Pressure-Induced Amorphisation in ZrW_2O_8: A Structural Analysis based on Reverse Monte Carlo Modelling of Neutron and X-ray Total Scattering

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Talk Outline

- The local structure of crystalline ZrW_2O_8 – where is the flexibility?
- The structure of pressure-induced amorphous ZrW_2O_8 – implications for PIA more generally

Negative Thermal Expansion Materials

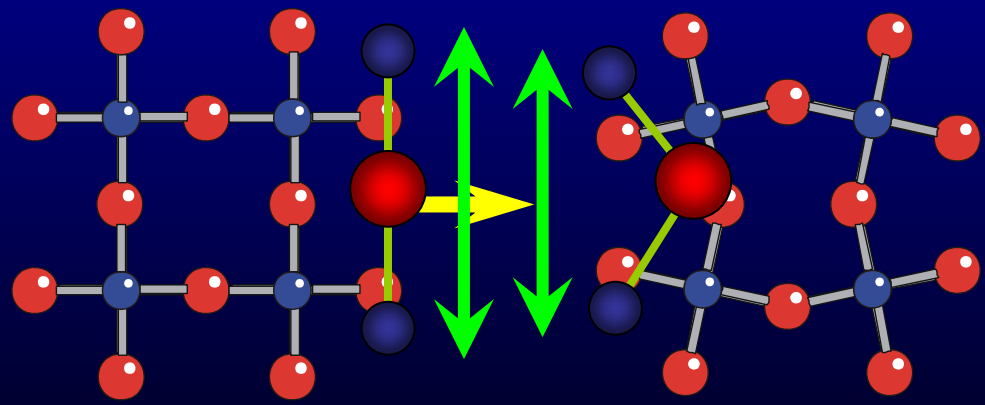
USES:

They can be mixed with POSITIVE thermal expansion (PTE) materials to produce composites with approximately ZERO thermal expansion (ZTE)

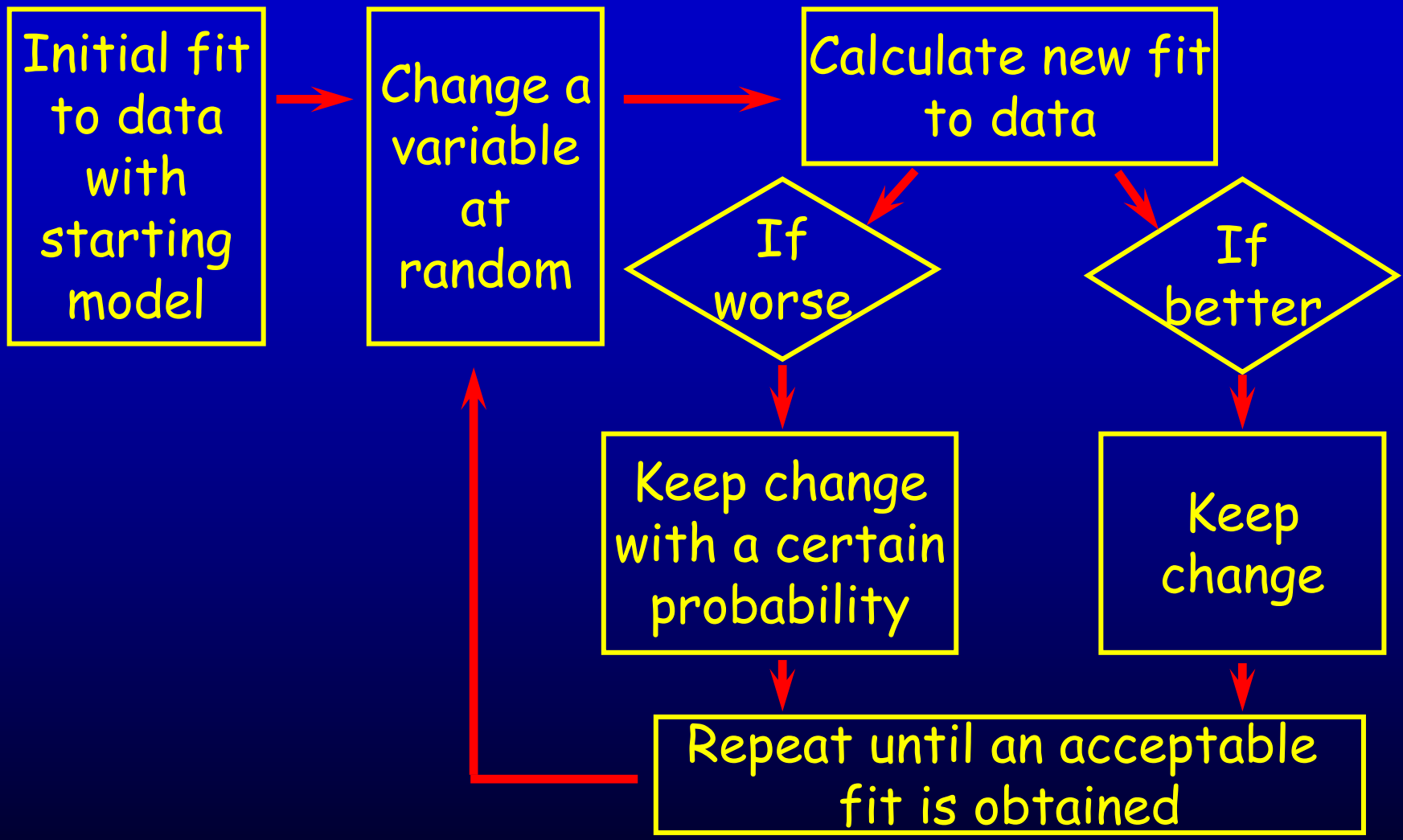
- High precision instruments
- Cooker hobs
- Astronomical telescope mirrors
- Casserole dishes

MECHANISM:

Since bonds expand when the material is heated, some other part of the structure must contract more than the bonds expand…



RMC Modelling Algorithm



RMC*Profile* for Modelling Crystalline Disorder

Use neutron and/or x-ray total scattering data collected at ISIS, ESRF etc.

Start with crystal structure from fitting the Bragg peaks

- Cell dimensions
- Density
- Initial atom positions

Refine with RMC

- Fit both S(Q) and *G*(r)
- Restrain bonds/polyhedra
- Fit Bragg profile

$$\chi^2_{RMC} = \sum_j \chi^2_j$$

$$\chi^2_{F(Q)} = \sum_j \left[F_{calc}(Q_j) - F_{box}(Q_j)\right]^2 / \sigma^2_{F(Q)}(Q_j)$$

$$\chi^2_{G(r)} = \sum_j \left[G_{calc}(r_j) - G_{expt}(r_j)\right]^2 / \sigma^2_{G(r)}(r_j)$$

$$\chi^2_{profile} = \sum_j \left[I_{calc}(t_j) - s' I_{expt}(t_j)\right]^2 / \sigma^2_{I(i)}(t_j)$$

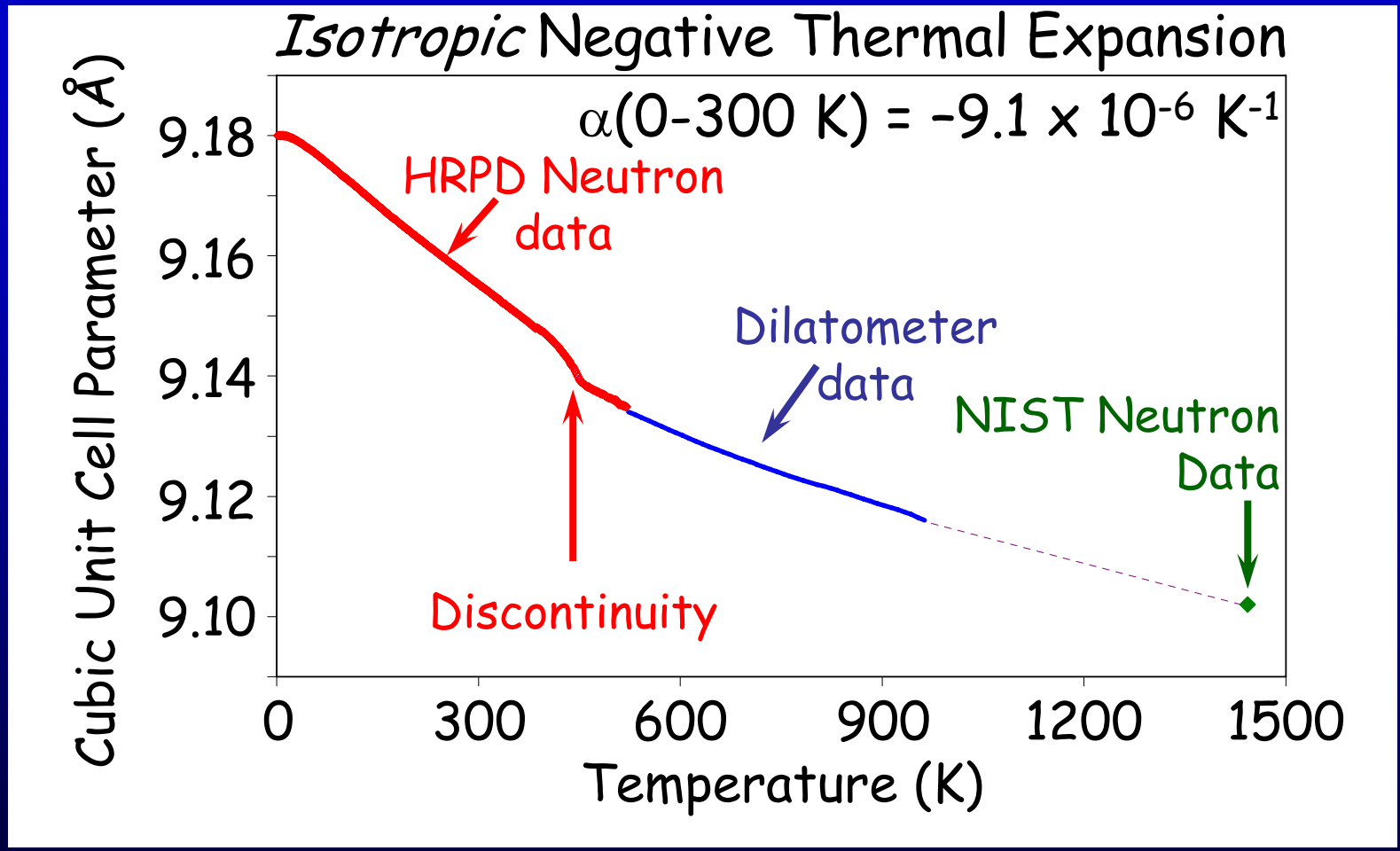
$$\chi^2_f = \sum_k w_k \left[f^{calc}_k - f^{req}_k\right]^2$$

$$I_{calc}(t_j) = \sum_{hkl} L_{hkl} \left|F(hkl)\right|^2 R_{hkl}(t_j - t_{hkl}) + B(t_j).$$

