Neutron powder diffraction studies of phase transitions and kinetics

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Bill Marshall, Stuart Hayward, Mainak Mookherjee,
Mark Welch, Michael Henderson, Gérard Syfosse, Howard Stone, …..

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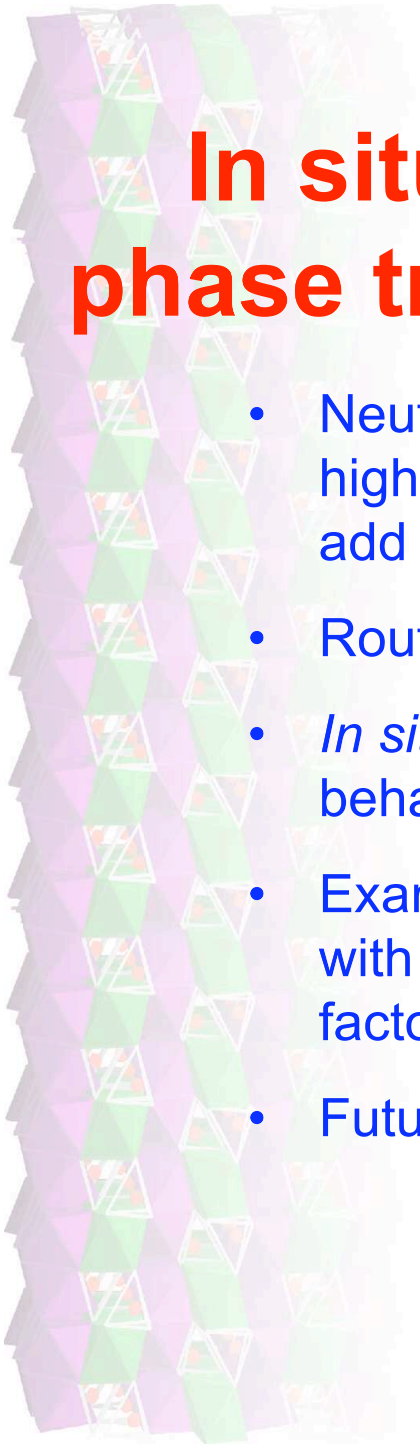
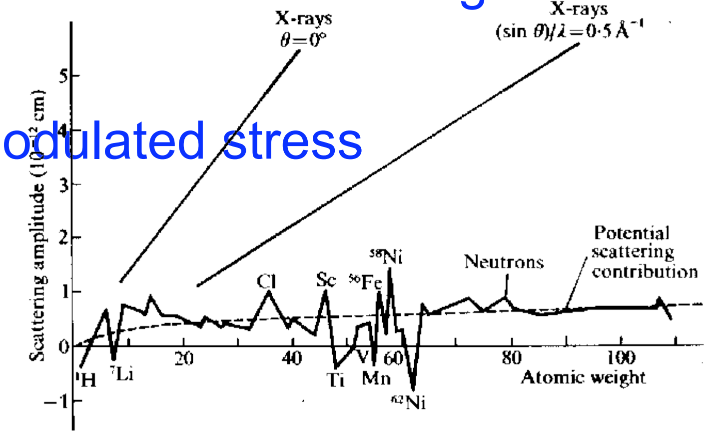


