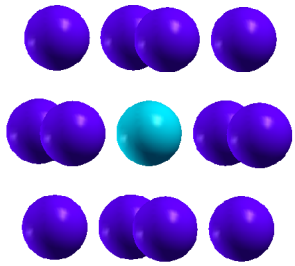
Hug *et al.*
Ultra **59** (1995) 121

Extended fine structure

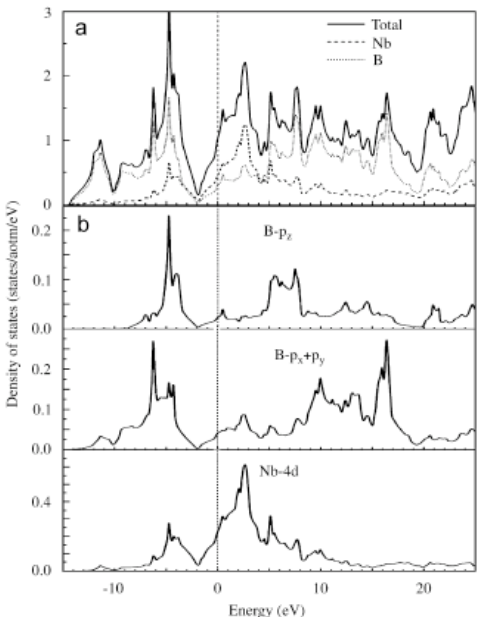
Aluminium metal

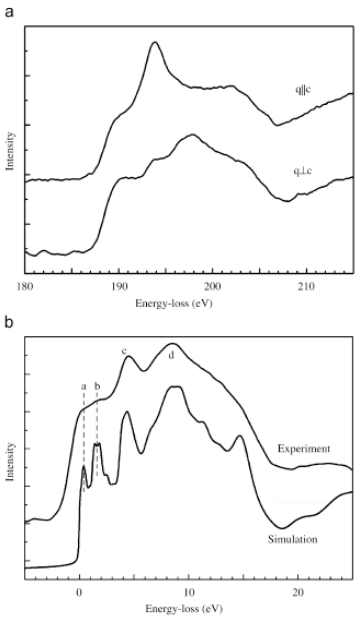


Al K-edge EXELFS and ELNES



Core hole – NbB_2



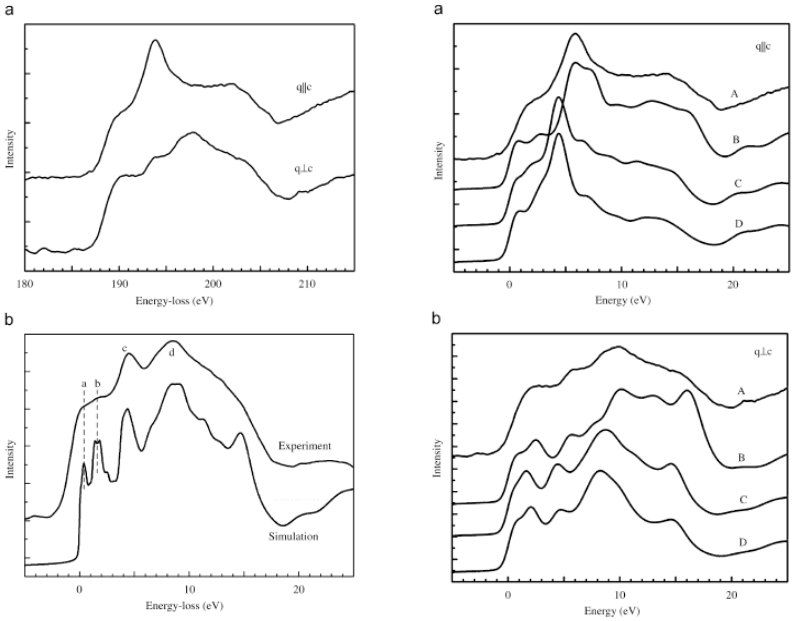


B K-edge

NbB_2

Ma *et al.* Ultra (2008) 320

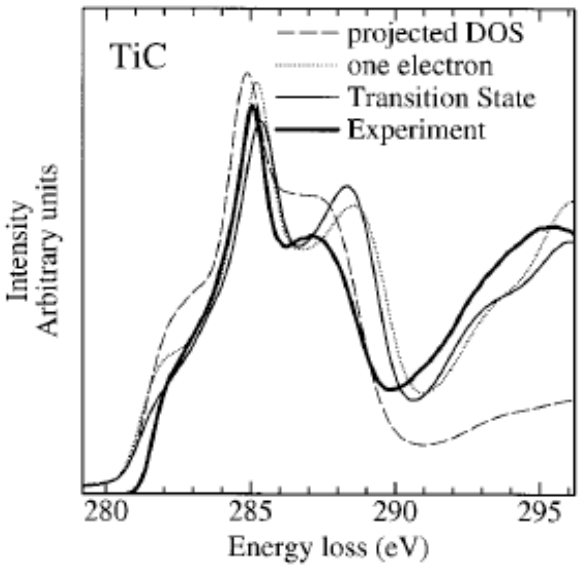
Core hole – NbB_2



Ma *et al.* Ultra (2008) 320

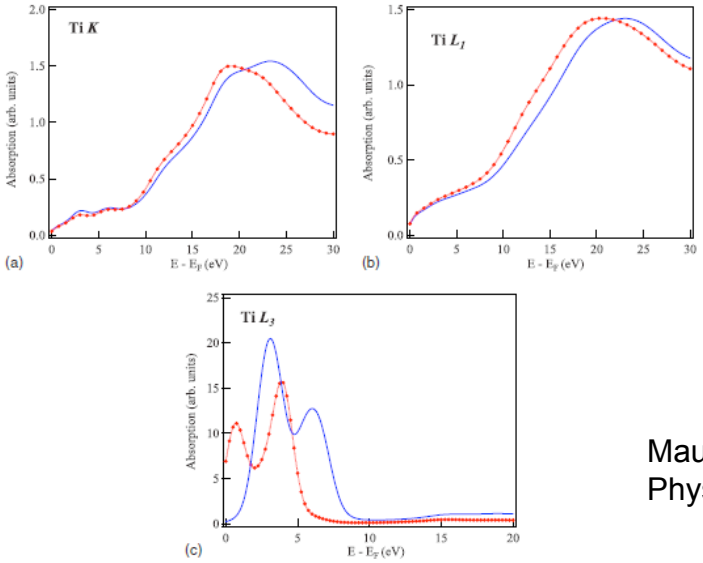
Core hole

- Slater transition state



