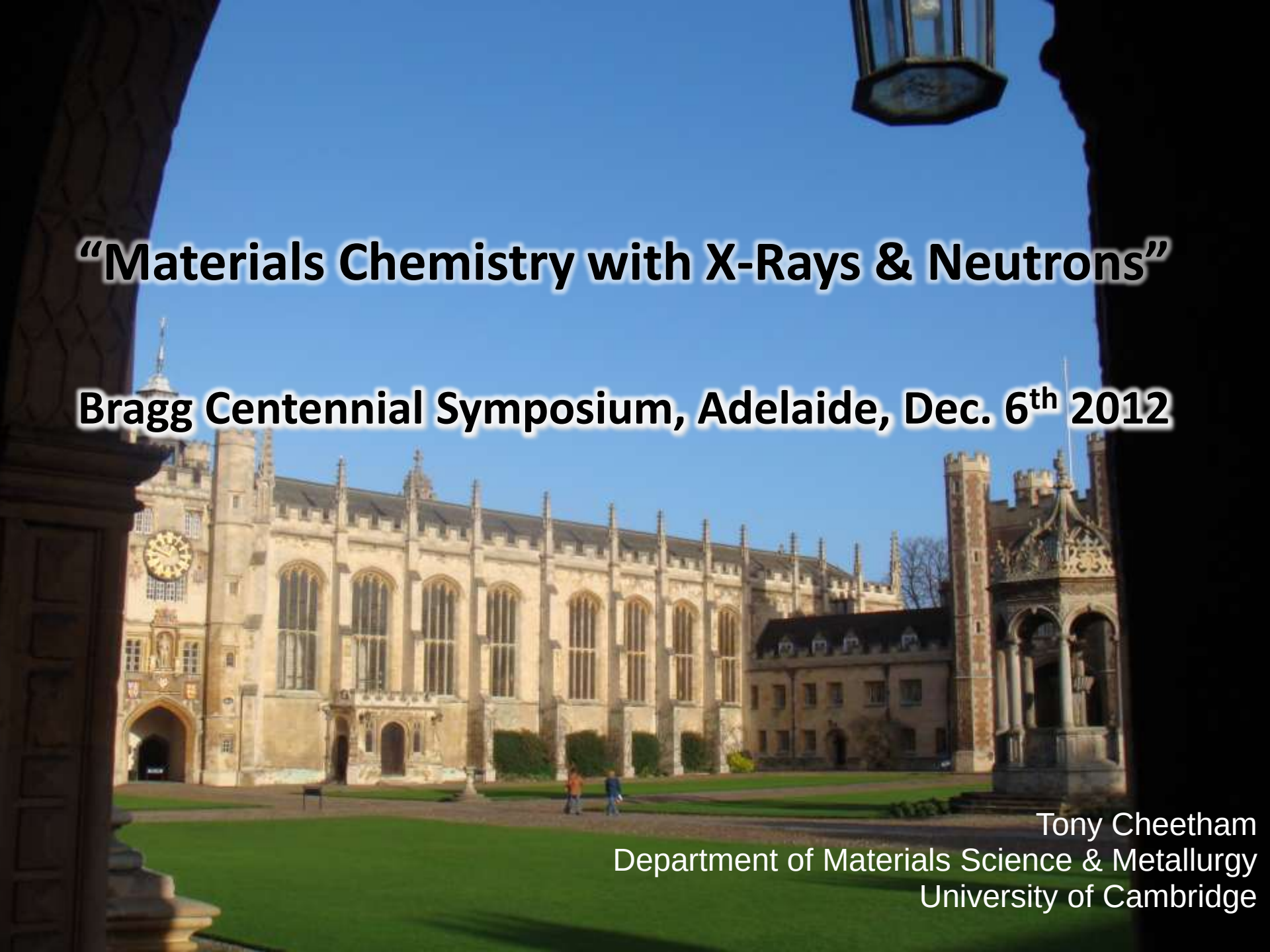


"Materials Chemistry with X-Rays & Neutrons"

Bragg Centennial Symposium, Adelaide, Dec. 6th 2012

Tony Cheetham
Department of Materials Science & Metallurgy
University of Cambridge

Outline of Talk

Some connections

Trinity College, Cambridge: 1909 ->

The Royal Institution: 1953 ->

Early achievements

– the Bragg equation and the interpretation of X-ray data

– the structures of diamond, zinc blende, rocksalt and fluorite were determined (and quartz by W.H.B)

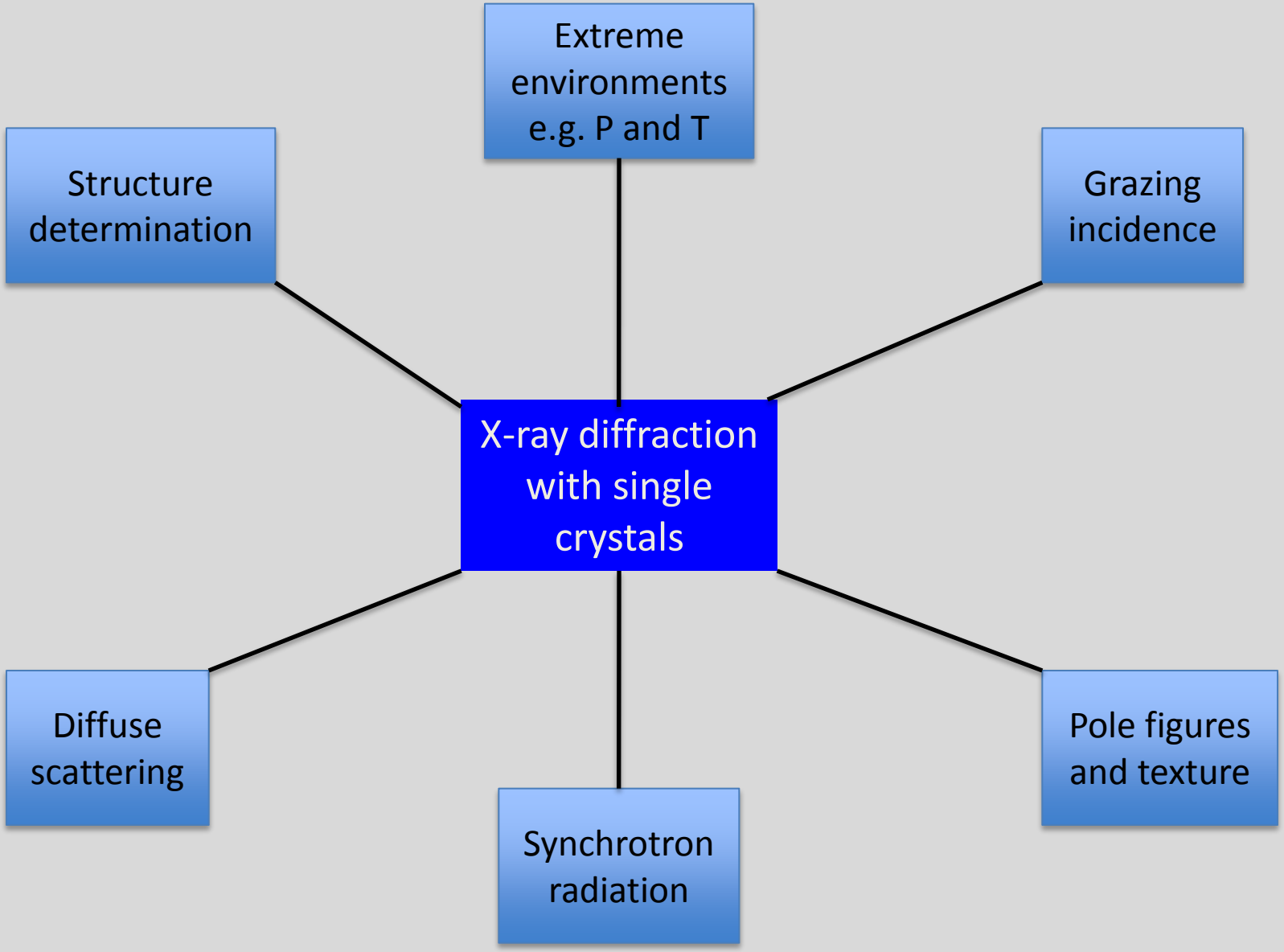
Materials chemistry with X-rays and neutrons

Ubiquitous use of single crystal X-rays methods

Use of neutrons

Powder methods and Rietveld refinement

Structure determination with powders


Extreme environments e.g. P and T
Structure determination
Grazing incidence
X-ray diffraction with single crystals
Diffuse scattering
Synchrotron radiation
Pole figures and texture

Impact of Single Crystal Methods

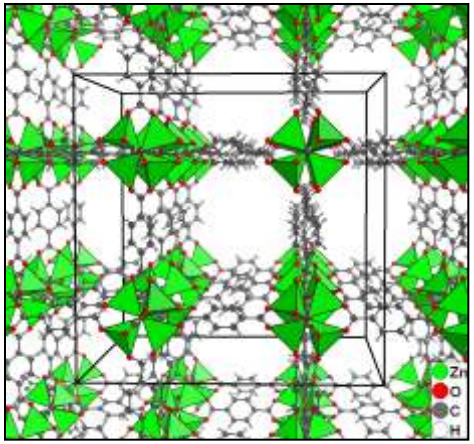
Structure determination

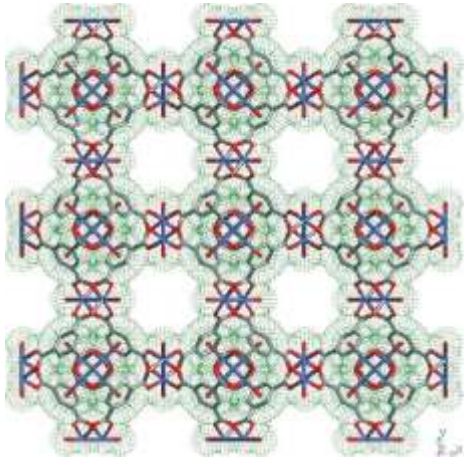
- Molecular crystals (organics and inorganics)
- Organometallics
- Supramolecular compounds
- Coordination compounds
- Crystalline polymers
- Compound semiconductors
- Minerals, e.g. aluminosilicates
- Metal oxides (ferroelectrics, superconductors, etc)
- Metal-organic frameworks