Tucker *et al*, *J Phys CM* **19** (2007) 335218

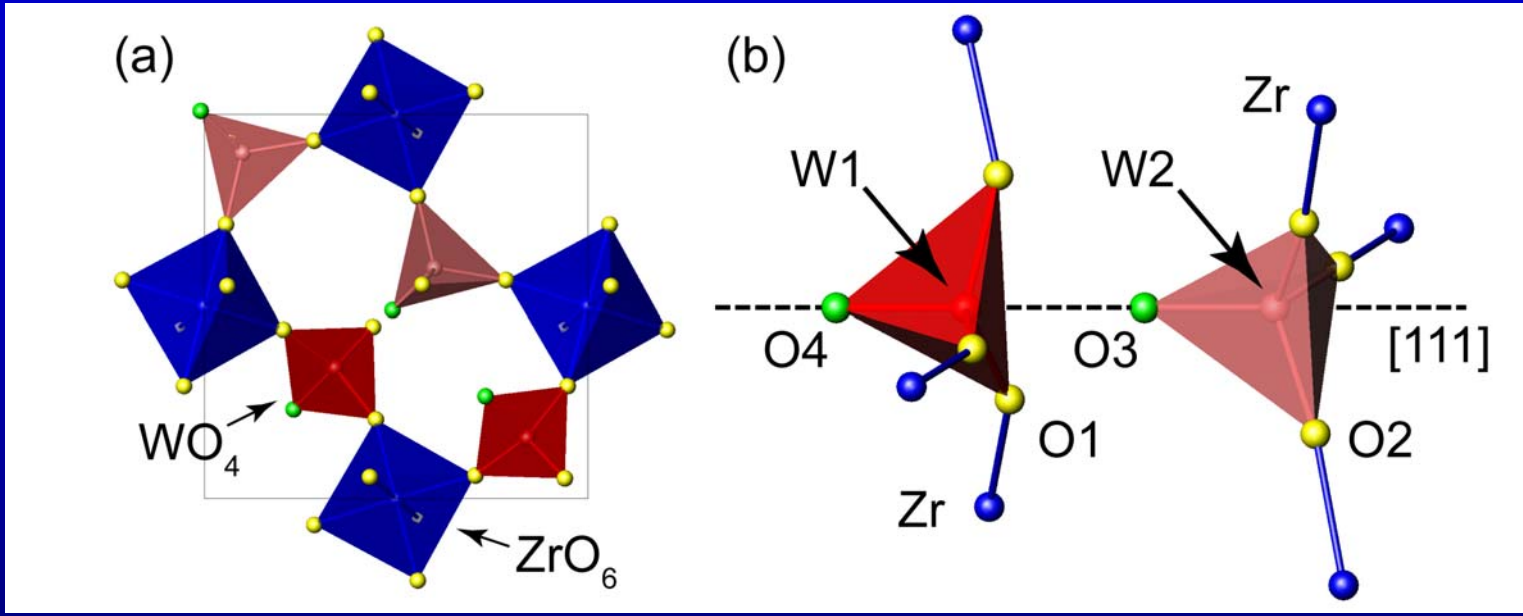
Produces a static 3-D atomistic model of the structure

Zirconium Tungstate, ZrW_2O_8



J S O Evans *et al*

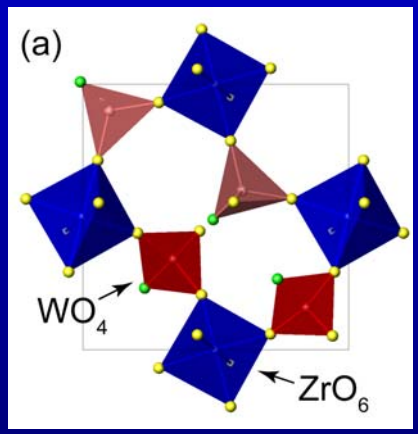
Structure of ZrW_2O_8

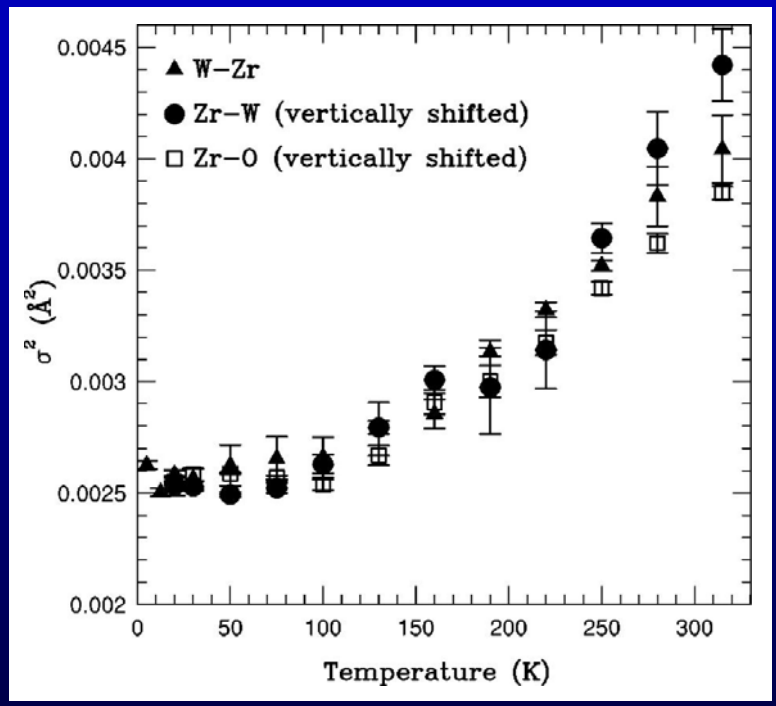


- A proposed mechanism for NTE is based on Rigid Unit Modes (RUMs).
- Flexible linkages facilitate the rotations and translations of the 'inflexible' polyhedra.
- The effect of increased rotations with increased temperature is to cause the polyhedral centres to come closer together

What are the 'rigid' polyhedra in ZrW_2O_8?

- Early work was based on 'rigid' units of ZrO_6 octahedra and WO_4 tetrahedra; the corner shared Zr-O-W linkages and under-bonded WO_4 tetrahedra provide the flexibility.