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

Core hole



r-TiO_2

Red – core hole
Blue – no core hole

Mauchamp *et al.*
Phys Rev B **79** (2009) 235106

Core hole – summary

- Core hole not always straight forward!
- 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

$MgCr_2O_4$

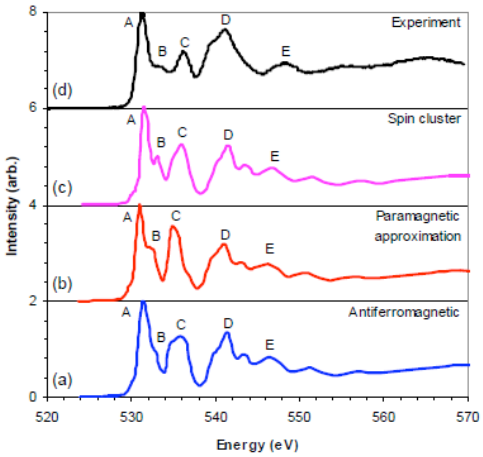
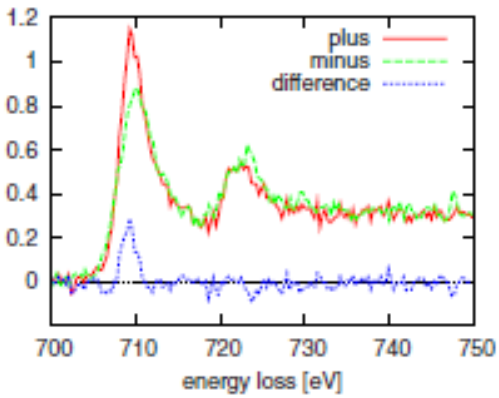


Figure 1 – Oxygen K-edge ELNES of $MgCr_2O_4$. (a) Long range AFM simulation, (b) paramagnetic simulation, (c) SRO 'spin clusters' simulation, (d) experimental spectrum.