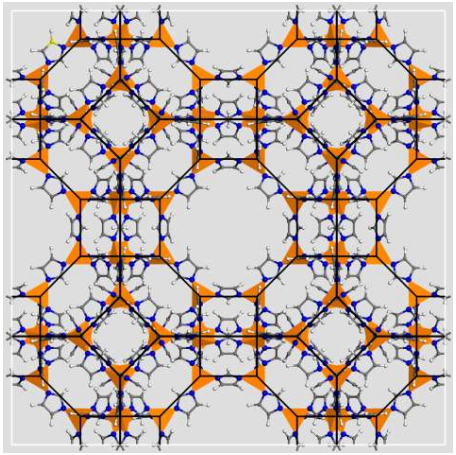
Special applications

- High pressure studies
- Structure of surfaces

Porous Metal-Organic Frameworks (MOFs)





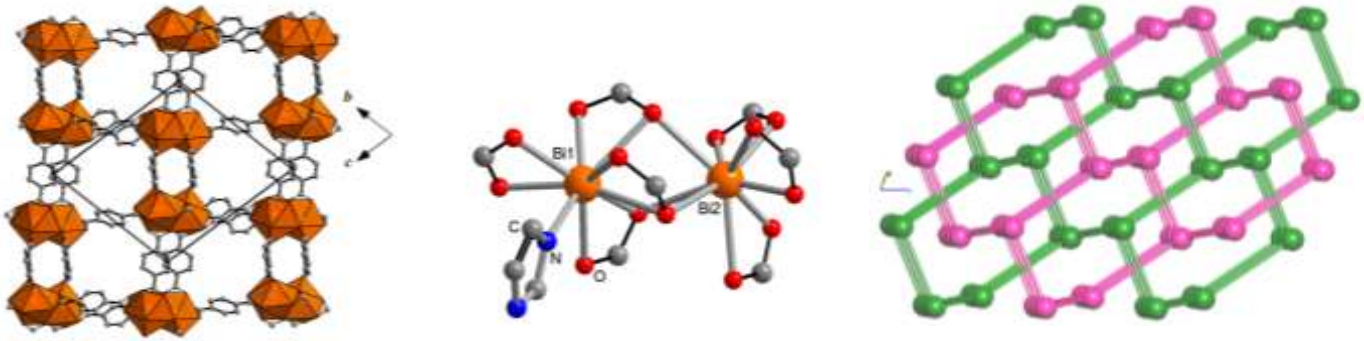


MOF-5 **HKUST-1** **ZIF-8**

- Porous MOFs are being explored for a wide variety of potential applications, including separations, hydrogen storage, catalysis, sensors and drug delivery
- Many frameworks are based upon simple inorganic structures established by Lawrence Bragg 100 years ago
- Many, such as MOF-5 above, adopt primitive cubic structures (**pcu**)

MOFs with the Diamond Topology (dia)

$[Bi_4(1,4\text{-BDC})_7(HIm)].(DMA)_2(DMF)_2$ adopts a 2-fold interpenetrated **dia** structure



$[Bi(1,4\text{-BDC})_2].(DMA)(DMF)$ forms a 3-fold interpentrated ***dia***

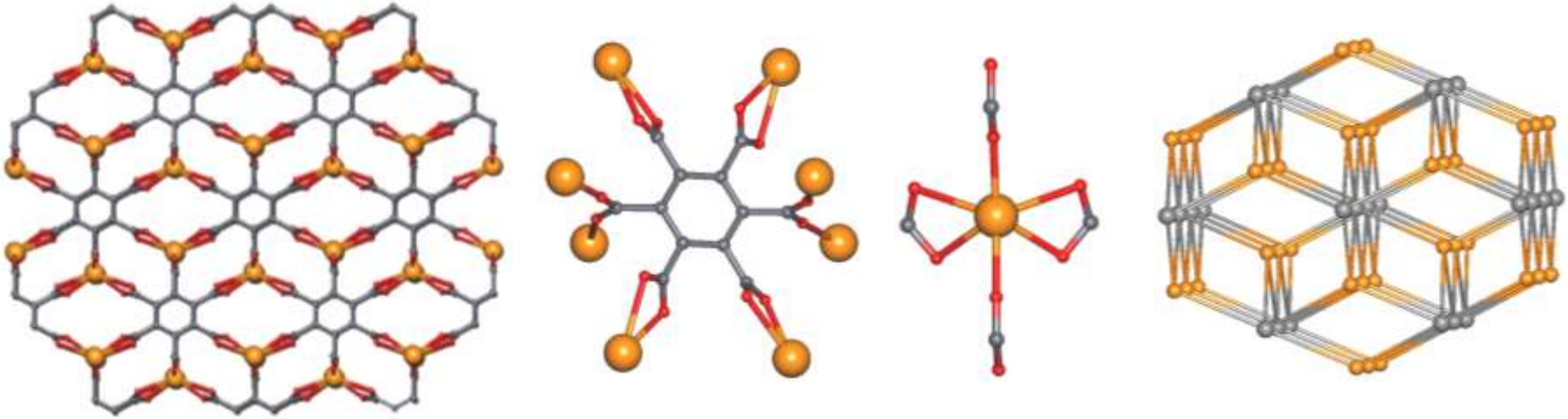
- There are around 500 such MOF structures

W. H. Bragg and W. L. Bragg, *Proc. Roy. Soc*. A 89, 277 (1913)

A. Thirumurugan and A. K. Cheetham*, Eur. J. Inorg. Chem.* **2010,** *3823*

MOFs with the Fluorite Topology (flu)

La_2 (mellitate)$(H_2O)_3$ *flu* net



There are 8- and 4- connected nodes

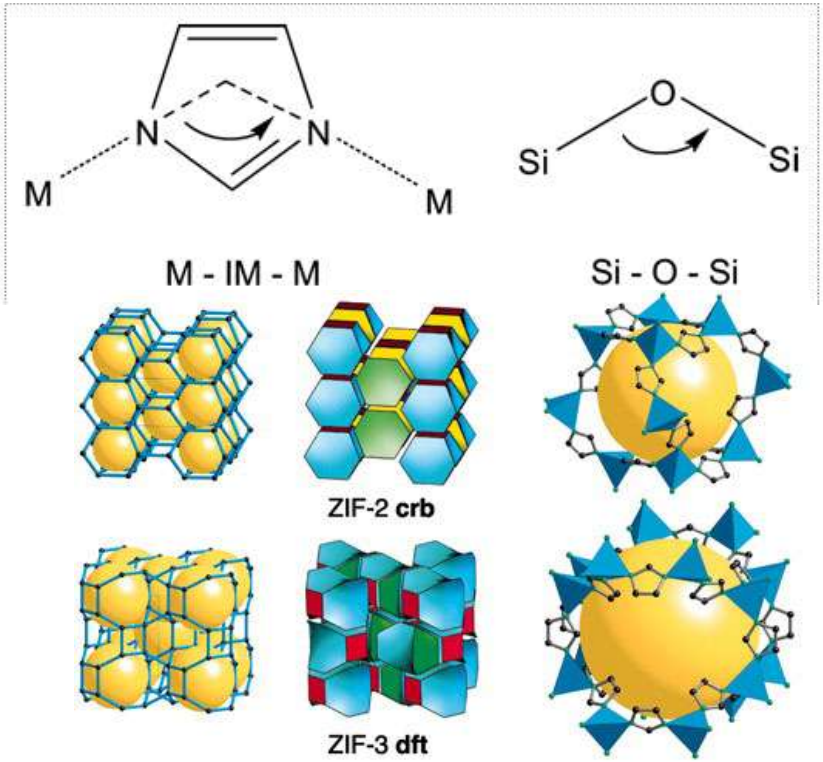
- There are around ~35 such structures

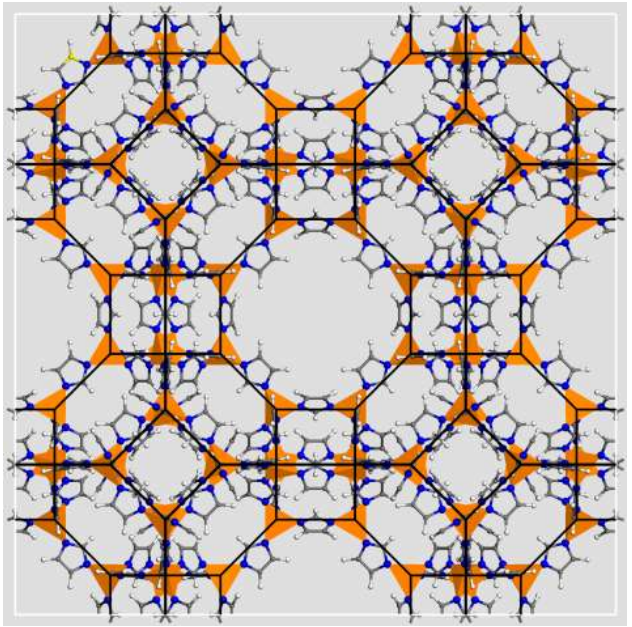
W. L. Bragg, *Proc. Roy. Soc*. A 89, 248 (1913)

SS-Y. Chui, A. Siu, X. Feng, ZY Zhang, TC-W. Mak and ID Williams, *Inorg. Chem. Commun*., 2001, 4, 467

ZIFs: Zeolitic Imidizolate Frameworks

- **In ZIFs, the Si-O-Si linkages found in silicates are replaced by Zn-Imidazolate-Zn linkages:**
- **$Zn(IM)_2$ is neutral and forms a range of zeolite analogues, such as LTA**

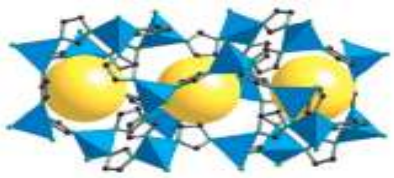




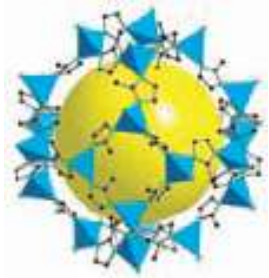
ZIF LTA-type structure
(i.e. zeolite-A)

The structure of α- and β-quartz
W. H. Bragg and R. E. Gibbs, *Proc. Roy. Soc*. A 109, 405 (1925)

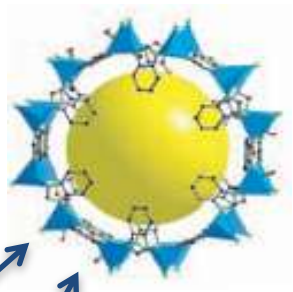
ZIF Topologies are Controlled by Substituents on the Imidazoles