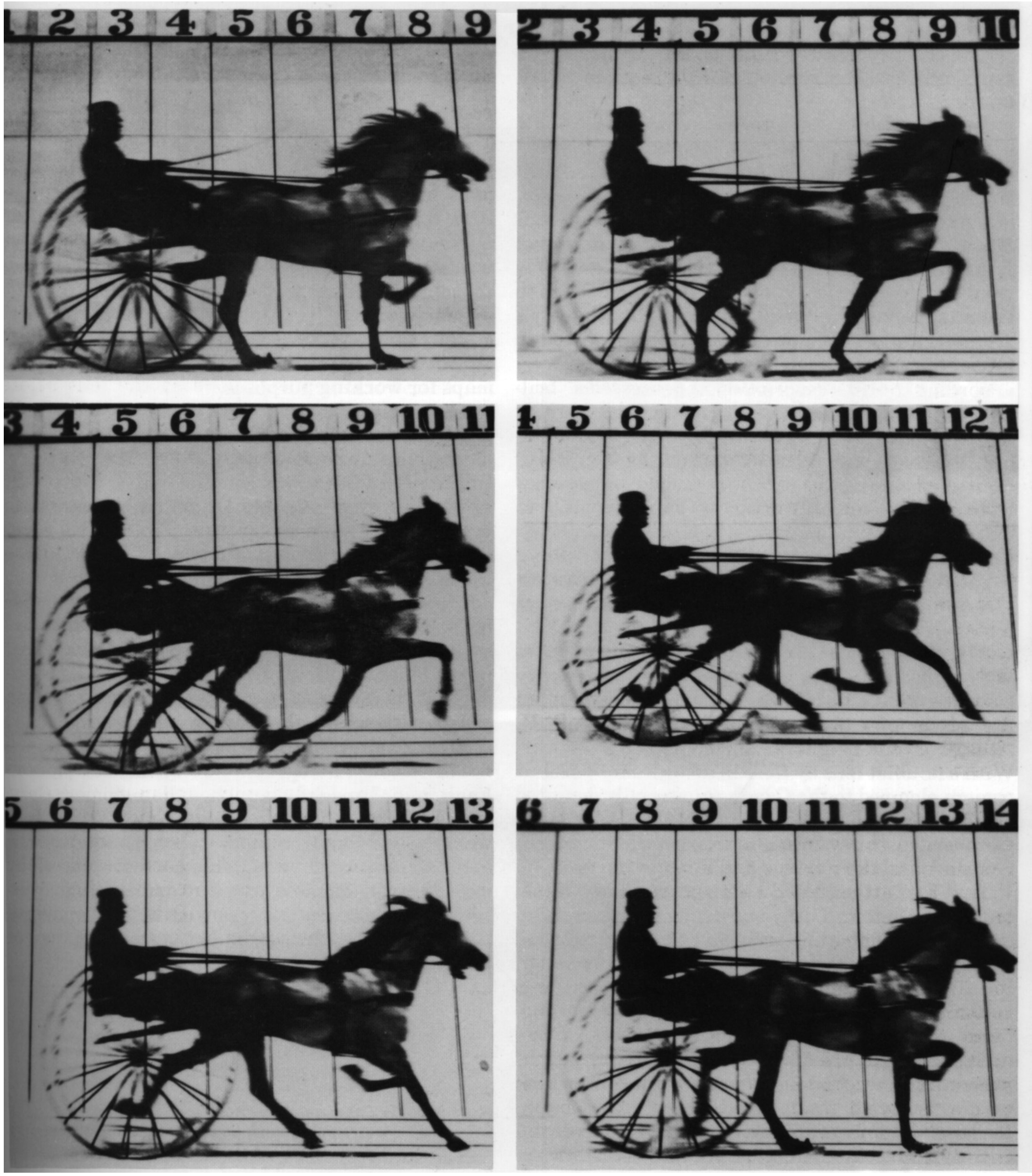
In situ high-P/T study essential for phase transitions by neutron scattering

- Neutrons ease in situ study: penetration through complex high-P/T sample environment - maintain fixed/buffered fO_2 - add external stress etc.
- Routes to fast neutron scattering studies
- *In situ* study is often essential if we want to understand real behaviour at deep Earth conditions
- Examples of cation order-disorder *in situ.* Complementarity with X-rays can be exploited, e.g. with different scattering factors
- Future prospects for high-P/T with modulated stress



The need for in situ study….

