Single Crystal Diffraction
Synchrotron applications

Cheiron School, Spring8, 2012

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Synchrotron radiation for single crystal diffraction

- Some properties of synchrotron radiation very valuable to single crystal diffraction
  - Very intense xray beam
  - Tunable wavelength
  - Broad energy spectrum
  - Pulsed structure
- Improve quality of some ‘standard’ studies
- Provides opportunities for studies and applications <u>not possible</u> with laboratory xray sources

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Intensity Formula for Diffracted Xrays

- $I_{hkl} = I^{o} (\lambda^3 /\omega) (V_x \, L \, p \, A/V^2) \, |F_{hkl}|^2$
  - I^o - incident beam intensity
  - V_x volume of crystal
  - λ^3 - increase λ 2x - increase scattering 8x
  - $|Fhkl|^2$ depends on unit cell contents – atomic scattering factor

- ω = rotation velocity of the crystal; L = Lorentz; p = the polarization factor; A = absorption factor ; V = volume of the unit cell

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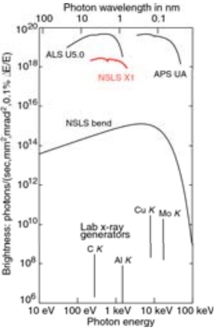
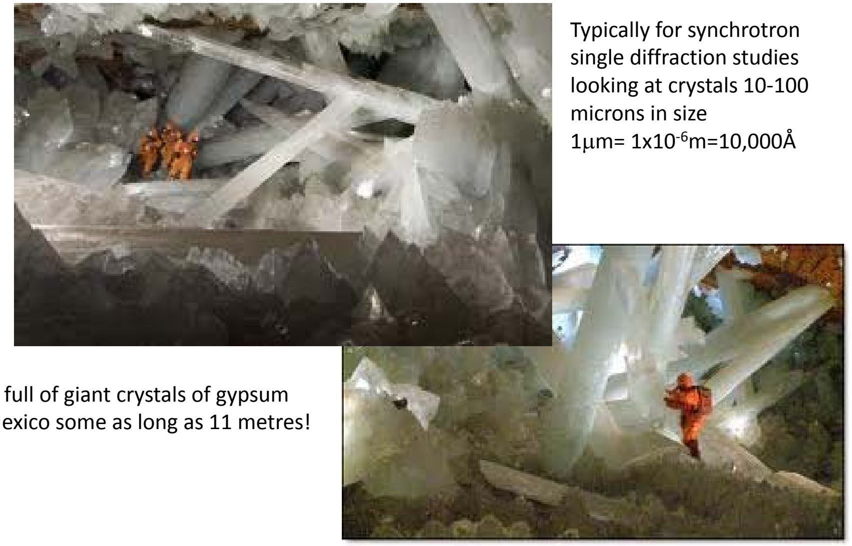
Small weakly diffracting crystals



- Use
  - very high intensity of synchrotron radiation
  - Focussed small beams
  - Longer wavelength xrays (tunability)
- Study crystals 10s microns (and smaller)
- Standard experiment but many exciting and scientifically important structures not possible using laboratory sources