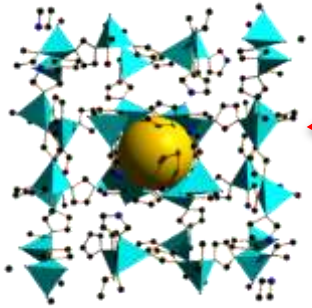
ZIF-4
(cag) Pbca



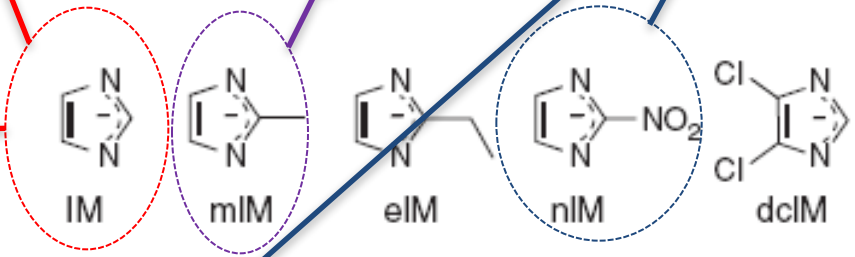
ZIF-8
(sod)
I-43m

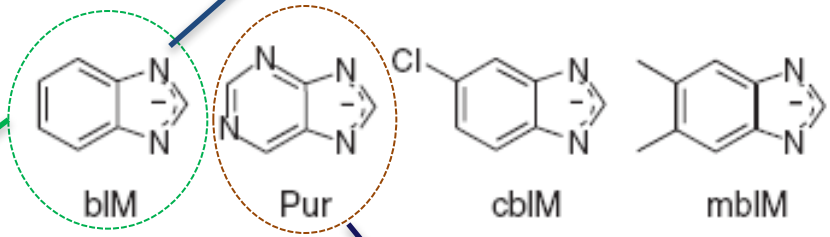


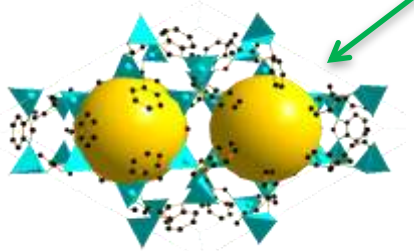
ZIF-68
(gme)
$P6_3/mmc$



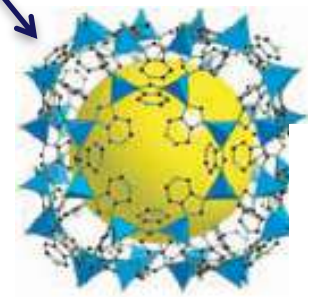
Dense (zni)
$I4_1cd$







ZIF-7 & ZIF-9
(sod) R-3

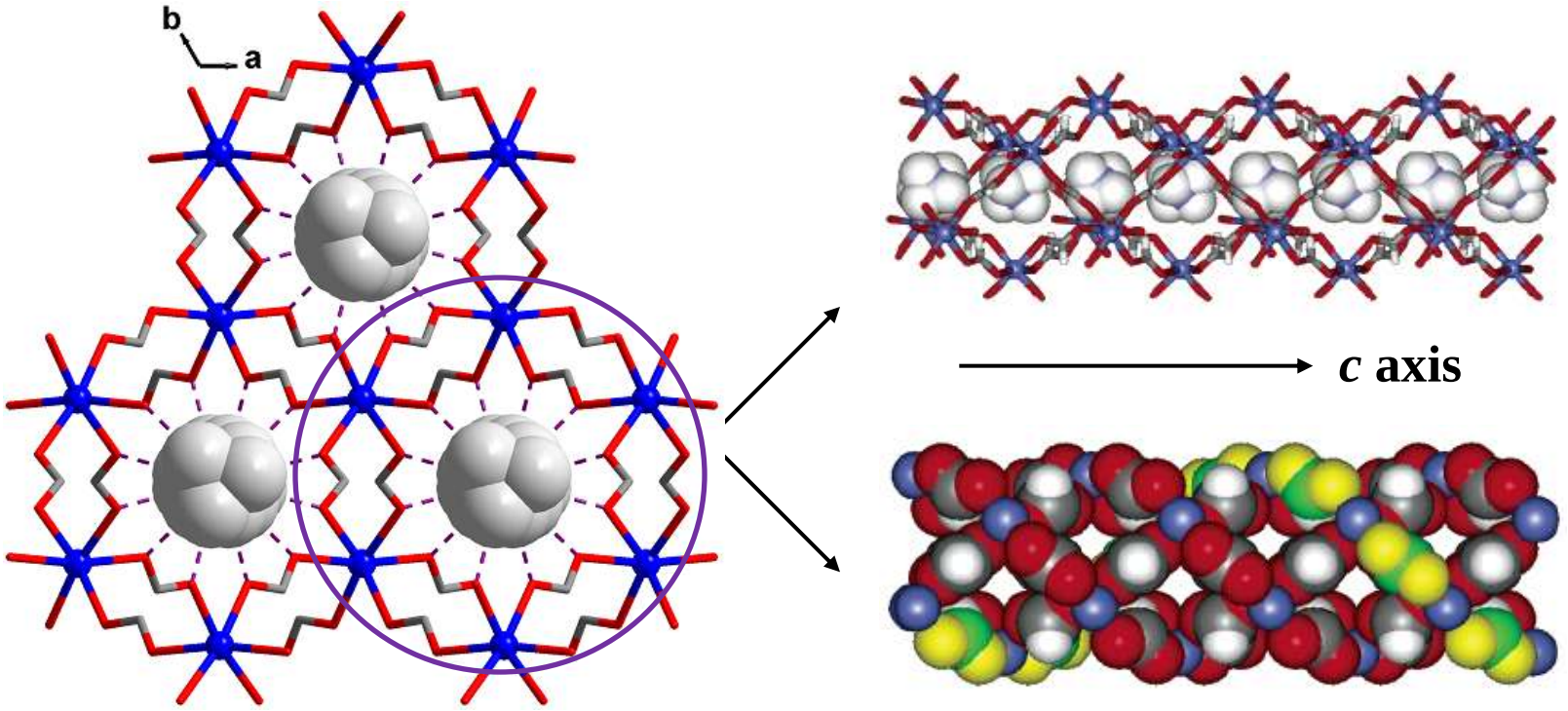


ZIF-20,
(LTA)
Pm-3m

$[NH_4][Zn(HCOO)_3]$

Highly anisotropic crystal structure, reported in 2006

Homochiral 3D framework



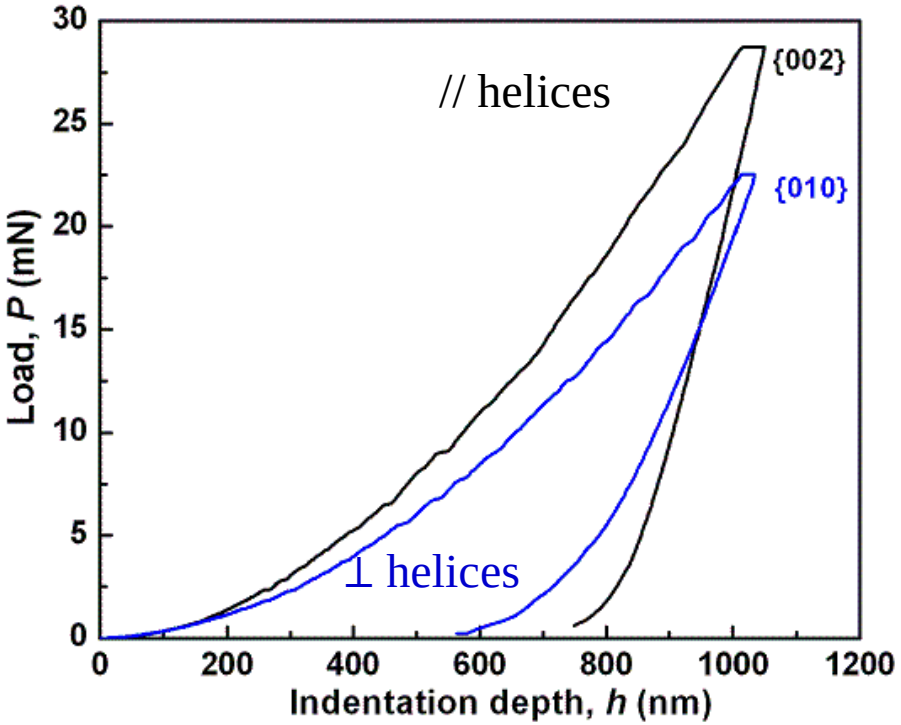
Triple helices along *c* axis

Inorg. Chem. **2006**, *46*, 437.

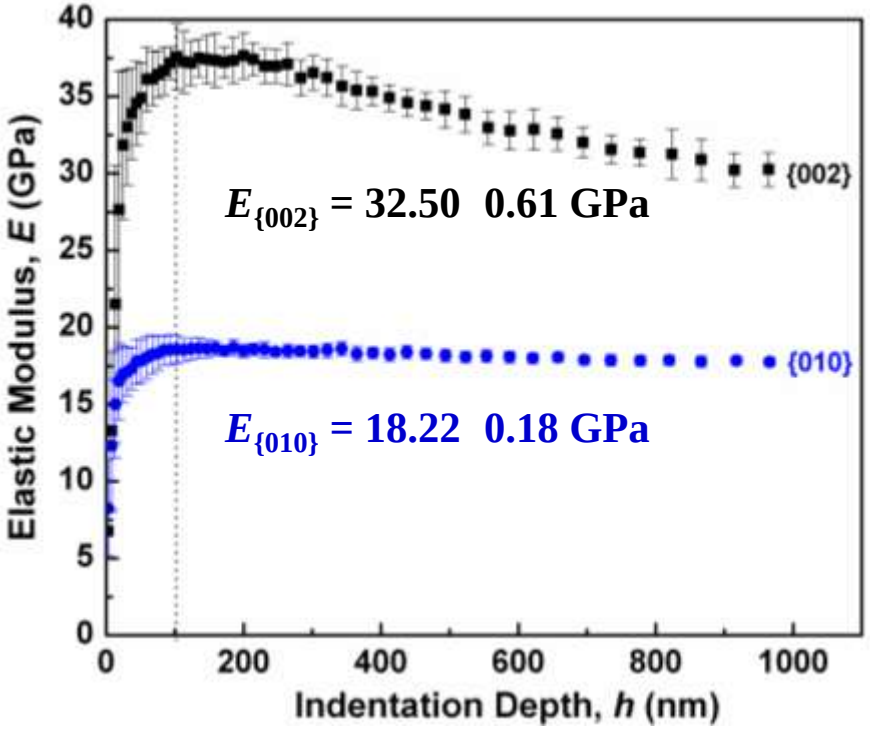
Mechanical Properties of $[NH_4][Zn(HCOO)_3]$