Eadweard Muybridge, "father of the motion picture", shows that a horse lifts all four hoofs in a gallop (1872):



principles of time-dependent diffraction studies:

- **Perturbation (T,P, pH etc.):**

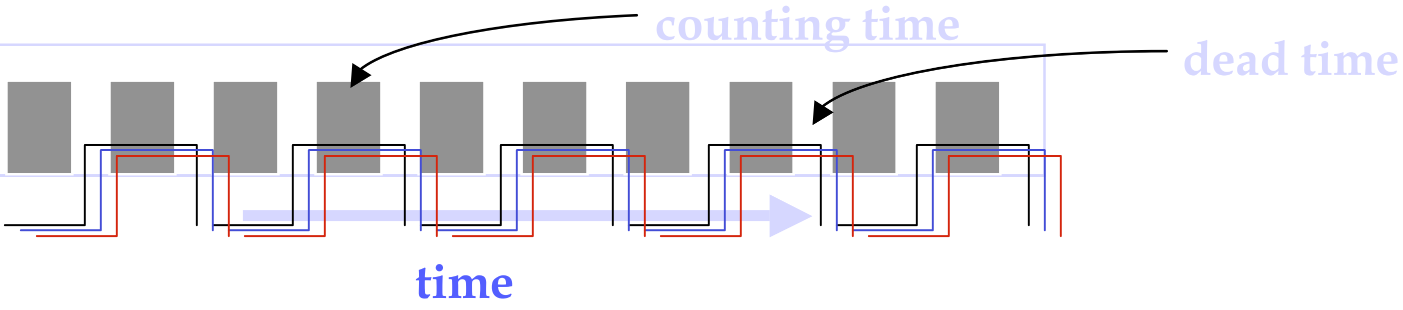
e.g. temperature ramp

e.g. temperature soak

e.g. temperature pulse

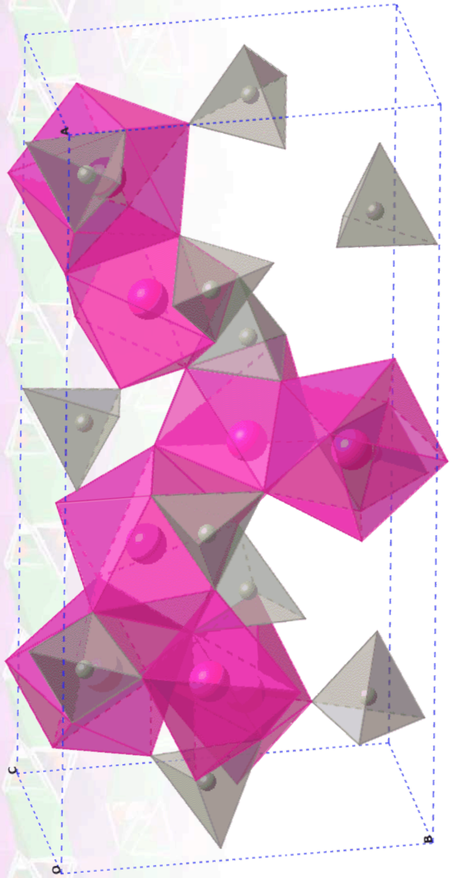