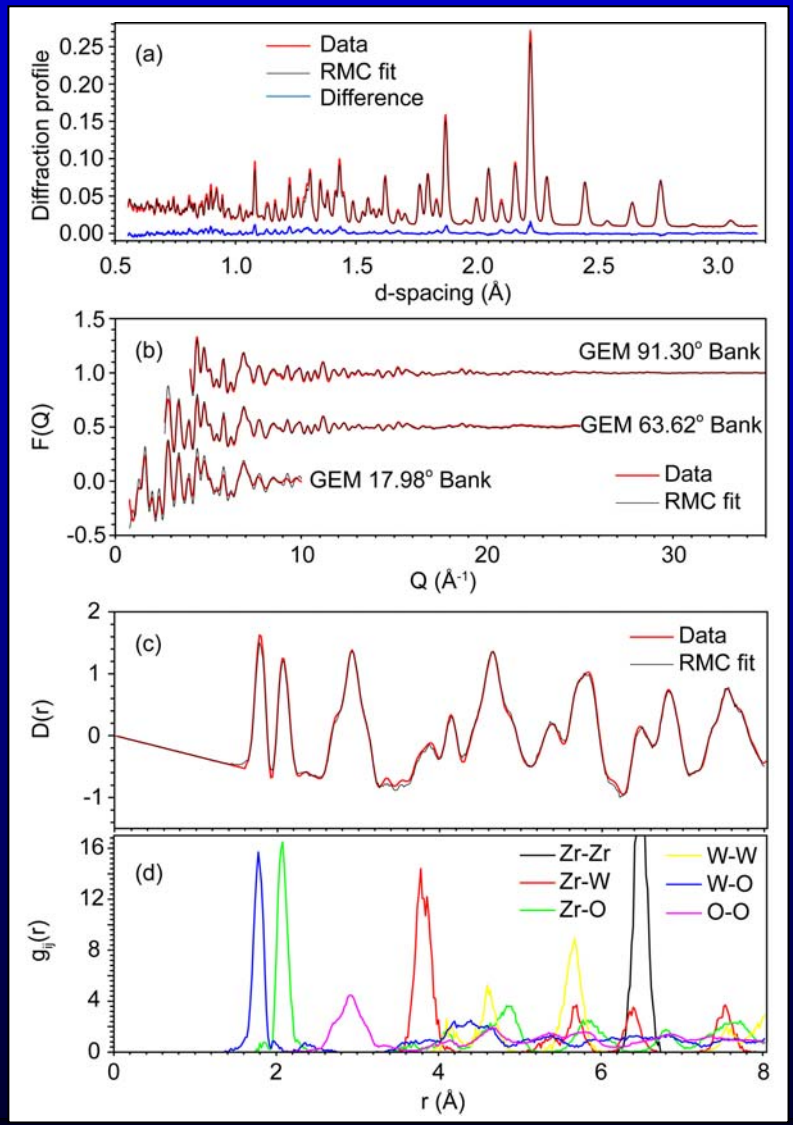




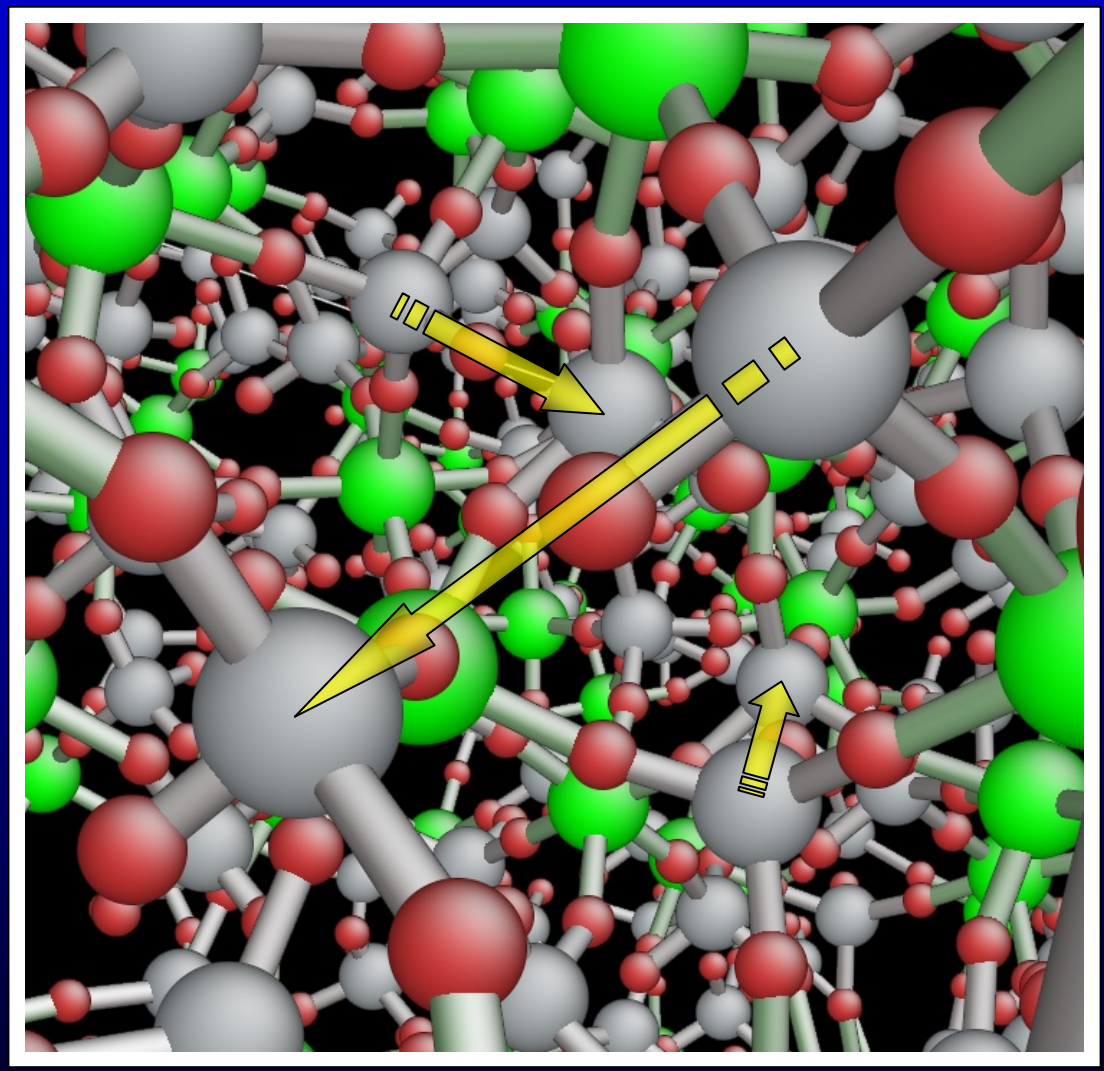
- XAFS work has challenged this assertion; a 'stiff' Zr-O-W linkage was observed [Cao *et al*/PRL 89 215902 (2002) & PRB **68** 014303 (2003)].

- We have used neutron total scattering to test these hypotheses.