- **Nanoindentation Study: high mechanical anisotropy**

P-h plots



Young's Modulus

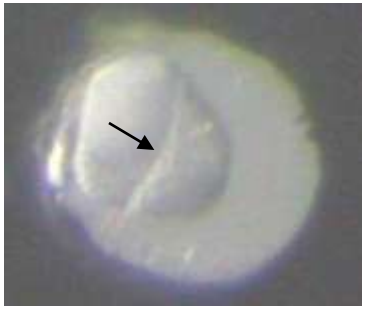


Li, Probert, Kosa, Bennett, Thirumurugan, Burwood, Parrinell, Howard & Cheetham, *JACS* (2012)

Compressibility of $[NH_4][Zn(HCOO)_3]$

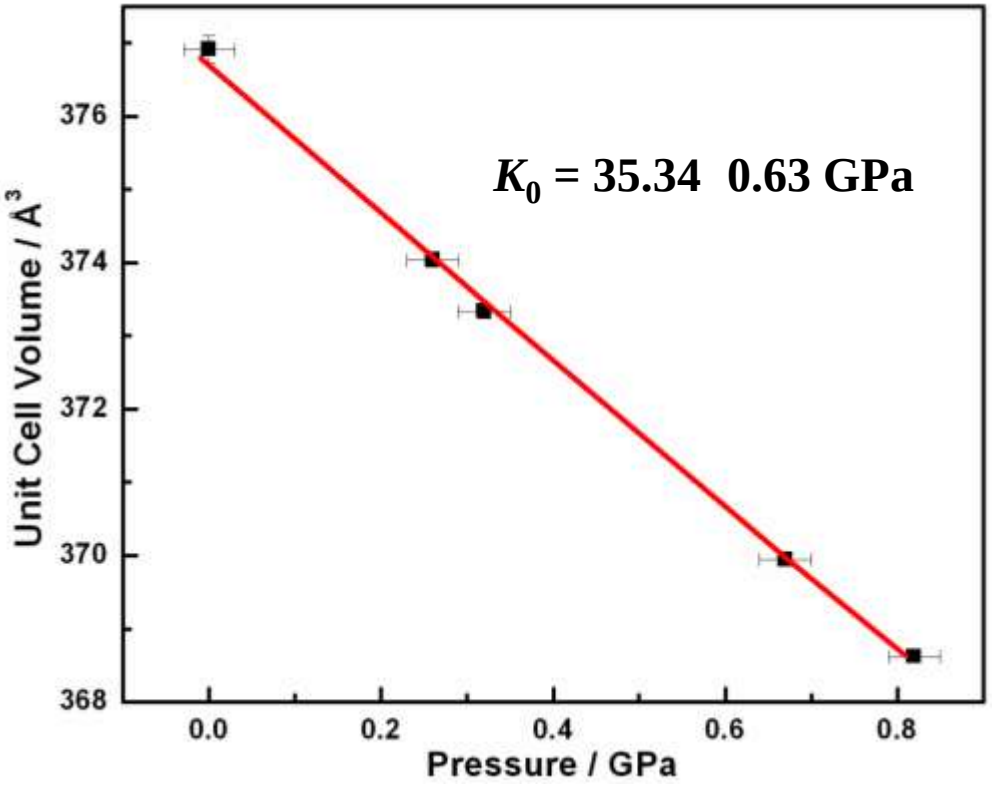
- **High-Pressure Single-Crystal X-ray Diffraction**

0.26 GPa



0.95 GPa

Birch-Murnaghan fitting

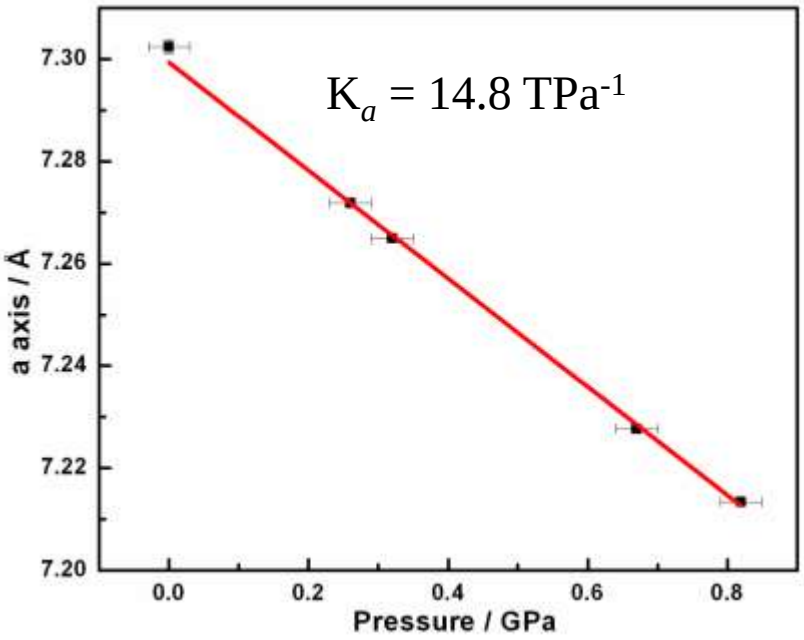


Li, Probert, Kosa, Bennett, Thirumurugan, Burwood, Parrinello, Howard & Cheetham, *J. Amer. Chem. Soc. 134* 11940, (2012)

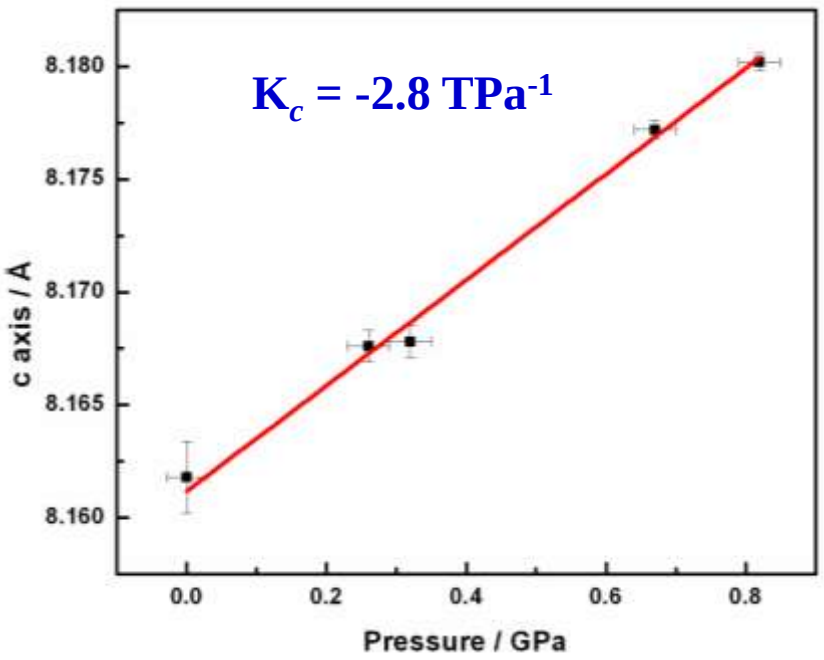
Negative Linear Compressibility in $[NH_4][Zn(HCOO)_3]$

Li, Probert, Kosa, Bennett, Thirumurugan, Burwood, Parrinello, Howard & Cheetham, *J. Amer. Chem. Soc.* 134, 11940 (2012)