- **Time-dependent measurement:**

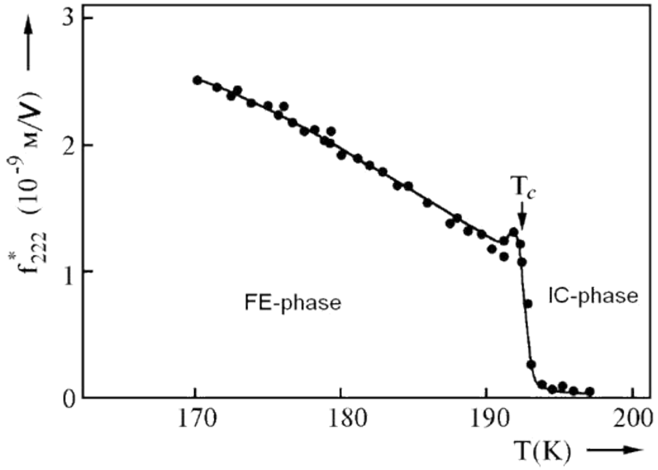
experiment

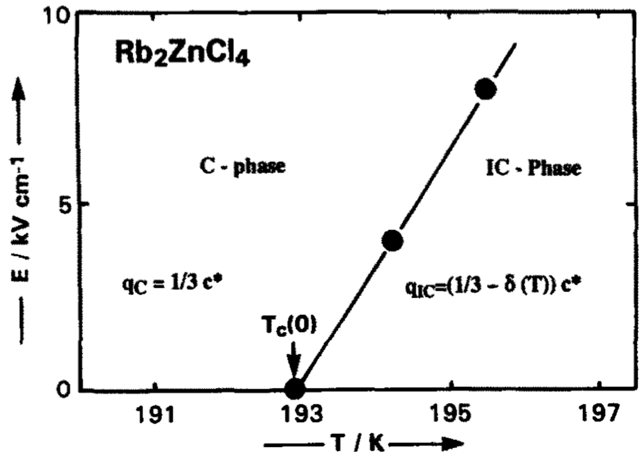


Stroboscopic neutron scattering: ic-c p.t. in Rb_2ZnCl_4

Eckold, Hagen & Steigenberger (1997) Physica B 234:151
Steigenberger, Eckold & Hagen (1994) Nucl Inst Meth Phys B 93: 316