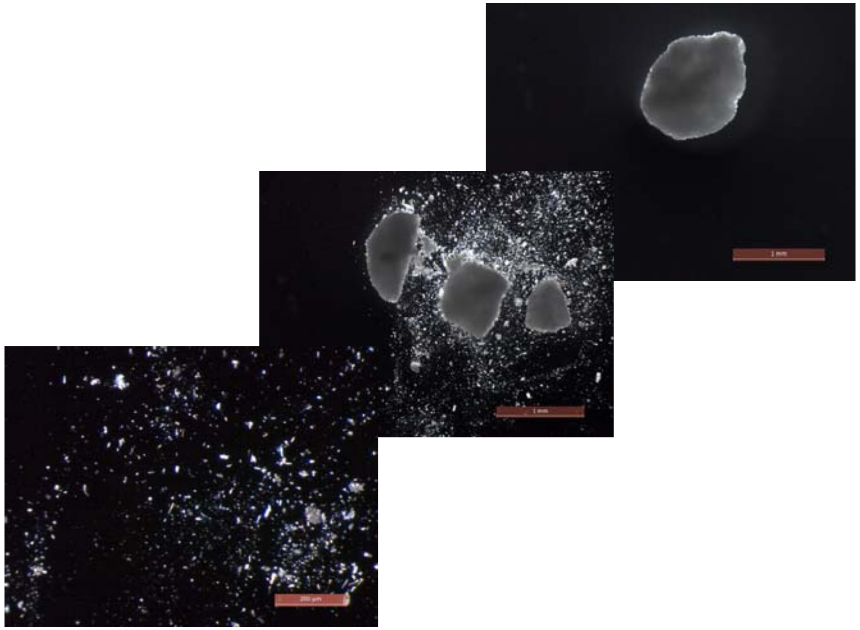
Crystal size

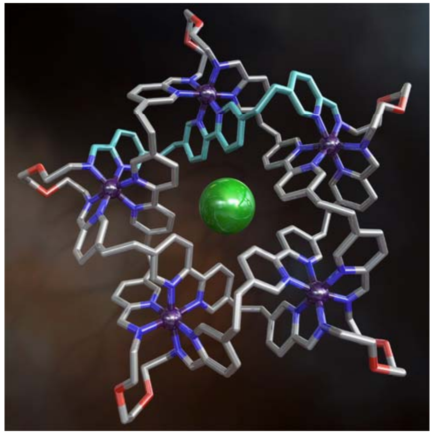


Typically for synchrotron single diffraction studies looking at crystals 10-100 microns in size

$1\mu m = 1x10^{-6}m = 10{,}000Å$

Cave full of giant crystals of gypsum in Mexico some as long as 11 metres!





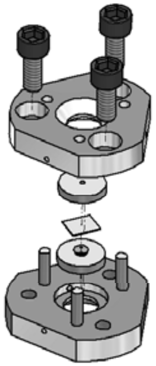
Leigh et al, *Nature Chem.* **4**, 15-20 (2012)
http://www.catenane.net/home/knot_paper_2011.html

Rapid data collection - automation

- Short data collections – sample changing becomes significant part of beamtime
- Robotic Sample Changer
  - Improved efficiency of screening samples
  - Reduce number and time spent on searches
  - Return to original crystal

High pressure studies

- Look at effect of pressure on structure
  - New polymorphs
  - New intermolecular interactions
  - Phase transitions



High pressure studies

- Experimental challenges
  - Diffraction data limited – shaded by pressure cell body that block xrays from sample or detector (40° cone)
  - High absorption by cell
  - Crystals relatively small
- Synchrotron radiation advantages
  - High xray flux – small crystals, improve statistics
  - Short wavelength (tunability) – improve completeness of data – compress diffraction pattern

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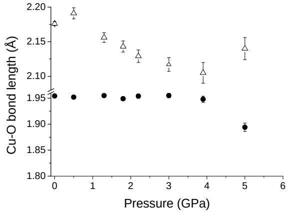
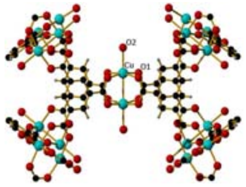
Diamond Anvil example

The effect of pressure on Cu-btc :
framework compression vs. guest inclusion

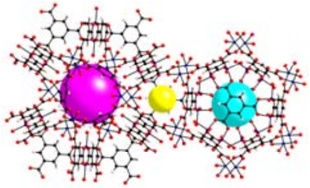
- Detailed structural data on the effect of high pressure on Cu-btc
  - Application of pressure causes solvent to be squeezed into the pores until a phase transition occurs, driven by the sudden compression and *expansion* of equatorial and axial Cu-O bonds
  - On increasing pressure further to 5.0 GPa, we enter a pore emptying region, with which the high pressure squeezes the solvent out of the pores; this is accomodated by the extension of the compliant (axial) Cu-O2 bond.
- Data collected on I19 at ~0.5GPa steps from ambient pressure to 5GPa



3 distinct but interconnected pore volumes in Cu-btc. Guest accessible cavities at (0,0,0) (pink), (1/2,1/2,1/2) (yellow) and (1/4,1/4,1/4) (blue) are shown.
1/2, 1/2) (blue, ~8.4 Å diameter), and (1/4, 1/4, 1/4) (yellow, ~5.4 Å diameter



Cu paddlewheel units present in Cu-btc showing the equatorial and axial Cu-O bonds, Cu-O1 and Cu-O2 respectively.