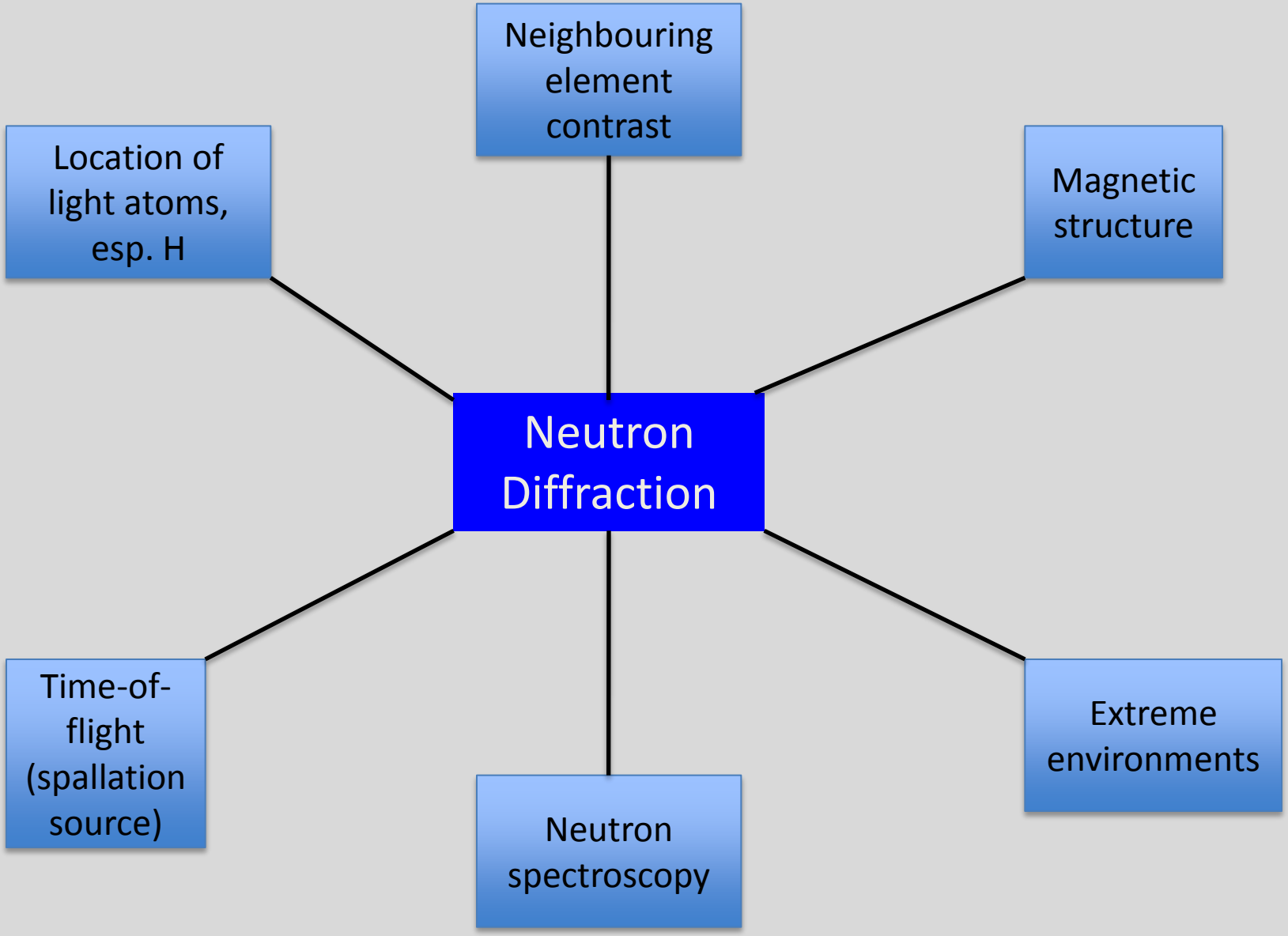
Shrinkage of *a* axis

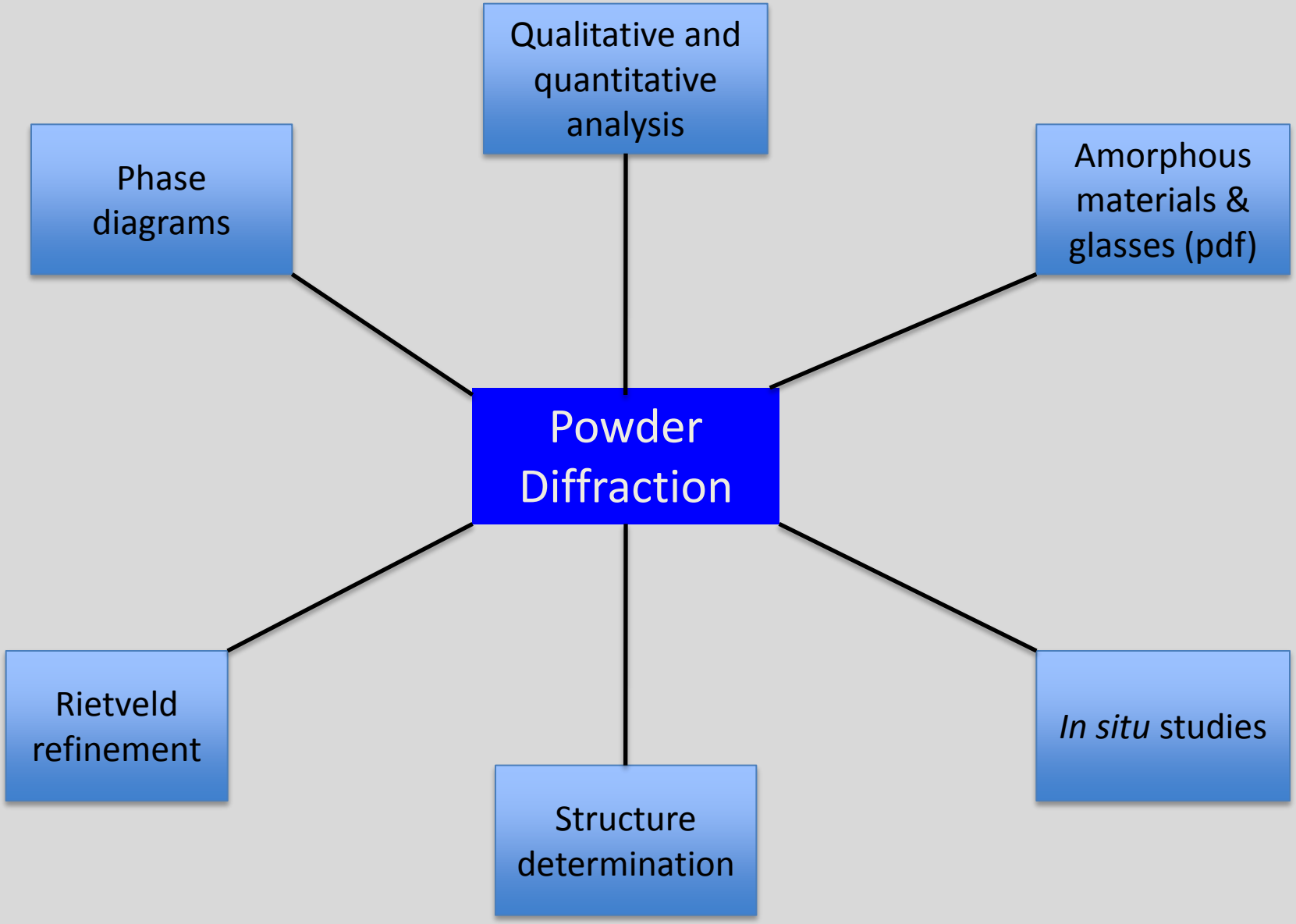


Expansion of *c* axis



Other examples: Inorganic materials: trigonal Se (-1.2 TPa^{-1}); α-cristobalite structured $BAsO_4$ (-2.0 TPa^{-1}); $Ag_3[Co(CN)_6]$ (-5.0 TPa^{-1}); $KMn[Ag(CN)_2]_3$ (-12.0 TPa^{-1})
Organic materials: $CD_3DO{\bullet}D_2O$ (-3.8 TPa^{-1}) *Science* **2011**, *331*, 742; *J. Am. Chem. Soc.* **2012**, DOI: ja20490


Neighbouring element contrast
Location of light atoms, esp. H
Magnetic structure
Neutron Diffraction
Time-of-flight (spallation source)
Neutron spectroscopy
Extreme environments


Qualitative and quantitative analysis
Phase diagrams
Amorphous materials & glasses (pdf)
Powder Diffraction
Rietveld refinement
Structure determination
In situ studies

Powder Diffraction – a Poor Man's Tool!

Pre-1970:

Table 1. Experimental and calculated structure factors

h, k, l	F^*_{obs}	F_{calc}
111	21.04 ± 0.21	20.80
200	23.60 ± 0.64	24.10
220	70.81 ± 0.18	70.81
311	23.07 ± 0.14	23.15
222	22.72 ± 0.37	22.86
400	62.60 ± 0.81	63.63
331	21.95 ± 0.37	21.64
420	22.36 ± 0.39	22.07
422	61.50 ± 1.03	60.68
440	55.60 ± 0.60	55.55
531	19.79 ± 0.65	19.49
620	51.37 ± 0.46	51.47

* Error given is a standard deviation arising from the counting statistics except for the (311), (222), (331), (420) and (531) peaks which also include an estimate of the error introduced in separating overlapping peaks.

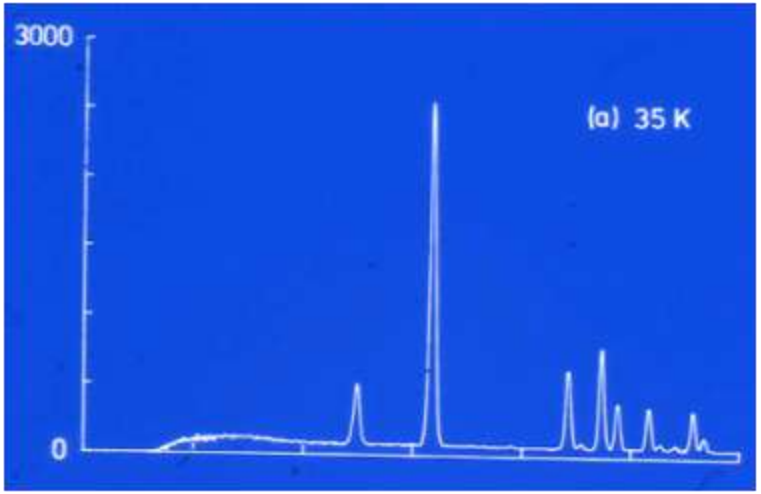


Table 2. (Ca/Y) $F_{2.10}$: *Structure parameters of average cell*

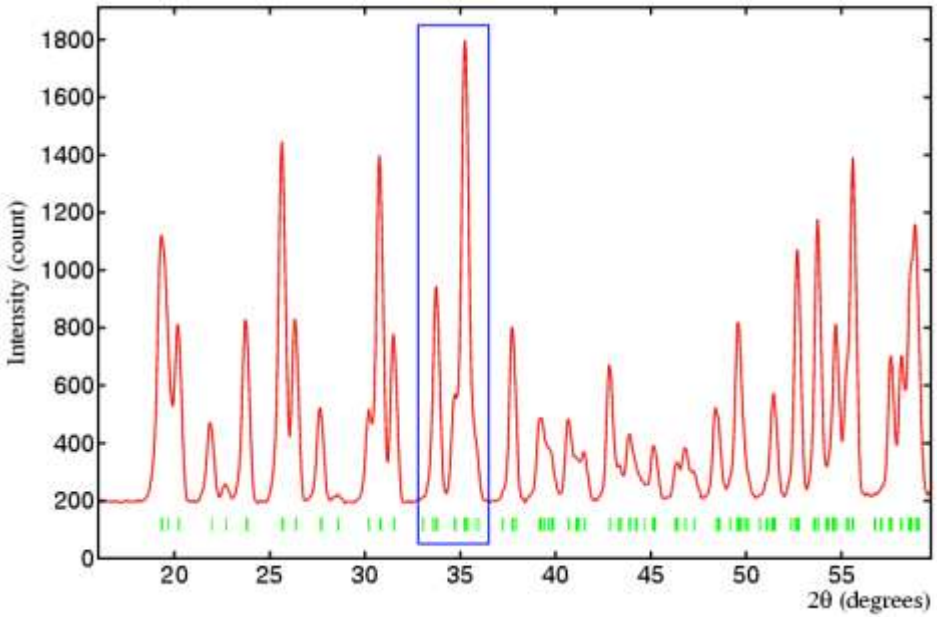
atom	co-ordinates in average cell			contribution to $2 + x$ in (Ca/Y) F_{2+x}
	x	y	z	
lattice F	0.25	0.25	0.25	1.88 (0.04)
interstitial F′	0.5	v	v	0.14 (0.03)
interstitial F″	w	w	w	0.08 (0.03)

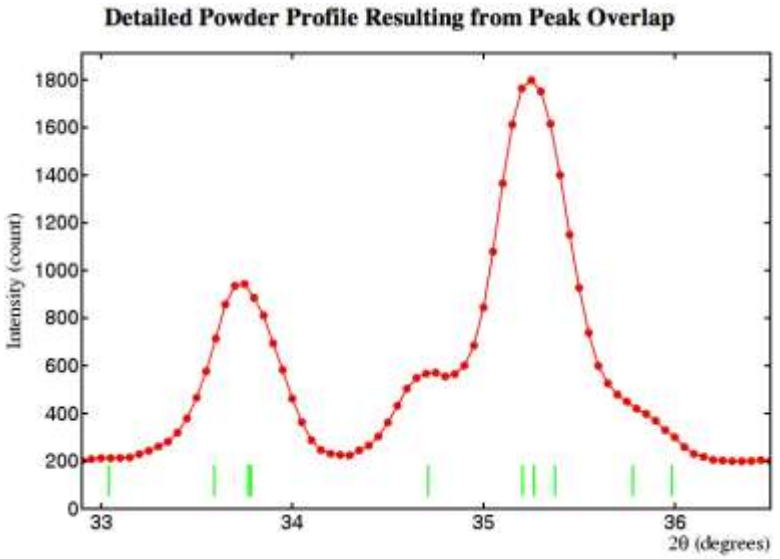
v = 0.36 (0.01), w = 0.42 (0.01), R_{index} = 0.85%.
Estimated standard deviations in parentheses.