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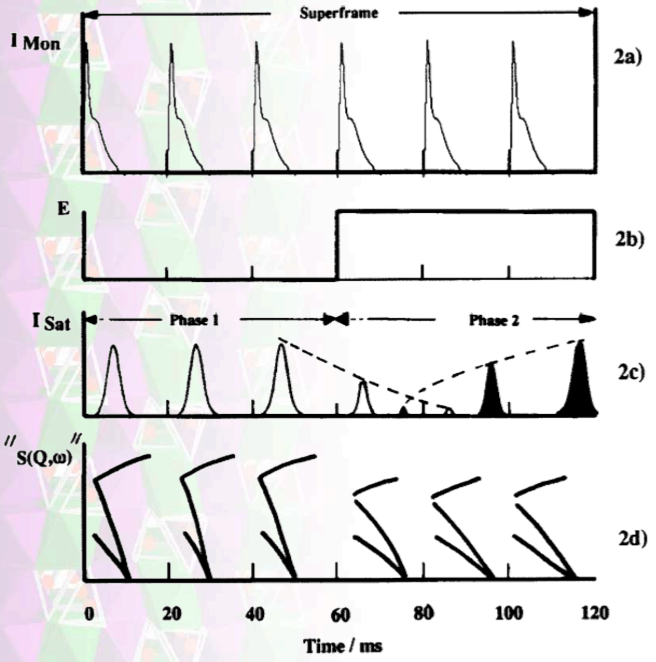