The effect of pressure on Cu-btc: framework compression *vs.* guest inclusion
Alexander J. Graham , Jin-Chong Tan , David R. Allan and Stephen A. Moggach
Chem. Commun., 2012,**48**, 1535-1537

Thanks to Stephen Moggach,
University of Edinburgh,UK

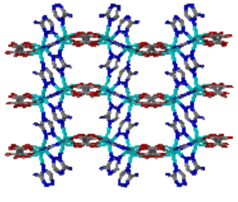
Gas Cell

Advantages of use with synchrotron radiation

- Smaller samples possible maximising gas penetration
- Rapid data collection allows monitoring in-situ monitoring of process and continuous evaluation
- Increased intensity overcome high background from borosilicate glass

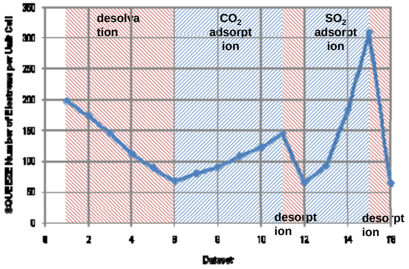
- Flow cell – used to flow a gas or put crystal under vacuum
- Crystals can be evacuated first with vacuum, in conjunction with heating from the Cryostream, then gases applied to sample
- Gases that can be used N_2, H_2, Ar, Kr, SO_2, CO_2, CO, Ne, HCl, H_2S, NO

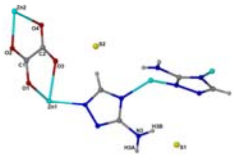
Gas Cell example



$Zn_2(ox)(atz)_2]\cdot 2MeOH$ (ox = oxalate, atz = 3-amino-1,2,4-triazolate)

- •Sample initially activated under vacuum,
- • collecting data as heated from 283 to 400K
- •Monitoring MeOH content until total desolvation ~22 hrs
- •Cell loaded with CO2, $e^{-}\rho$ monitored
- •CO2 removed under vacuum
- •SO2 loaded into environmental gas cell
- •Increase in $e^{-}\rho$ – location of 2 S-atom sites

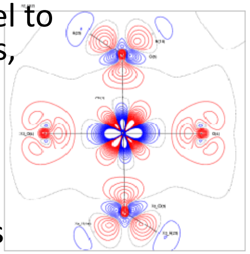




Crystal structure of $[Zn_2(ox)(atz)_2]\cdot 0.42SO_2$, indicating the sulfur positions within the pores

Thanks to Anna Warren, I19

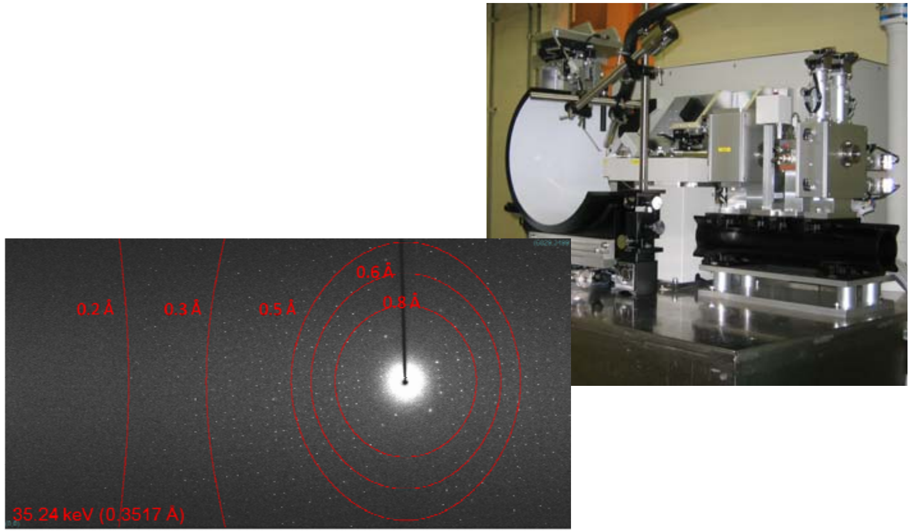
Charge density studies



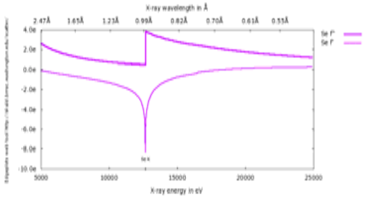
- Similar experiment – much more information
- Extend conventional spherical atom model to explore electron density – bonding effects, electronic structure and properties
- More complicated model, many more parameters and relatively small effect
- Need accurate, highly redundant, high resolution data including weak reflections
- Short wavelength, high intensity, high quality beam – increase resolution, reduce systematic errors, measure weak reflections accurately

P. Coppens, B.B. Iversen & F.K. Larsen, Coord. Chem. Rev., 249, 179-195,2005
use of synchrotron radiation for charge density studies

Spring-8 BL02B1 – short wavelength, high resolution, high quality data



Anomalous scattering



- Close to absorption edge scattering factor no longer wavelength independent
- f = f^0 + f' + if"
  - – f^0 scattering of unperturbed atom, f' + if" real and imaginary parts of anomalous scattering
- Magnitudes of f' and f" can change by several electrons

MAD

- Multiwavelength Anomalous Diffraction
- An approach to solving the phase problemin protein structure by comparing structure factors collected at different wavelengths, including the absorption edge of a heavy-atom scatterer.
- W. Hendrickson (Hendrickson, W. A., 1991, *Determination of macromolecular structures from anomalous diffraction of synchrotron radiation*. *Science*, **254**, 51–58.)