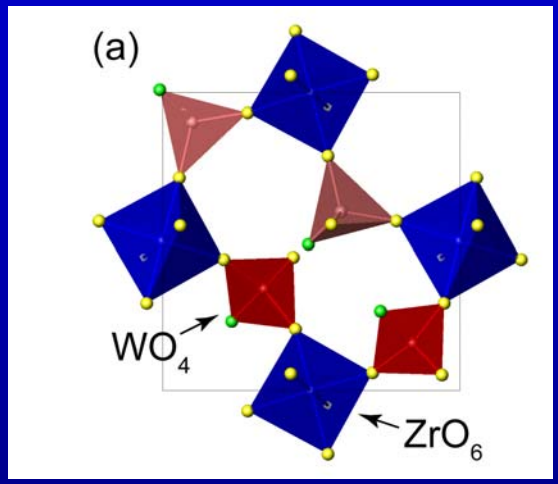
RMCProfile results from α-ZrW_2O_8

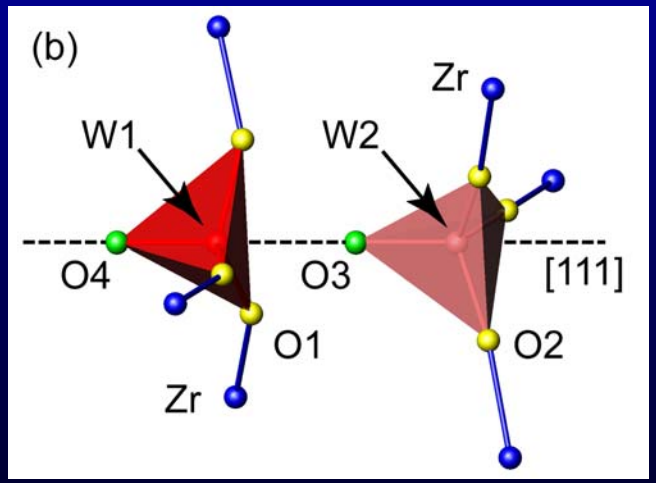


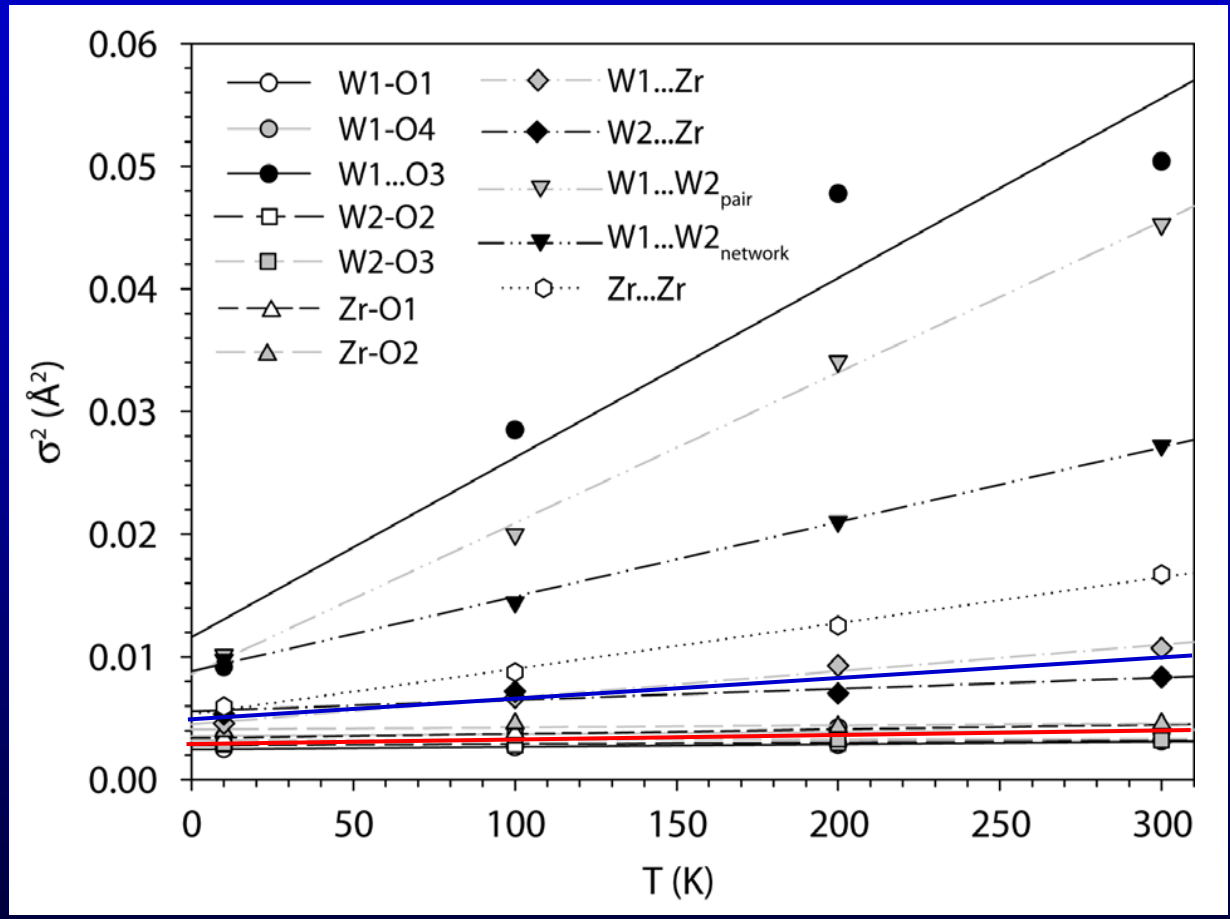
Local Structure in ZrW_2O_8



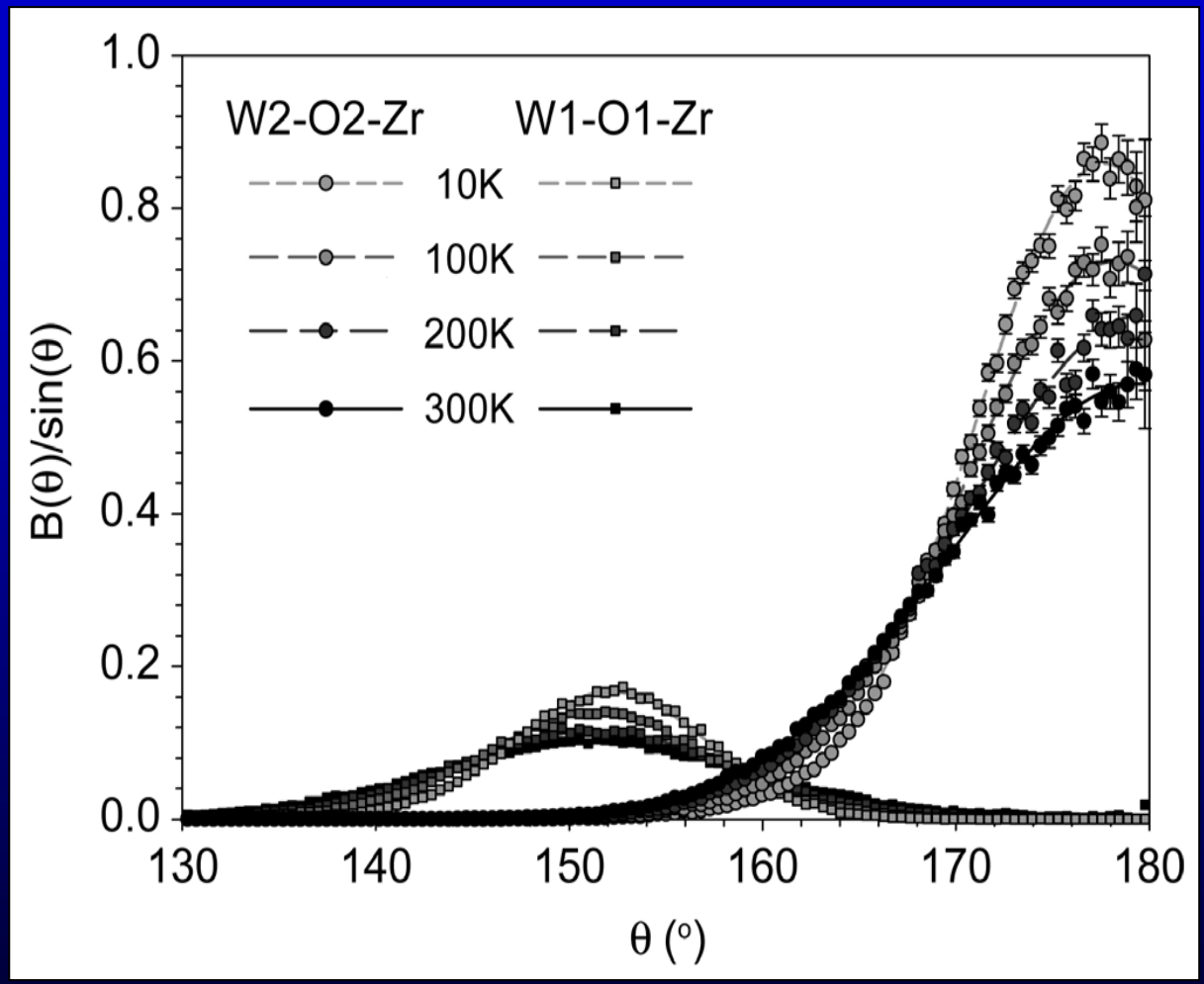
Linkage Flexibility in ZrW_2O_8

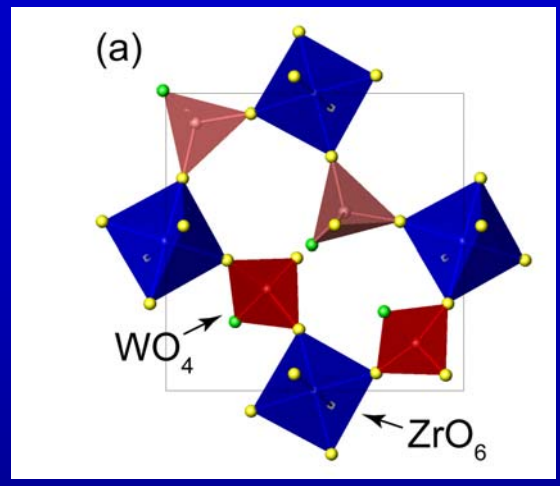


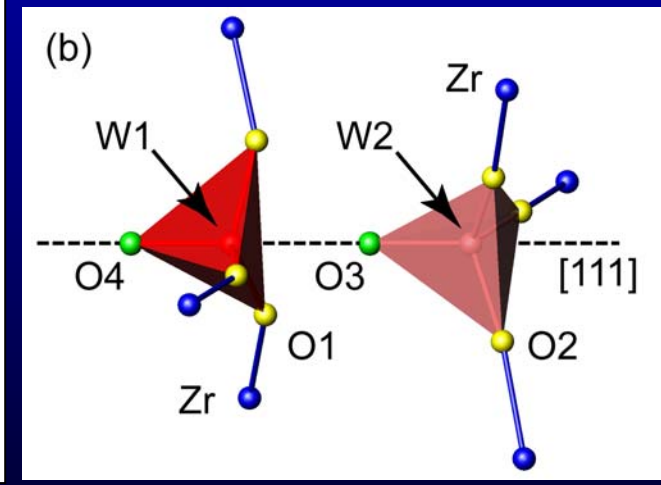