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

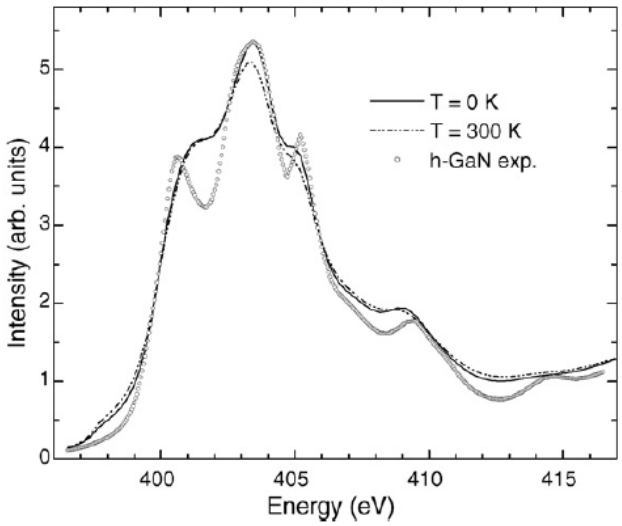
Magnetic circular dichroism



Schattschneider *et al.*
Phys Rev B **78** (2008) 104413

http://www.chiraltem.physics.at/Chi-What-is-ChiralTEM.htm

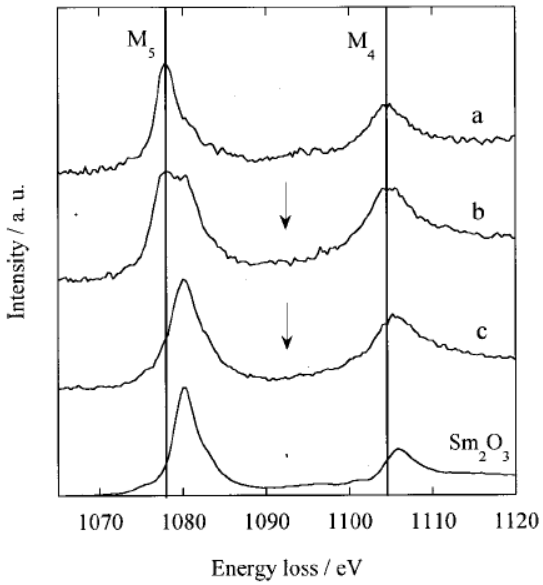
Temperature



FEFF8 calculation including Debye-Waller factors

Moreno *et al.*
Micron **38** (2007) 1

Valence state



Oakzaki *et al.*
J. Chem. Phys. (2000) **113** 9593

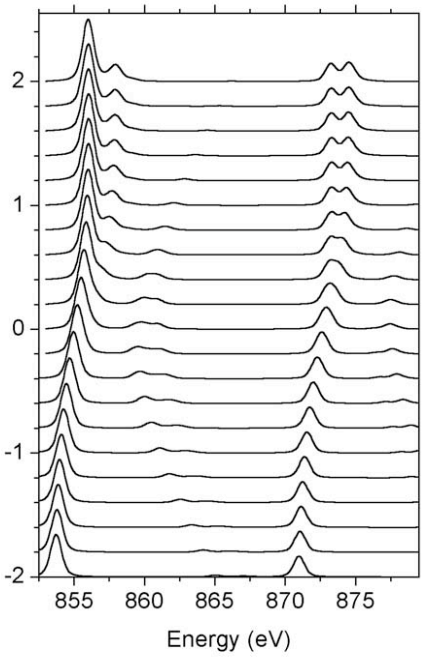
Sm atom inside a fullerene cage

$Sm^{2+} \longrightarrow Sm^{3+}$

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

Multiplet calculations



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

Things to think about when simulating spectra

- What information do you want?
  - Low-loss / core-loss
  - ELNES / EXELFS
  - Bonding / valence state

Things to think about when simulating spectra

- 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

Things to think about when simulating spectra

- 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?

Acknowledgements

- David Cockayne, Duc Nguyen-Manh, David Pankhurst, Seung Mi Lee
- Gianluigi Botton, Sorin Lazar
- Jonathan Yates, Chris Pickard, Shang-Peng Gao
- David McComb, David Eustace, James Perkins
- Kevin Jorissen
- Andrew Scott