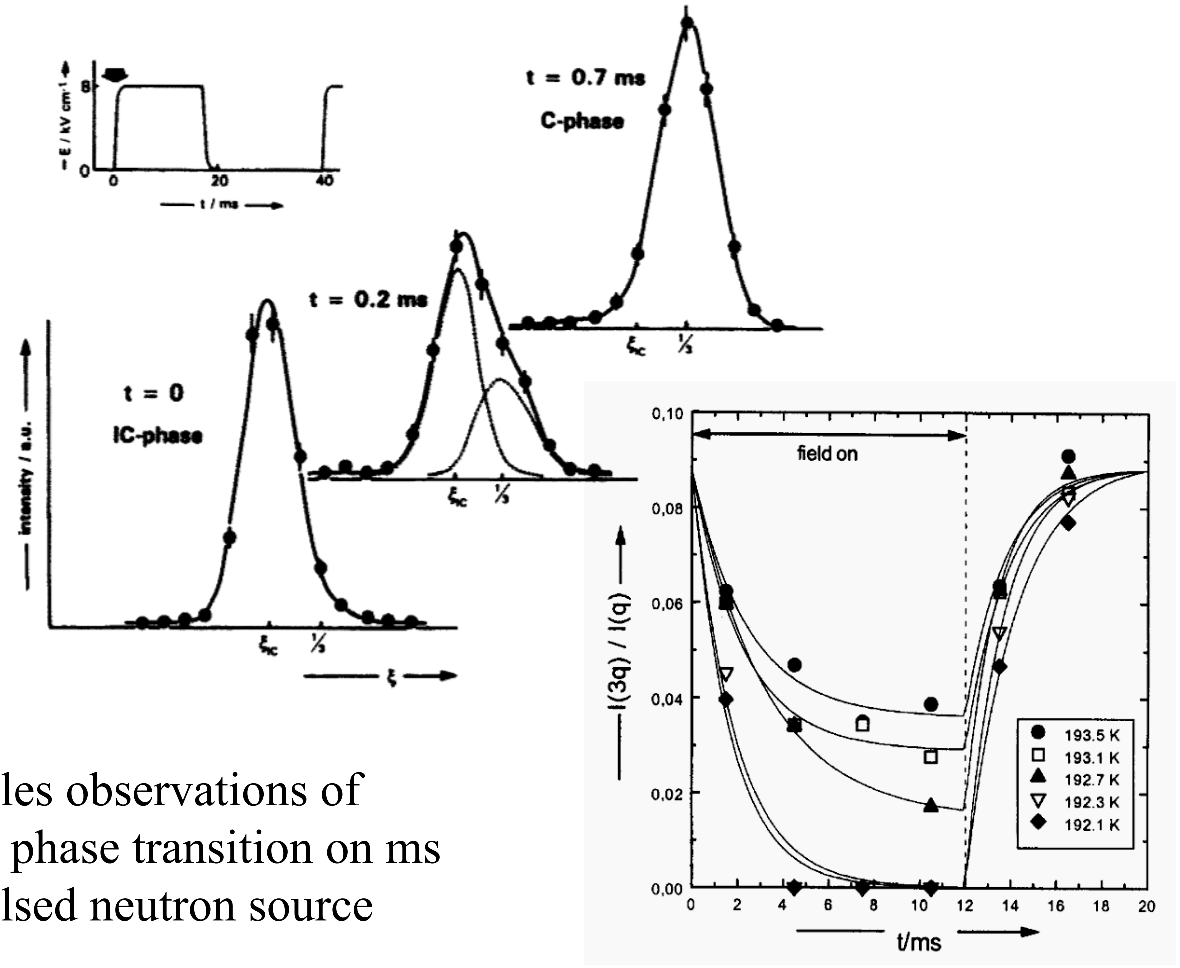
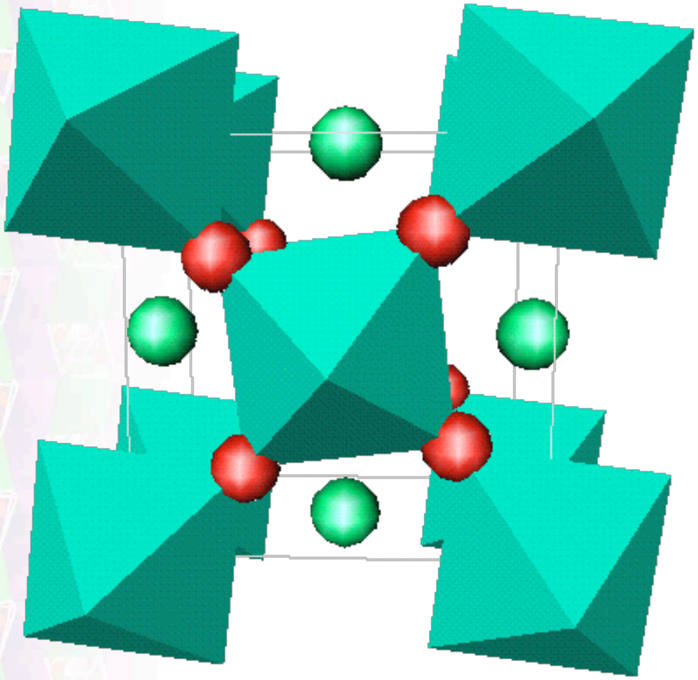
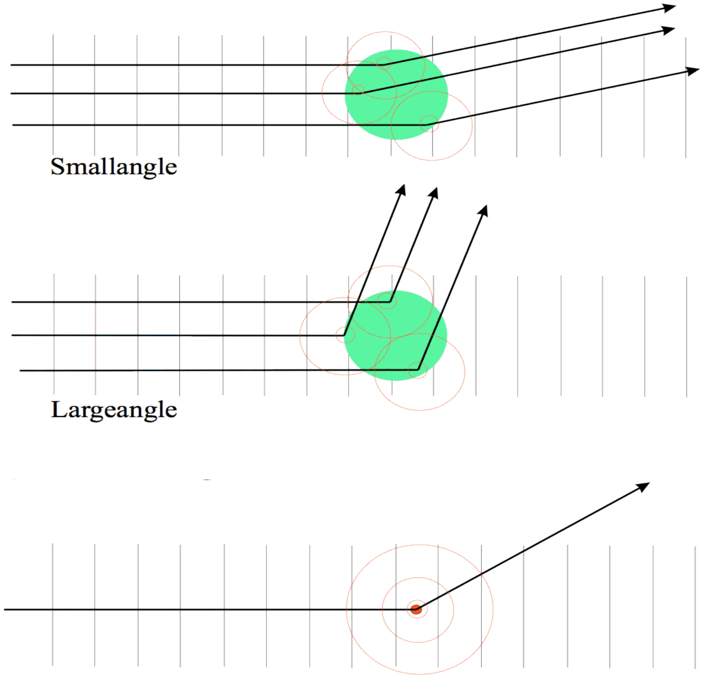