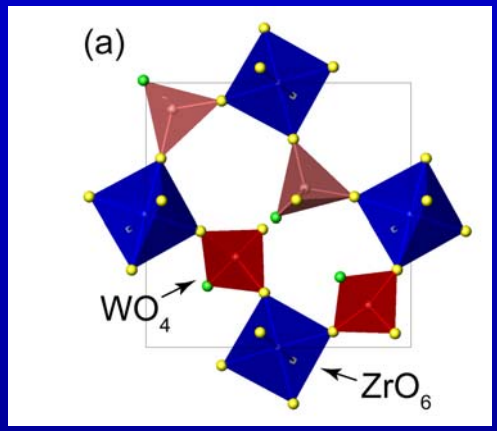
W-O-Zr Bond Angles in ZrW_2O_8

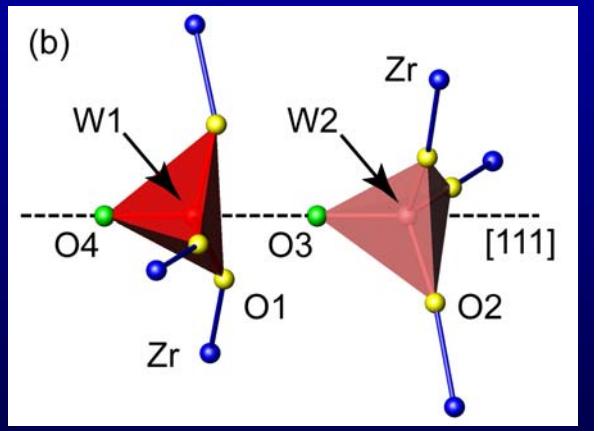


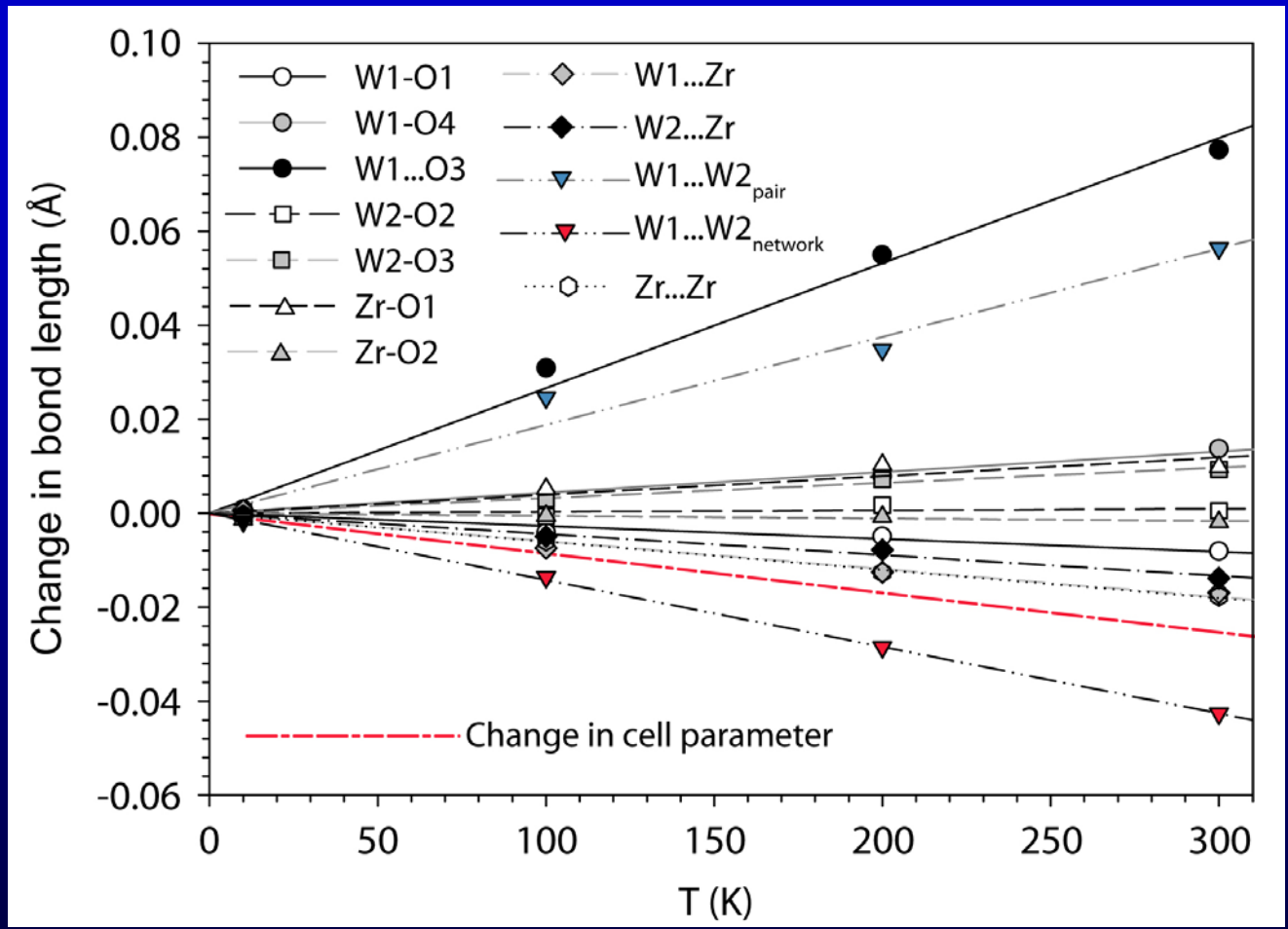




'Bond' Length Changes in ZrW_2O_8

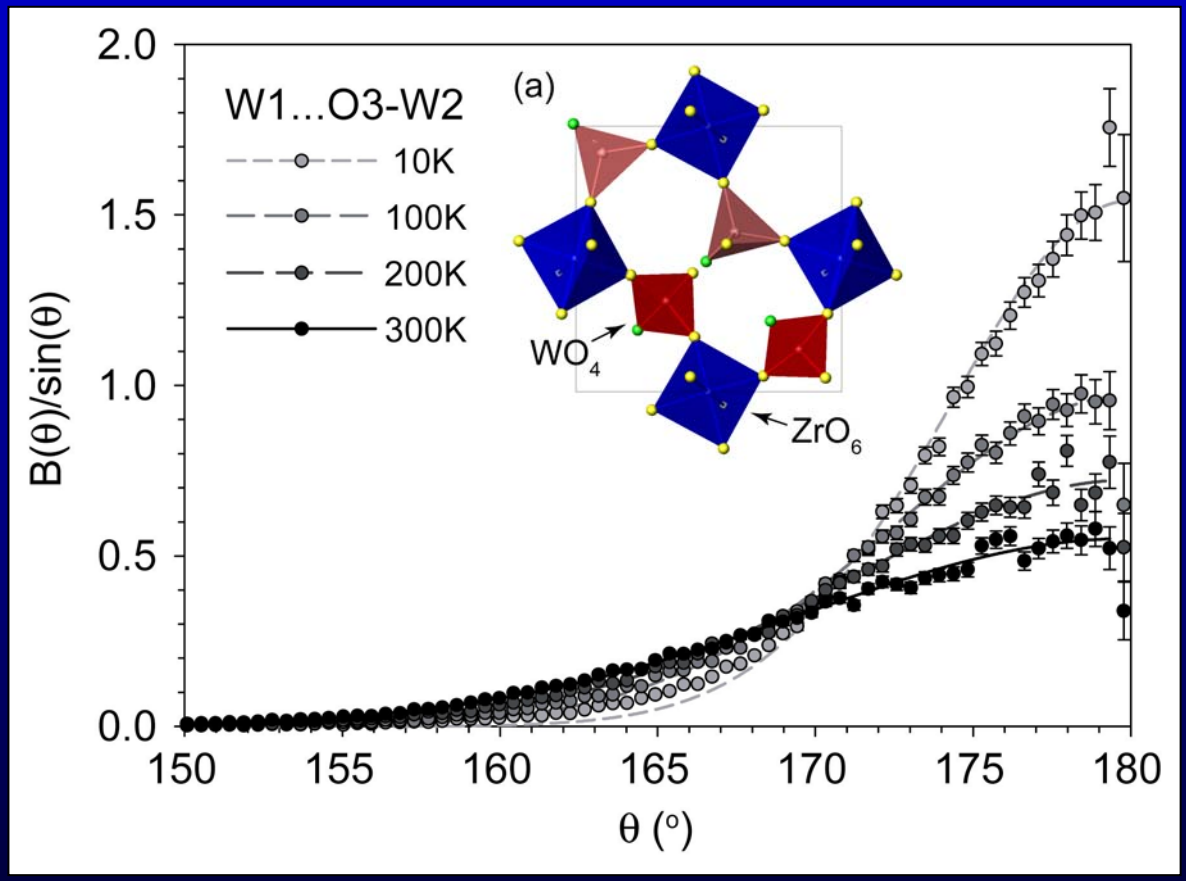




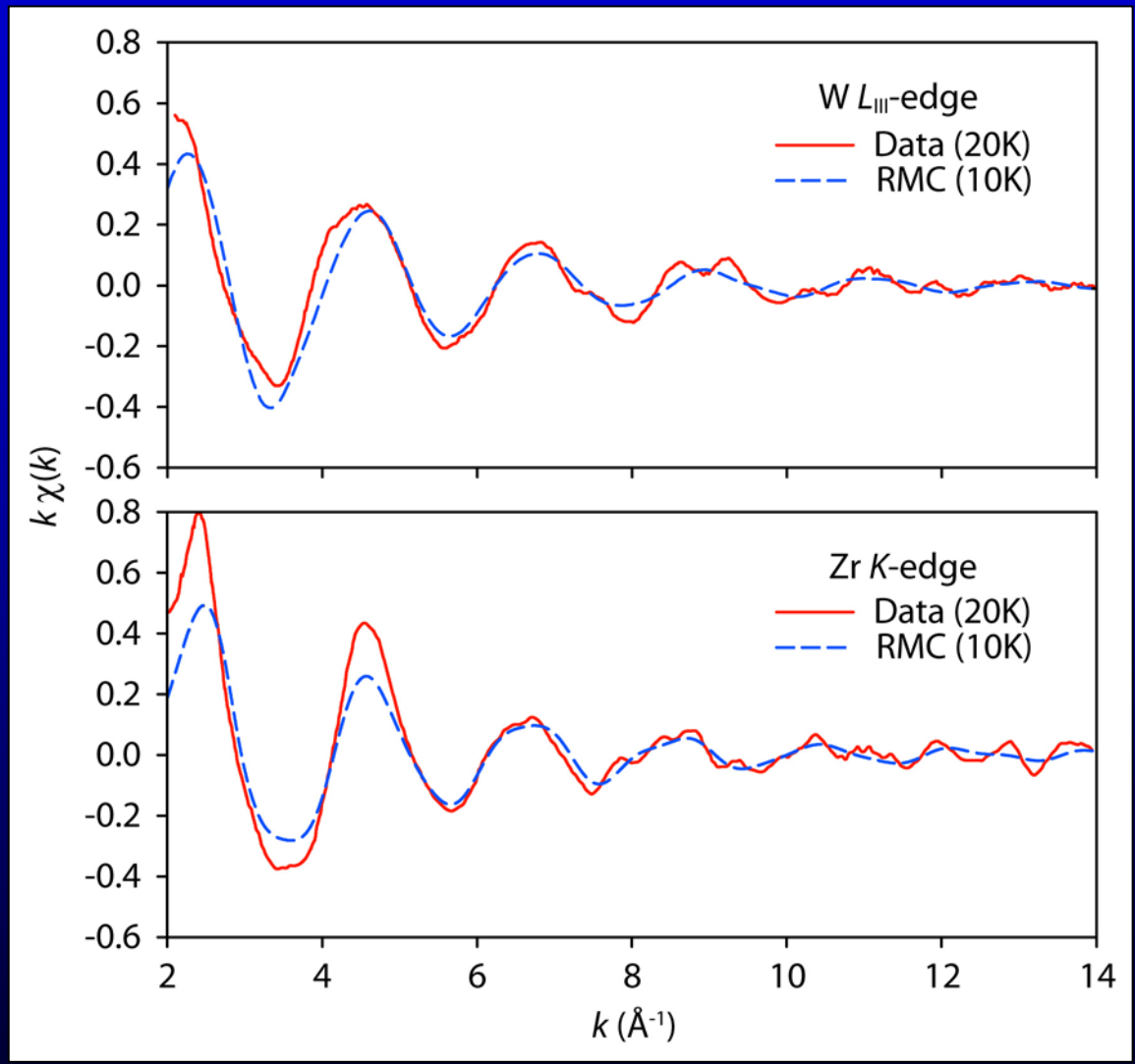


How might we understand the large local W1…W2 bond expansion?