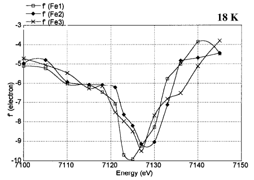
Anomalous scattering

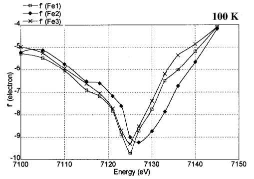
- Element and valence specific diffraction
- identify and locate different elements even on same site e.g. Fe and Co or Fe(II)/Fe(III), Gd(I)/Gd(III), Eu(II)/Eu(III)
- Edge differ 2-6eV for increase of 1 in oxidation state
- Use data collected at several wavelengths around absorption edge and refine f’ at each site to identify valence state
- Review by Madeleine Helliwell, J. Synchrotron Rad (2000), **7**, 139-147

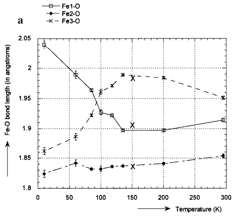
Multitemperature Resonance-Diffraction and Structural Study of the Mixed-Valence Complex [$Fe_3O(OOCC(CH_3)_3)_6(C_5H_5N)_3$]

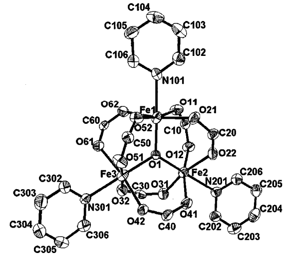
Multi-temperature structural data showed valence trapping to occur on cooling.
Room temperature have 2/3 of sites with intermediate geometry between Fe(II) and Fe(III)
At low temperature 2 x Fe(III) and 1 x Fe(II)

Data collected at 13 energies and 4 temperatures and f’ at each of the Fe sites refined for each case
Determine absorption edge position for each site at each temperature









Wu et al, Inorg. Chem. ***1998, 37, 6078-6083***

Photocrystallography

- Use single crystal diffraction to investigate structural changes induced by light
- Light of appropriate wavelength excite electron to excited states
- change in electron distribution – atomic displacements and sometimes photoisomerism or solid-state reaction

Photocrystallography

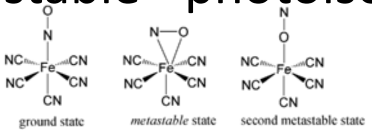
Range of timescales

- Irreversible – standard experiment before and after structure
- Metastable – excited state long lived as long as environment retained – e.g. Low temperature
- Microsecond and shorter lived species – time resolved studies
- Feature article J.M. Cole Acta Cryst. (2008). A64, 259–271
- *And tutorial review in Analyst*, 2011, **136**, 448-455

Metastable excited states

- Metastable – excited state long lived as long as environment retained – e.g. Low temperature
- Typically partial conversion ~20% - 'disordered' structure with ground state
- Experimental steps – collect ground state structure (in dark at low temperature) – irradiate – collect activated structure (mix of ground state and metastable state)
- Advantage with synchrotron radiation – small crystal and rapid data collection

Metastable - photoisomerism

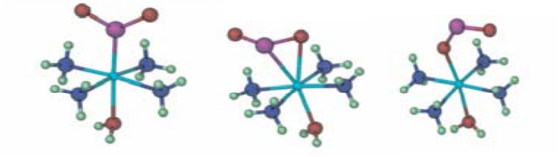


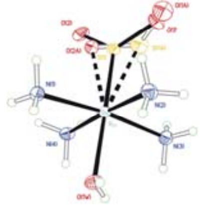
- First complex studied by photocrystallographic techniques $Na_2[Fe(CN)_5(NO)]$ - 2 photoactivated metastable complexes - linkage isomers of the ''ground state'' nitrosyl complex

Coppens et al, J. Am. Chem. Soc., 119, 2669 (1997).