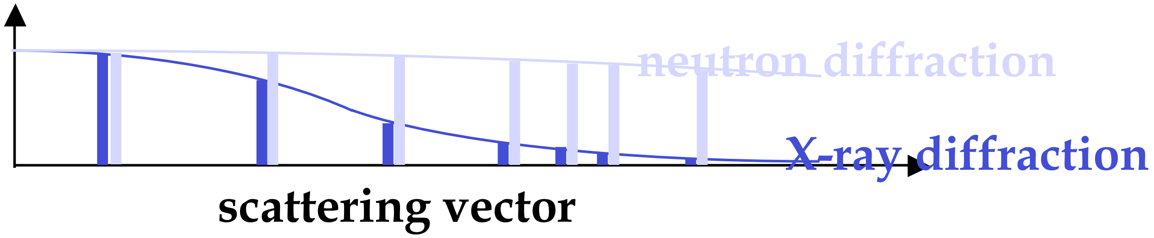


Stroboscopic scattering enables observations of ferroelectric responses at the phase transition on ms time scales, synching to a pulsed neutron source

strains and tilts in oxide perovskites

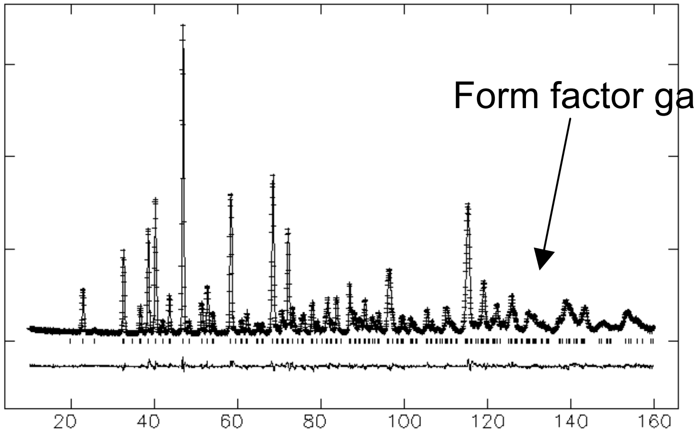




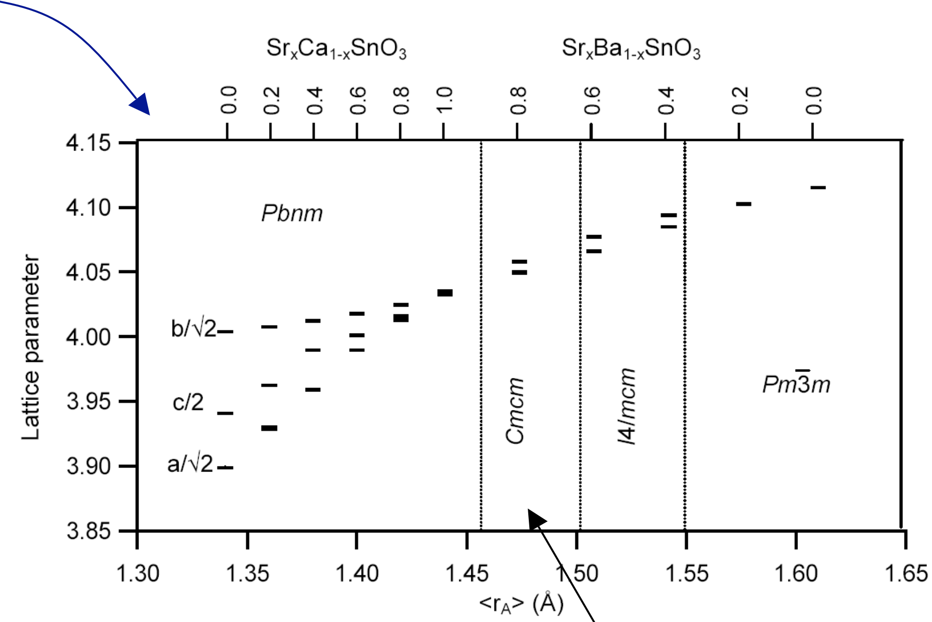


strains and tilts in oxide perovskites

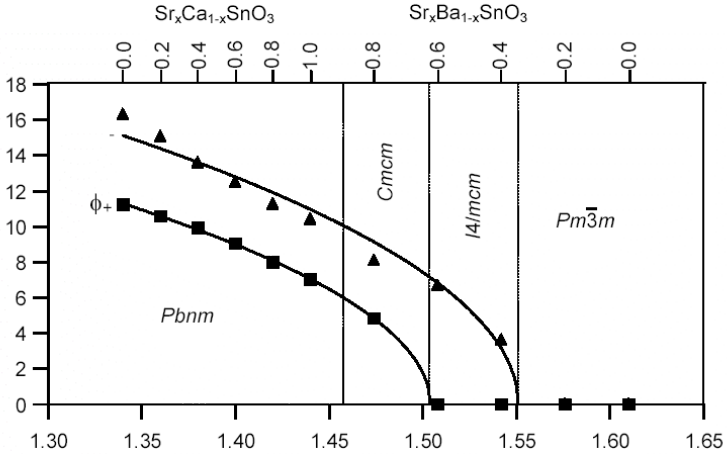
Mountstevens, Redfern, Attfield (2005) Phys Rev B 71: 220102
Mountstevens, Attfield, Redfern (2003) J Phys Cond Matt 15: 8315.