Cheetham et al., *Solid State Comm*. 8, 171 (1970)

Powder Diffraction – Complex Patterns???

How to proceed with overlapping peaks?



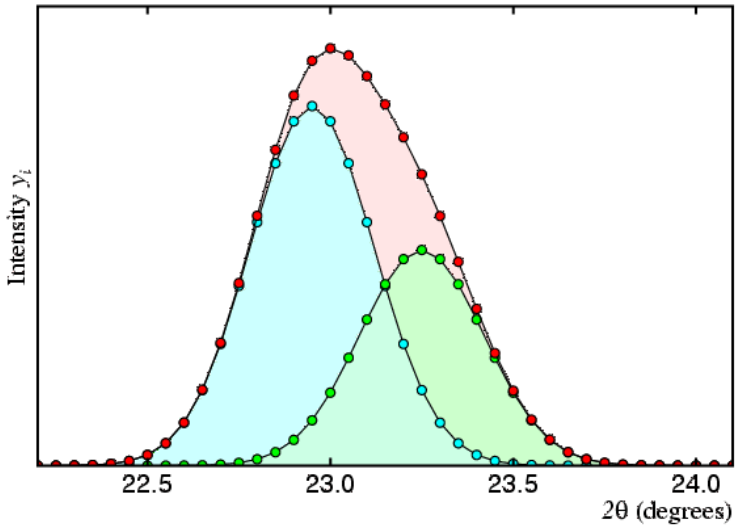


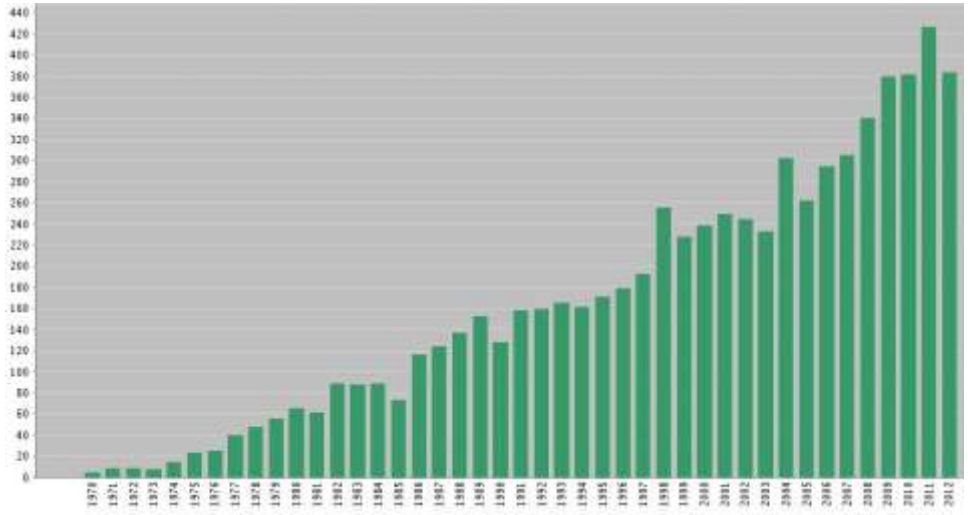
There are 10 peaks in the highlighted region!

Rietveld Method - 1969

Available 1972 onwards:

The Rietveld method analyses powder diffraction data by a curve-fitting procedure, rather than measuring individual I_{hkl} values. Initially used a Gaussian shape function for neutron data, it was extended in 1977 to X-ray data (with more complex shape functions).





H. M. Rietveld, *J. Appl. Cryst.* 2, 65 (1969) – 7099 citations

11,355 papers have Rietveld in the abstract or key words!

Rietveld Method Refinement of Complex Structures: $TiNb_2O_7$ and $Ti_2Nb_{10}O_{29}$

Post-1972:

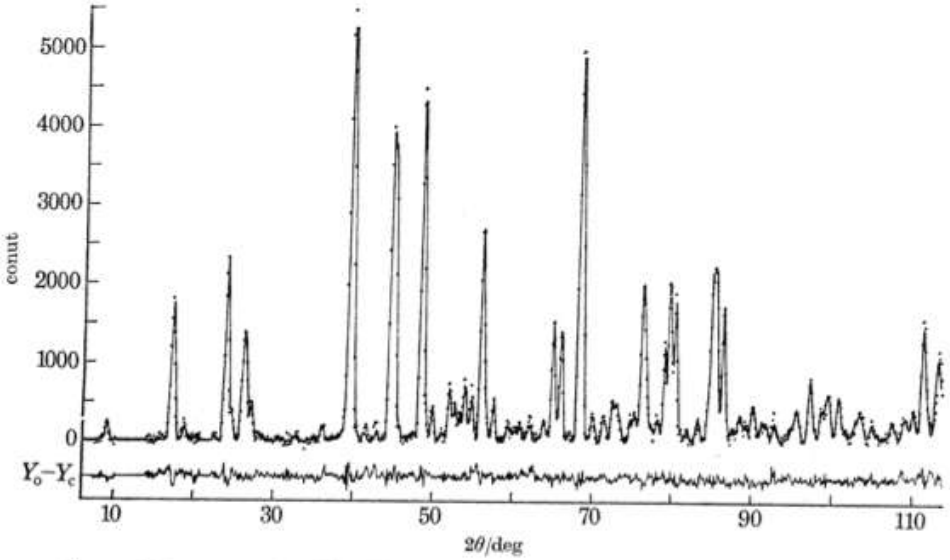


FIGURE 3. Neutron powder diffraction profile for $TiNb_2O_7$. Lines and points represent calculated and observed profiles, respectively. A difference curve is shown.

TABLE 3. FRACTIONAL ATOMIC COORDINATES FOR ORTHO-$Ti_2Nb_{10}O_{29}$

(Value in parentheses is the estimated standard deviation in the last place.)

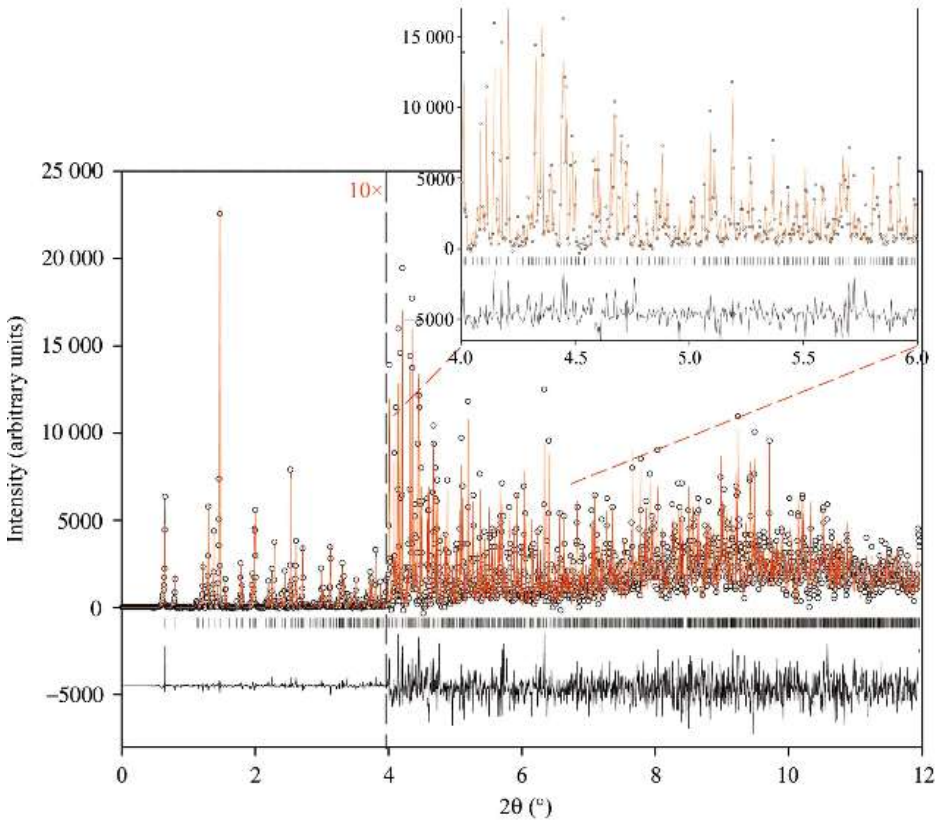
atom	x	y	z
M 1	0.0503 (6)	0	0.0387 (11)
M 2	0.0496 (12)	0	0.6758 (18)
M 3	0.0497 (5)	0	0.8492 (10)
M 4	0.1812 (7)	0	0.8546 (9)
M 5	0.1833 (7)	0	0.6688 (8)
M 6	0.1827 (7)	0	0.0366 (10)
O 1	¼	0	0.0370 (15)
O 2	¼	0	0.6624 (15)
O 3	¼	0	0.8497 (15)
O 4	0.0363 (5)	0	0.5594 (11)
O 5	0.0424 (6)	0	0.1493 (10)
O 6	0.0436 (6)	0	0.7582 (10)
O 7	0.0307 (6)	0	0.3488 (12)
O 8	0.0249 (6)	0	0.9490 (11)
O 9	0.1079 (6)	0	0.0419 (11)
O 10	0.1155 (7)	0	0.6673 (9)
O 11	0.1116 (6)	0	0.8571 (9)
O 12	0.1824 (6)	0	0.5620 (10)
O 13	0.1788 (7)	0	0.1401 (8)
O 14	0.1854 (6)	0	0.7547 (8)
O 15	0.1771 (7)	0	0.3514 (12)
O 16	0.1758 (6)	0	0.9478 (10)

Remember that the Rietveld method is for *refinement* only and does not *solve* structures. It requires prior knowledge of the unit cell, space group, and approximate starting coordinates for the least

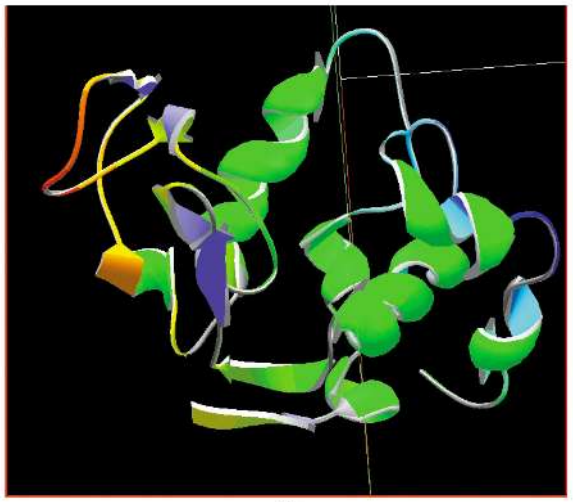
Von Dreele & Cheetham, *Proc. Roy. Soc*. A 338, 331 (1974)

Very Complex Structures – Proteins!