W1…O3-W2 Bond Angles in ZrW_2O_8



RMC-derived model and XAFS data



Data from *Cao et al* *PRB* **68** 014303 (2003)

ZrW_2O_8 Crystal Summary

- ZrW_2O_8 does not possess a 'stiff' Zr-O-W linkage; we believe that difficult XAFS multiple scattering corrections could have produced this conclusion
- The temperature-dependence of the widths of the $g_{ij}(r)$ peaks are consistent with a simple RUM model of the structure
- It is the under-bonded WO_4 tetrahedra which give the structure the flexibility needed for the significant NTE effect
- The structural units undergo a complex combination of translational and rotational motion

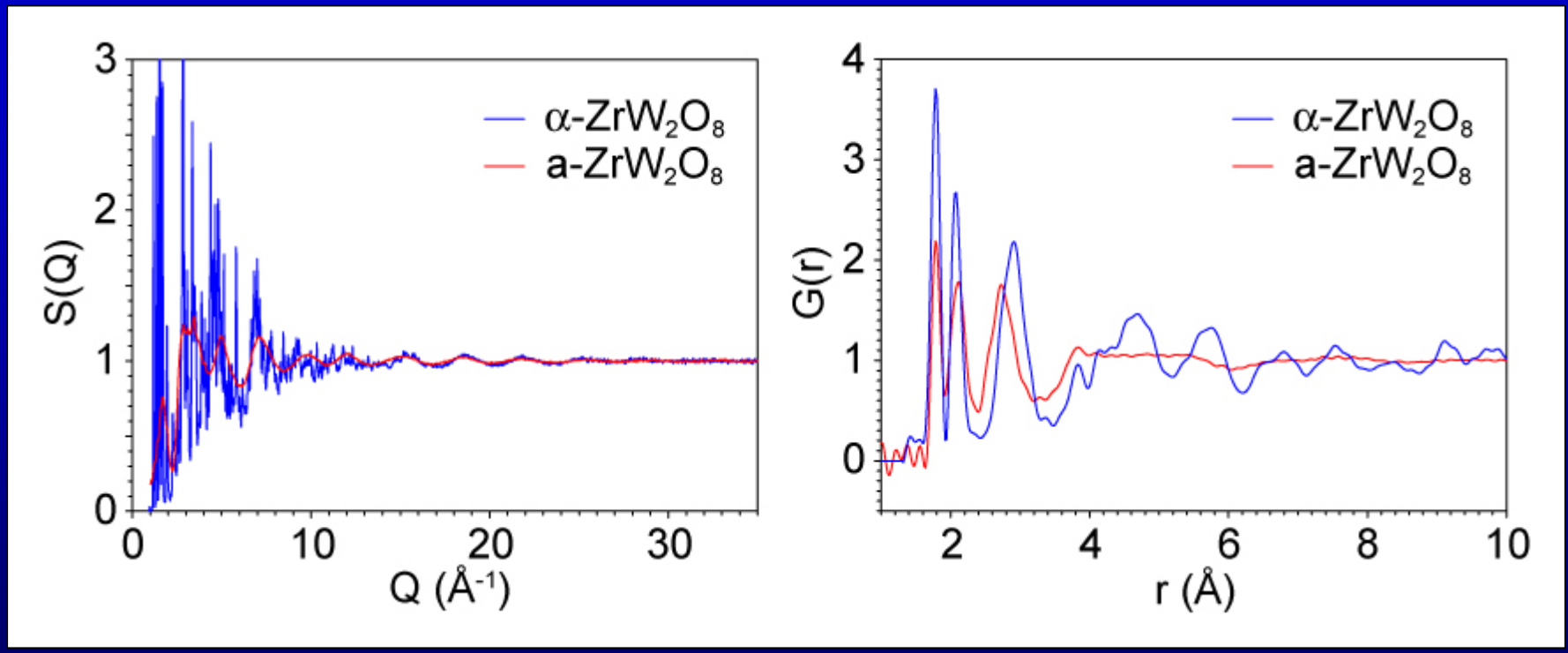
Tucker *et al, PRL* **95** (2005) 255501; *J Phys CM* **19** (2007) 335215

High pressure amorphisation of ZrW_2O_8

Cubic α-ZrW_2O_8 $\xrightarrow{<0.5\ GPa}$ Orthorhombic γ-ZrW_2O_8 $\xrightarrow{>2.4\ GPa}$ Amorphous ZrW_2O_8

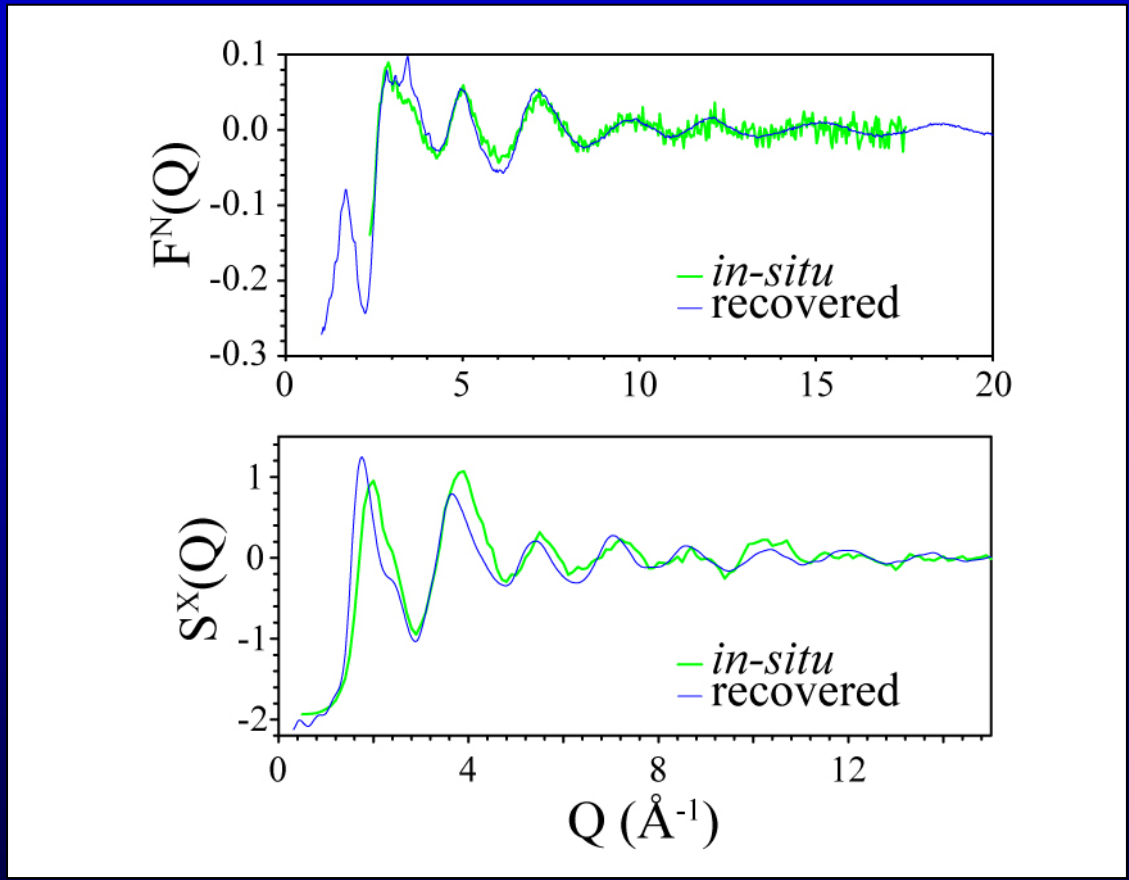
- Amorphous ZrW_2O_8 can be recovered to room pressure
- Recovered amorphous ZrW_2O_8 is ~26% more dense than crystalline ZrW_2O_8 (0.0721 c.f. 0.0573 atoms/$Å^3$)
- Neutron diffraction on GEM at ISIS on ~1cm^3 of sample recovered from ~4 GPa; X-ray diffraction on ID31 at ESRF
- What is it's structure?