- $[Ru(NH_3)_4(H_2O)(1\text{-}SO_2)][\text{tosylate}]_2$ studied by Coppens *et al* and ground state and one metastable state determined, 2nd metastable structure determined by Raithby *et al*

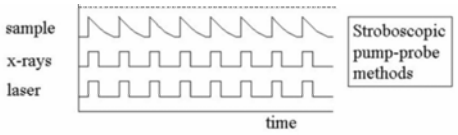
Coppens et al Inorg. Chem., 124, 9241 (2002 and Inorg. Chem., 42, 140 (2003). P.R. Raithby et al, Chem. Comm., 2448 (2006).

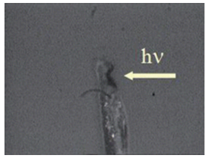




Short-lived species – time resolved studies

- Microsecond lifetimes - reversible on short timescale
- use stroboscopic (optical)pump-(xray)probe techniques
- Laser pump excited state and probe excited structure with synchronised xray probe very short delay after laser pulse
- Need synchrotron radiation – sufficient photos per chopper cycle where chopper pulse of photons
- Limited time resolution with monochromatic beam – throwing many photons away





Coppens et al Acta Cryst A66, 179-188, 2010

Picosecond lifetimes – Laue method

- Polychromatic experiments using larger bandwidths increase flux by 1000x or more compared to monochromatic beam
- Collect data with a single synchrotron pulse.
- Laser pulse followed by single X-ray pulse - time resolution determined by the largest width of the pump and the probe pulses.
- With femtosecond lasers time resolution determined by width of synchrotron pulse, typically 50–160 ps, depending on fill pattern

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Laue Method

- Stationary crystal
- White (or pink) beam – polychromatic
- Very fast shutter
- Simple experimental set up but much more complicated data processing – wavelength dependent effects
- Wavelength normalisation – different incident intensity, sample diffracting power and detector response

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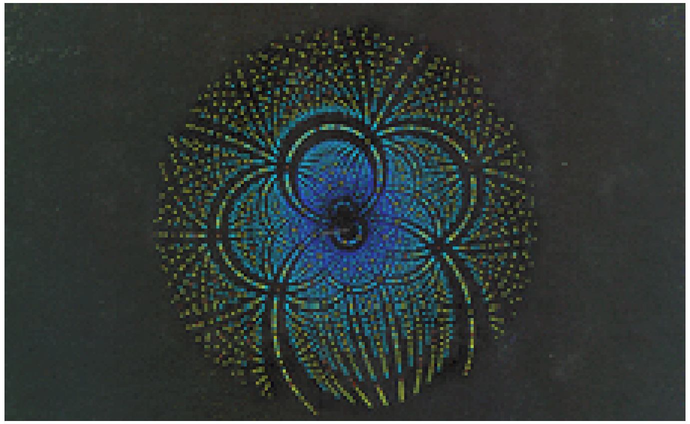

Simulation of Laue diffraction pattern for a lanthanum complex with spots colour-coded for wavelength. Short wavelengths in blue and then through the rainbow colours to red at the longest wavelengths. Actual wavelength bandpass used in this simulation is 0.5–1.5 Å.

M. Harding, Acta Crvst. (1995). B51,432-446

Laue Method

Considerable work to improve accuracy and quality of time resolved studies using Laue techniques

- The development of Laue techniques for single-pulse diffraction of chemical complexes
  - [Coppens *et al* Acta Cryst. (2011). A67, 319–326]
- Time-resolved Laue diffraction of excited species at atomic resolution: 100 ps single-pulse diffraction of the excited state of the organometallic complex $Rh_2(\mu\text{-}PNP)_2(PNP)_2\cdot BPh_4$
  - [Coppens et al *Chem. Commun.*, 2011, **47**, 1704-1706]

A Time-resolved X-ray Beamline

- http://pfwww.kek.jp/adachis/NW14/NW14.htm
- NW14A is an insertion device beamline aiming for time-resolved X-ray diffraction, scattering and absorption experiments. This beamline is particularly suitable for studying ultrafast dynamics in condensed matter systems such as organic and inorganic crystals, biological systems, liquids etc. Structural dynamics triggered by optical laser pulses is captured with the synchronized pump-and-probe system. With the relatively large amount of X-ray photon flux derived from the undulators, it is possible to produce atomic-scale movies of the photo-induced phenomena with 100-ps resolution.
- J. Synchrotron Rad. (2007). 14, 313–319

Future

Much shorter lifetimes studied using the XFEL?