2005: Synchrotron X-ray diffraction with proteins



Solution and refinement of the structure of hexagonal turkey egg-white lysozyme: hexagonal, space group $P6_122$, unit-cell parameters a=71.0862 (3), c=85.0276 (5) A

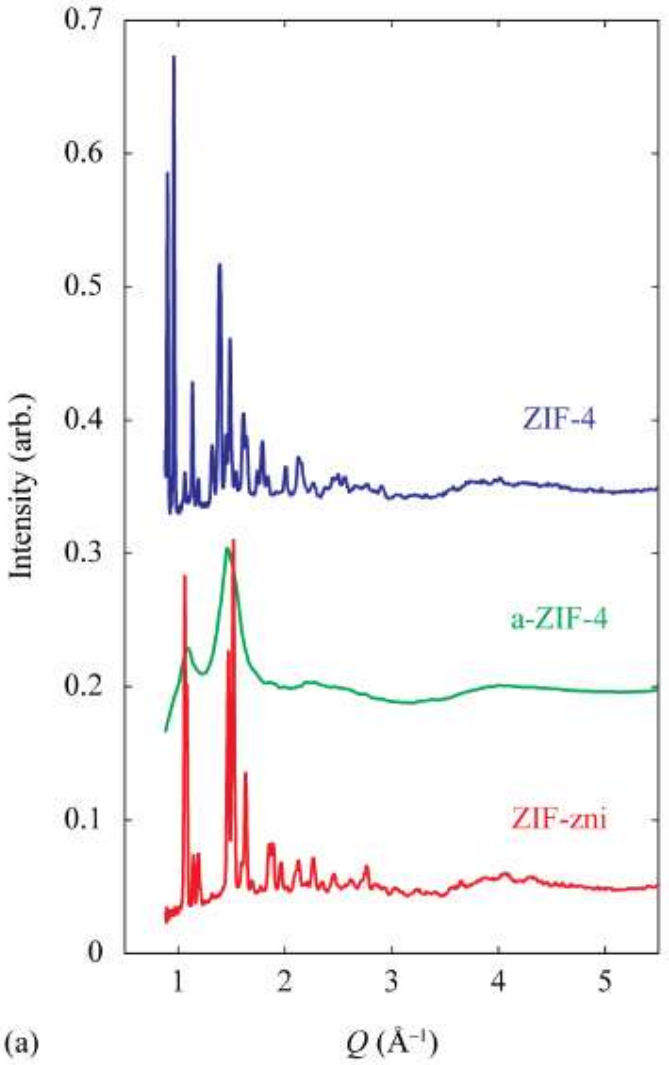


Margiolaki, Wright, Fitch, Fox & Von Dreele, *Acta Cryst.* D61, 423 (2005)

Can we make Amorphous ZIFs?

Silica is well-known as a glass-forming material. Can we do the same thing with a ZIF?

High Temperature Neutron Diffraction of ZIF-4

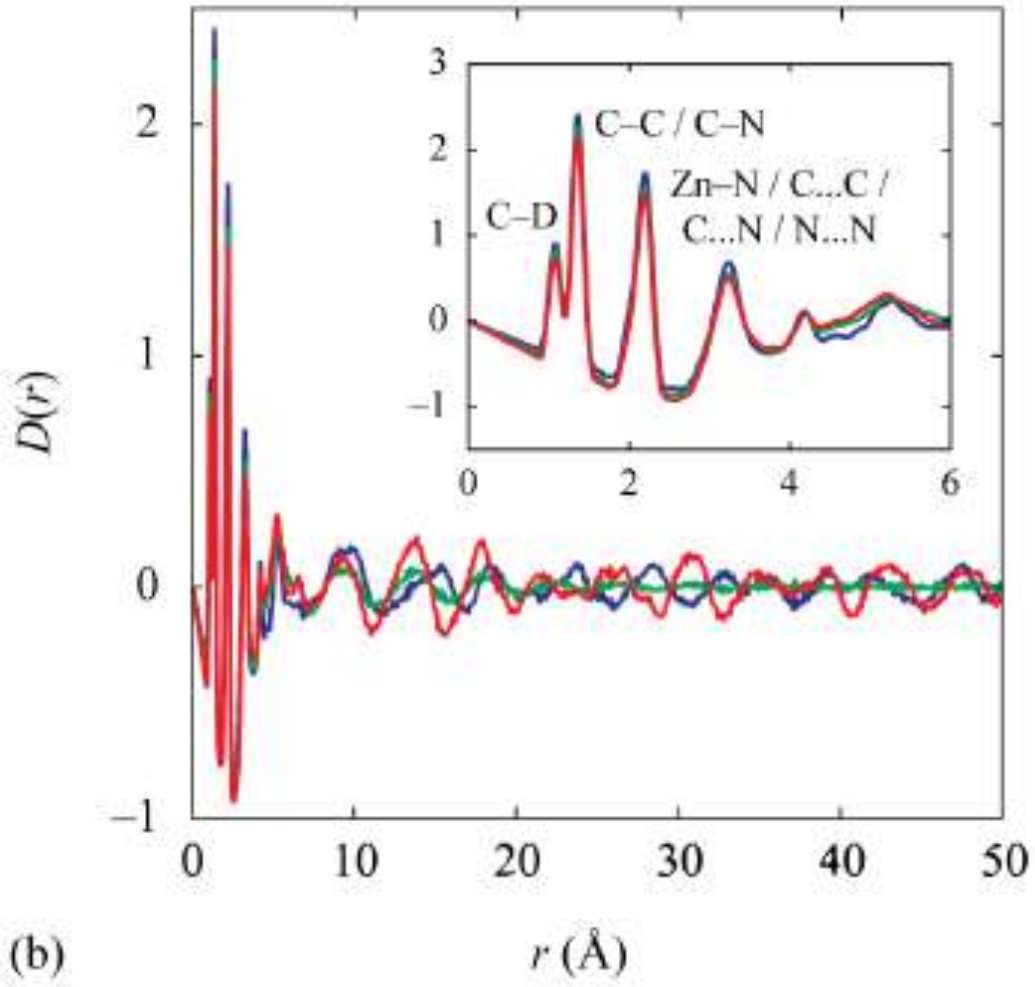


Data collection with perdeuterated ZIF-4 at ISIS

The initial ZIF-4 has an open structure which becomes apparently amorphous at ~300°C and then recrystallises as the dense ZIF (zni) at ~400°C

Bennett, Goodwin, Dove, Keen, Tucker, Barney, Soper, Bithell, Tan & Cheetham
Phys. Rev. Lett. 104, 115503 (2010)

Pair Distribution Functions

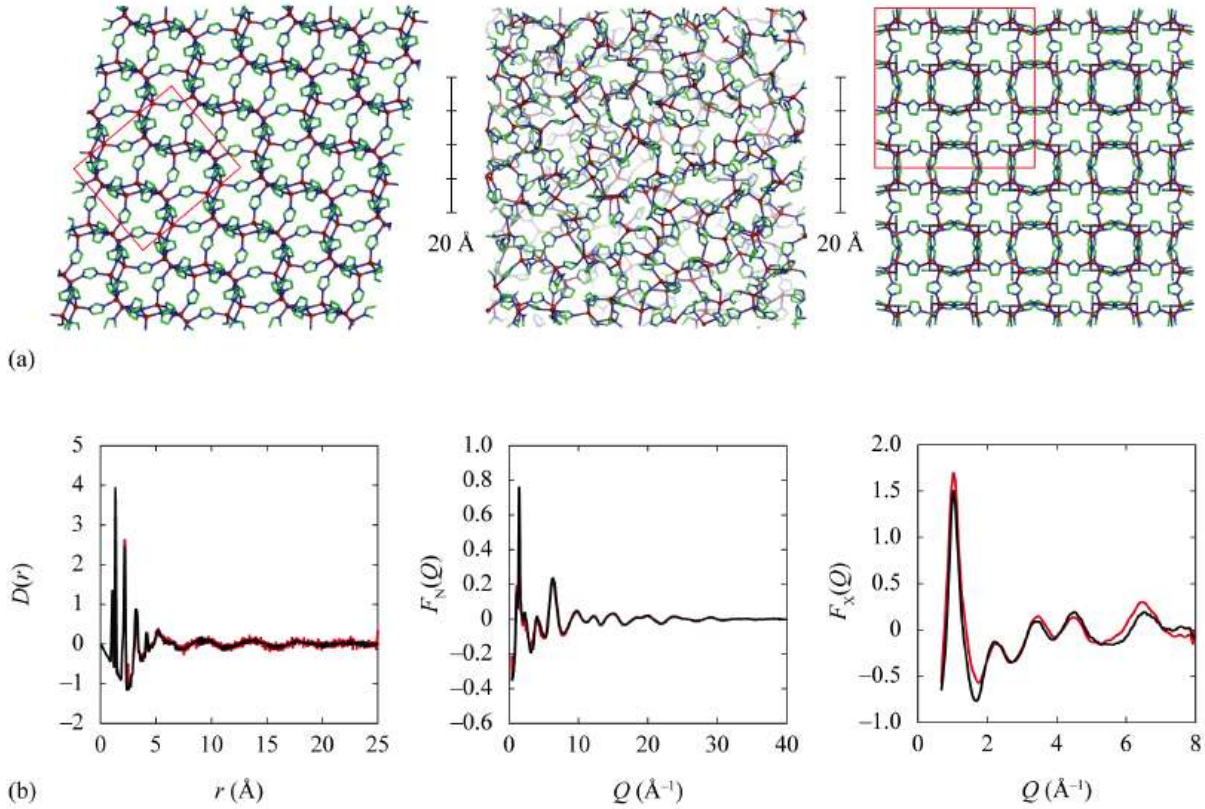


Key points:

- PDFs of ZIF-4, a-ZIF, and zni are very different at large r
- PDFs are very similar at short R (less than 10Å)

Structure of Amorphous ZIF by RMC

Model of the a-ZIF derived from Reverse Monte Carlo simulations



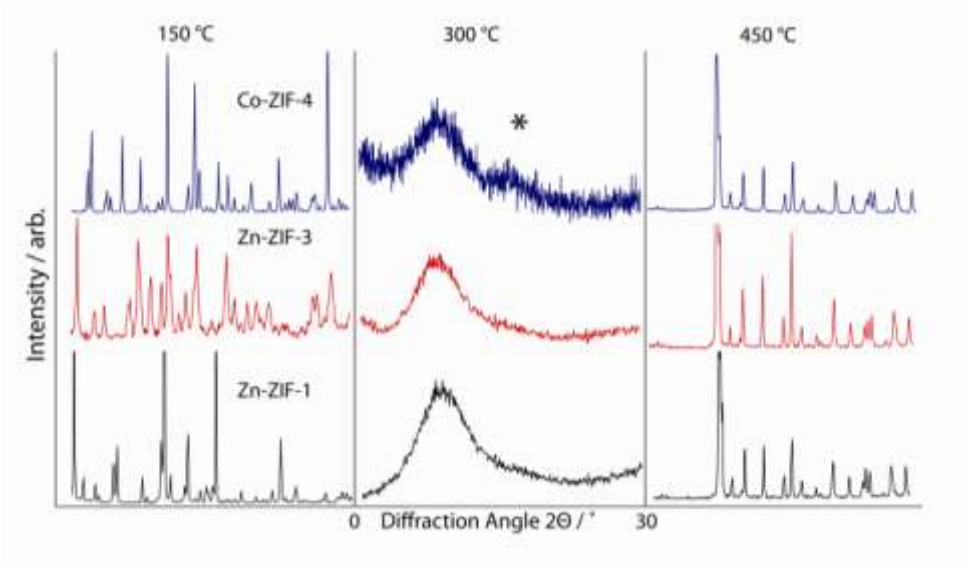
ZIF-4 a-ZIF zni

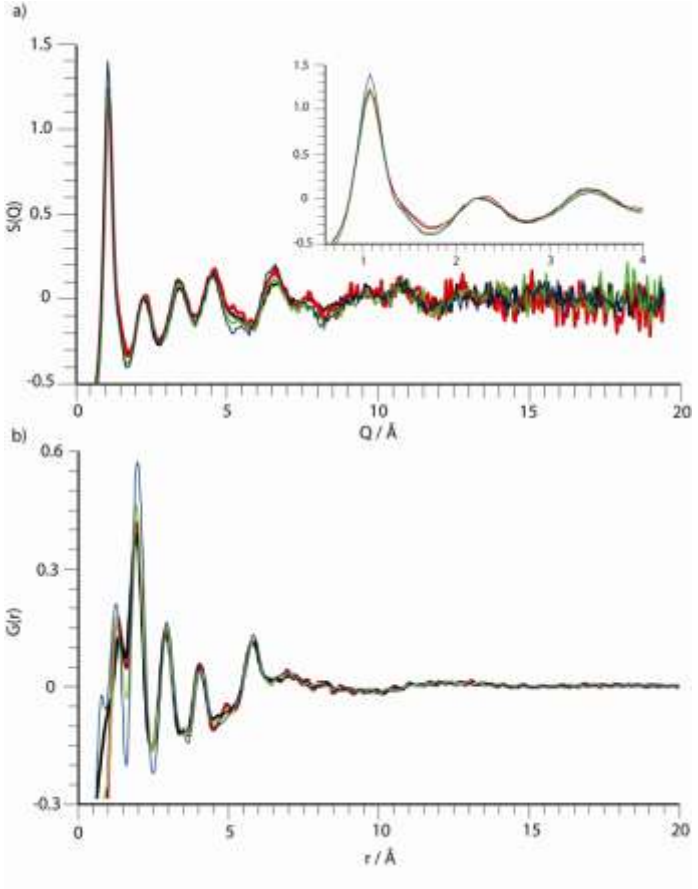
Formation of a-ZIF is irreversible on cooling. It can be brought to room temp.

Bennett et al. *PRL*, 104, 115503 (2010)

Can we make Amorphous ZIFs from other ZIF Frameworks by Heating?

The *Unsubstituted* ZIFs – ZIF-1, ZIF-3 and Co-ZIF-4 all undergo amorphization to give *a*-ZIF with the same structure as before, according to the X-ray pdfs and densities

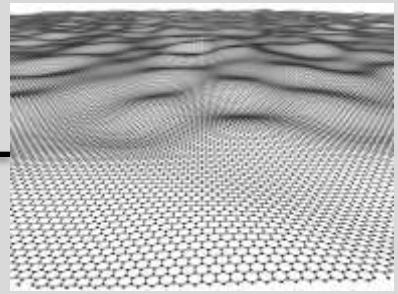




T. D. Bennett, D. A. Keen, J-C. Tan, E. R. Barney, A. L. Goodwin, and A. K. Cheetham, *Angew. Chemie Intl. Ed*. 50, 3067 (2011)

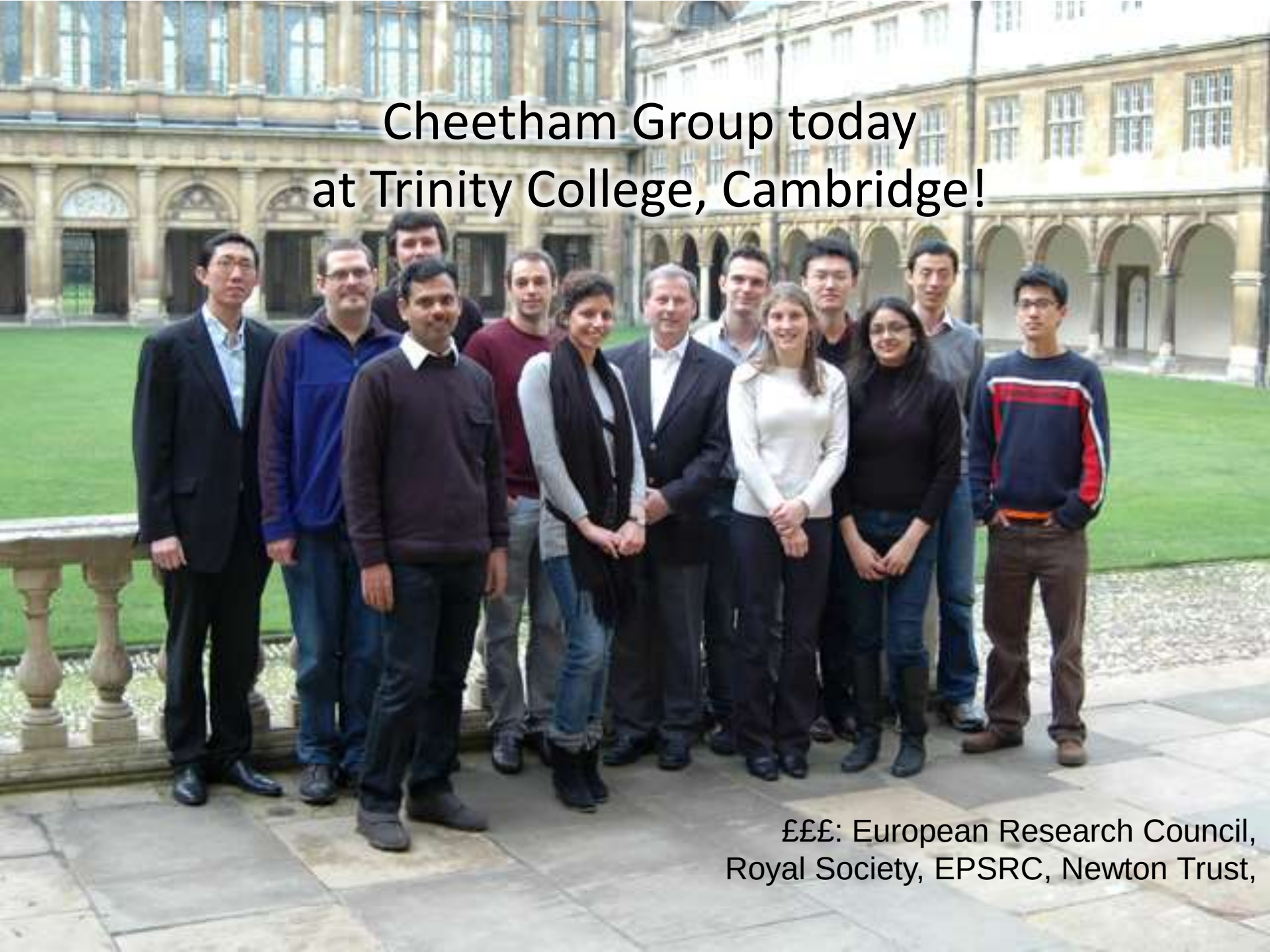
Major New Classes of Materials in the last 40 years

- Supramolecular materials (1970s) *
- Quasicrystals (1982) *
- Conducting polymers (1982) *
- Lithium electrodes for batteries (1984) ¶
- High temperature superconductors (1986) *
- Buckeyball, C_{60} (1985) *
- Carbon nanotubes (1991) §
- Quantum dots (1992) §
- GaN semiconductors (1993) #
- Colossal magnetoresistive manganates (1993)
- Inorganic-organic framework materials (1995)
- Graphene (2004) *



* Nobel prize § Kavli prize
¶ Japan Prize # Millenium Prize

Cheetham Group today at Trinity College, Cambridge!



£££: European Research Council, Royal Society, EPSRC, Newton Trust,