ZrW_2O_8 Total Neutron Scattering Data

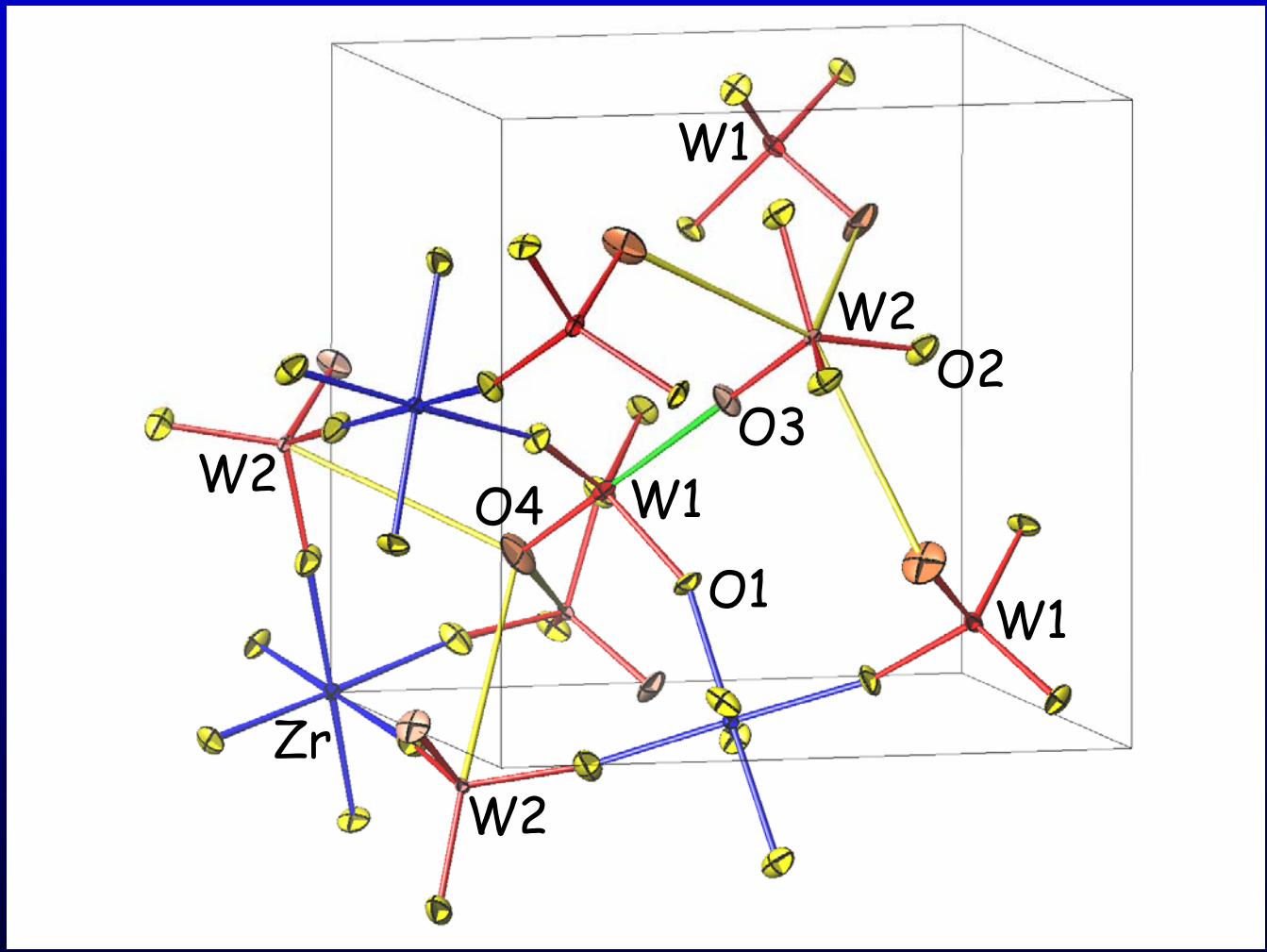


- 1st G(r) peak ⇒ W-O co-ord change from 4 to 3
- 2nd G(r) peak ⇒ Zr-O/W-O co-ord change from 6 + 0 to 6 + 2
- 3rd G(r) peak reflects the increased O-O packing

Comparison with *In-situ* Data

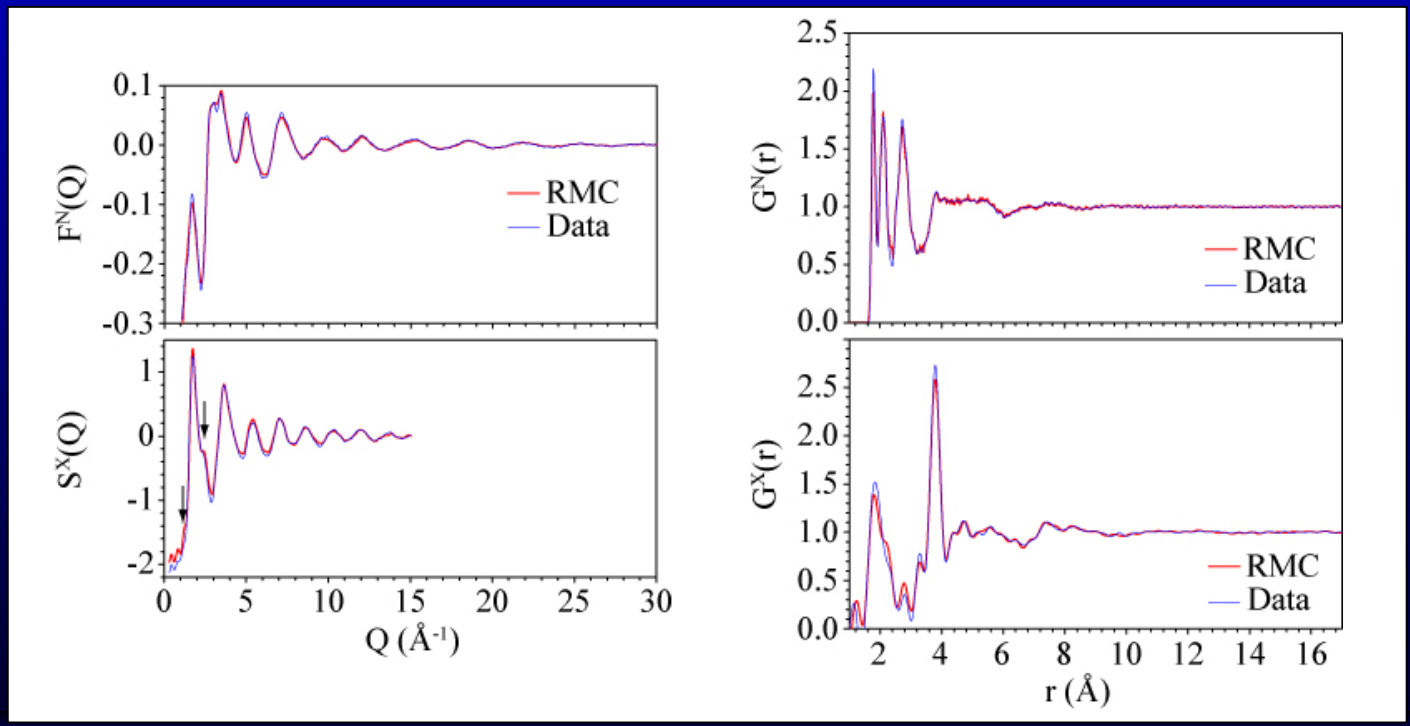


Forming 'Amorphous' Model from α-ZrW_2O_8



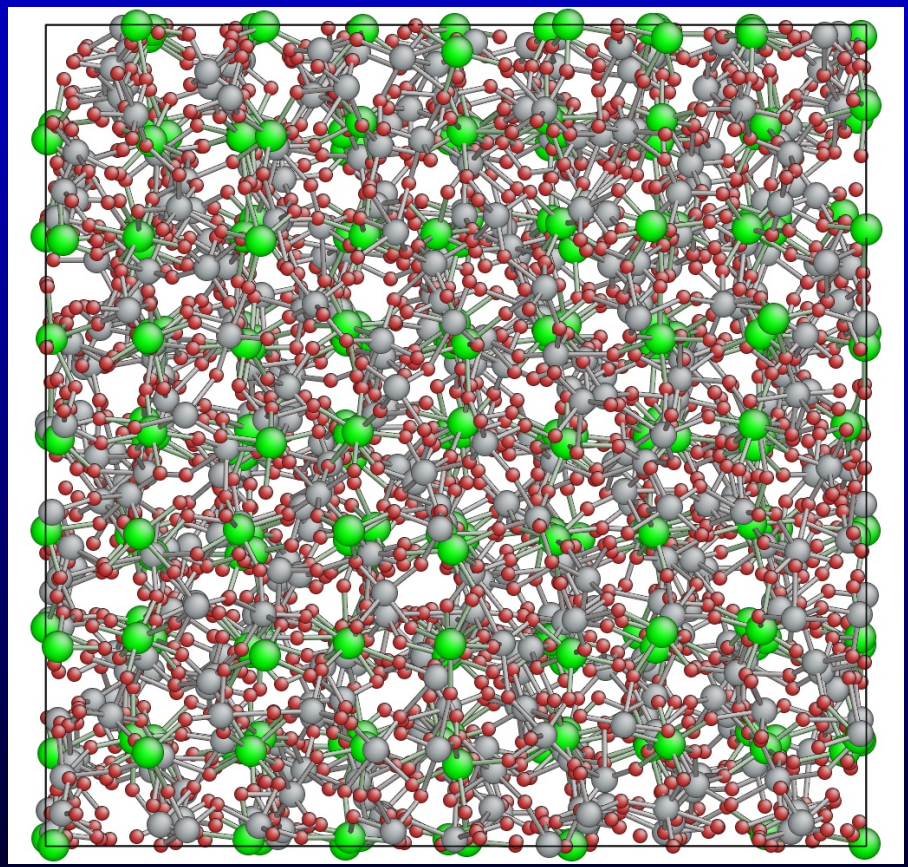
RMC Goodness-of-Fit Parameters

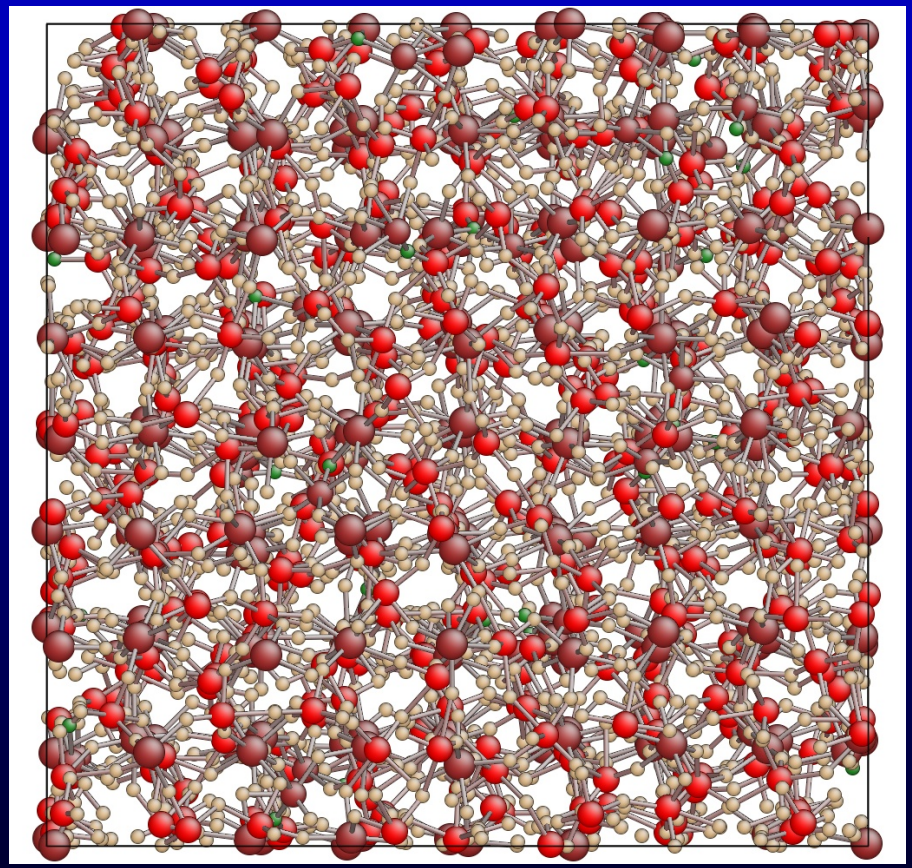
Model	Coordination ZrO	Coordination WO	$G^N(r)$	$F^N(Q)$	$S^X(Q)$
(a)	7	4/5	3.4	1.5	11.8
(b)	6	5	1.6	0.6	5.4
(c)	6	<5>	1.8	0.6	6.2



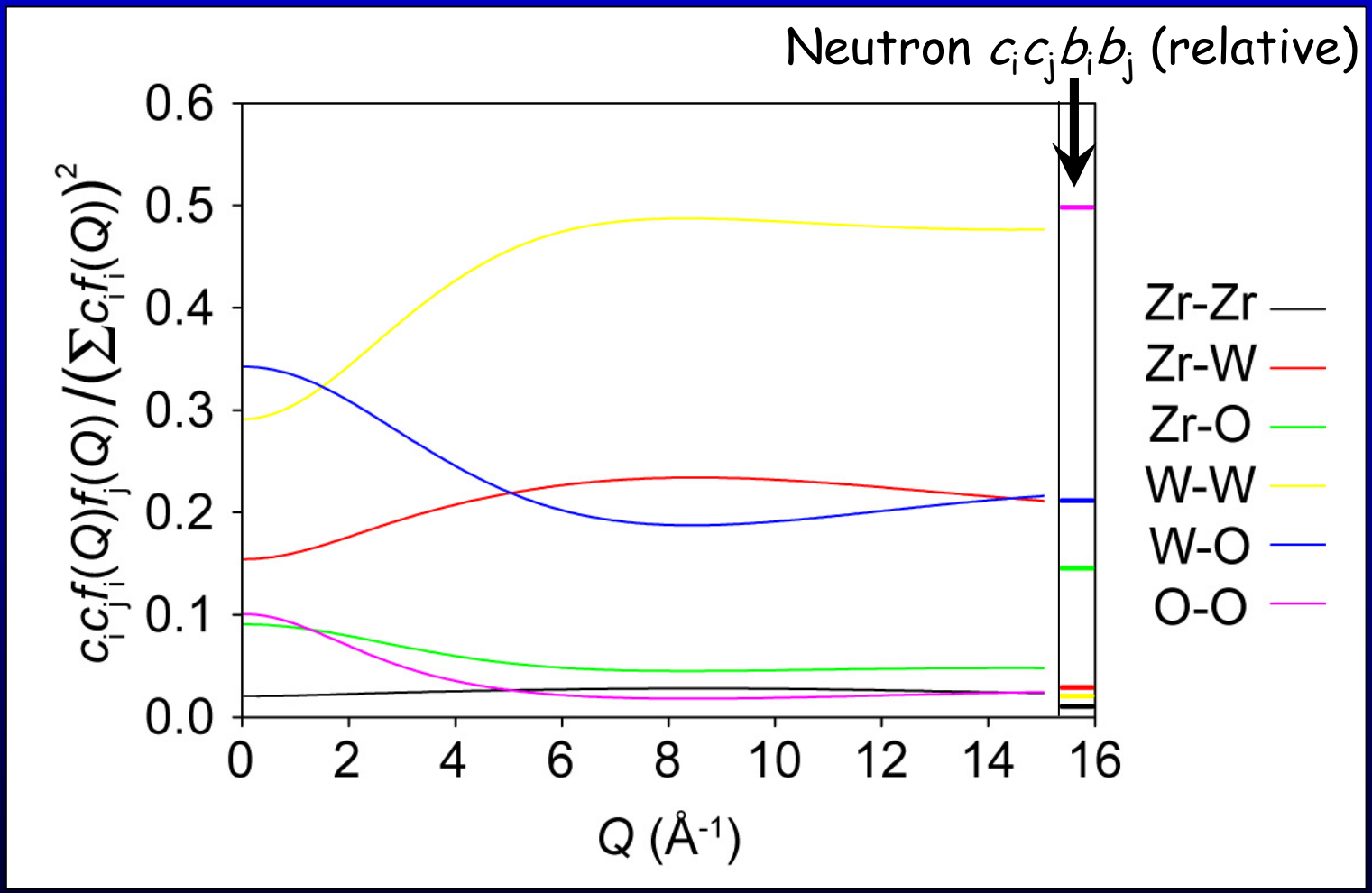
ZrW_2O_8 Amorphous Model (b): W-O-W Links

Co-ordination: 1 – turquoise 3 – green 5 – red 7 - purple
2 – lt brown 4 – grey 6 – brown

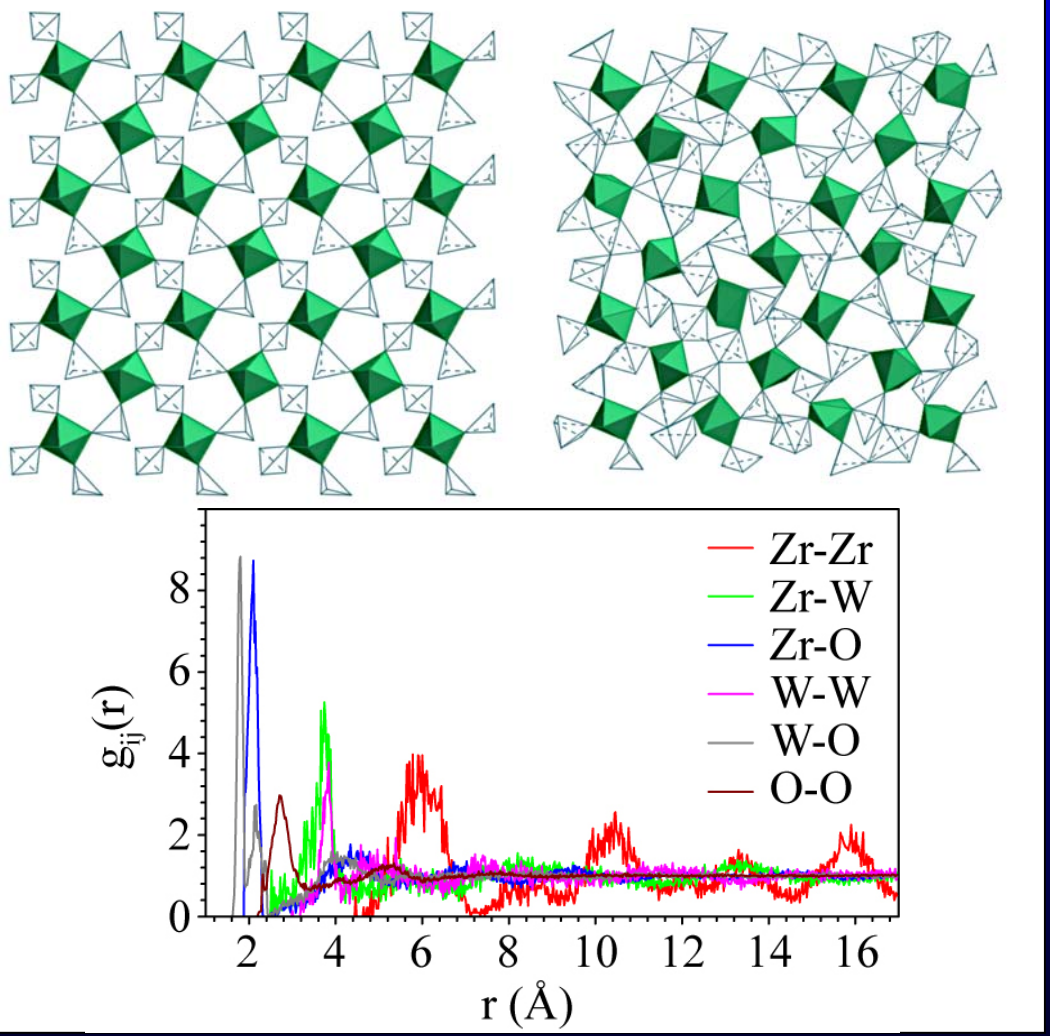




X-ray and Neutron Weighting Factors for ZrW_2O_8



Amorphous-like Connectivity Within a Periodic Zirconium Array



- Model formed with "ice-rules" from crystal structure
- Displacive phase transition plus bond formation
- Correct density, sensible bond lengths and appropriate polyhedra
- Concerted rotations and translations of polyhedra allow the structure to fold in on itself and increase its density
- This is an appealing model!

Keen *et al*, *PRL* **98** (2007) 225501

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