Form factor gains



Low strain orthorhombic state

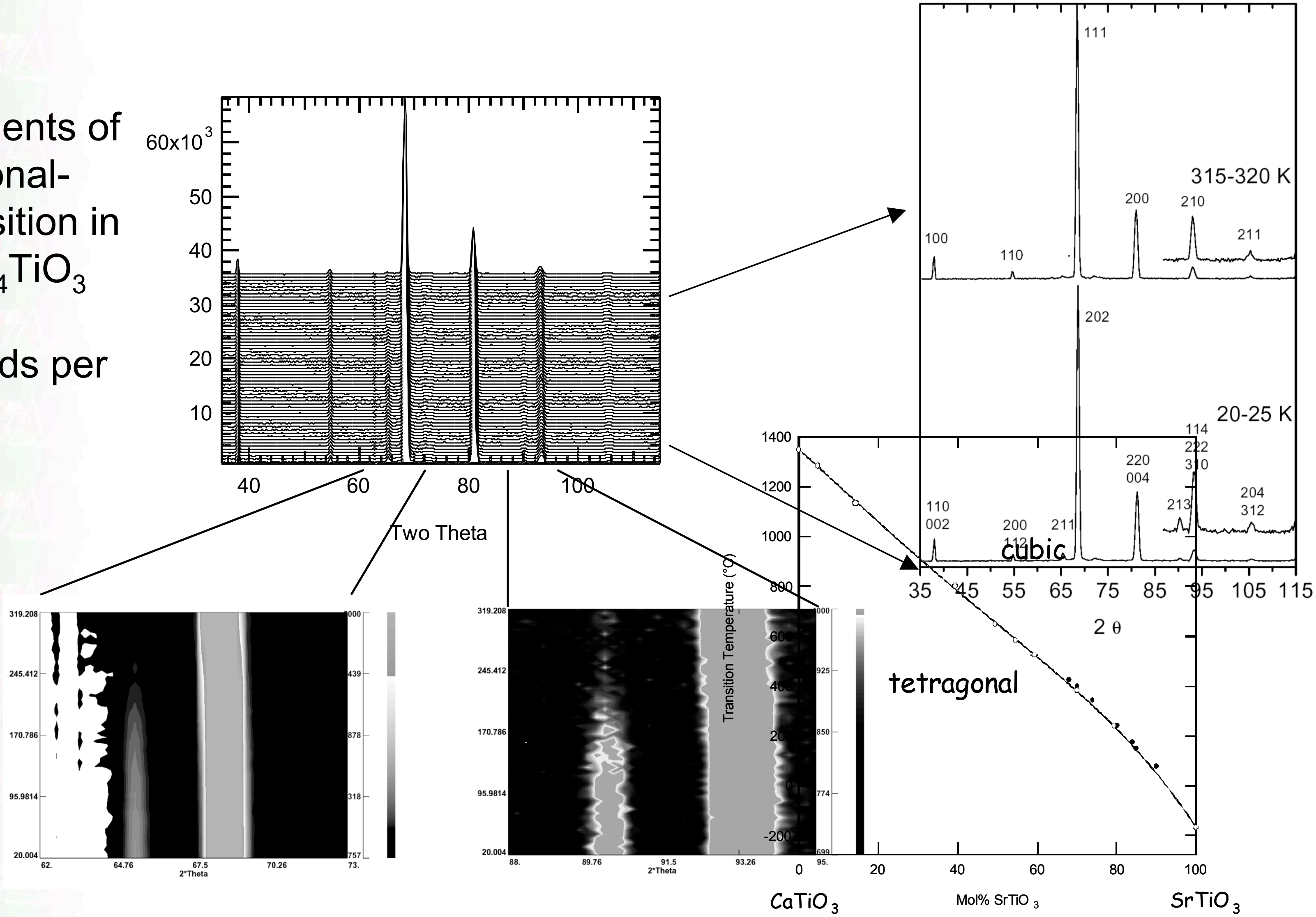


Pbnm (a+b-b-) →
Cmcm (a0b+c-) →
I4/mcm (a0a0c-) →
Pm-3m (a0a0a0)

High-*T-t* resolution with high flux (D1B)

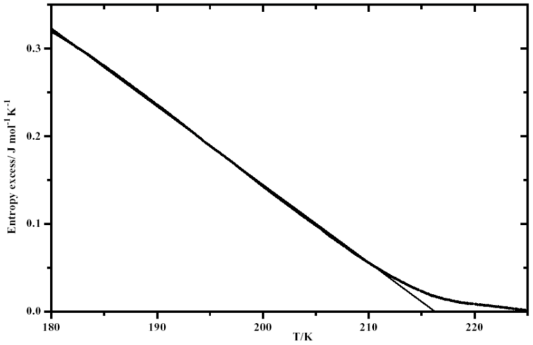
Low-T measurements of the tetragonal-cubic transition in $Sr_{0.96}Ca_{0.04}TiO_3$

300 seconds per pattern



thermodynamics of *I4/mcm-Pm3m* transition

Combine entropy measurements with order parameter measurements to derive a Landau potential



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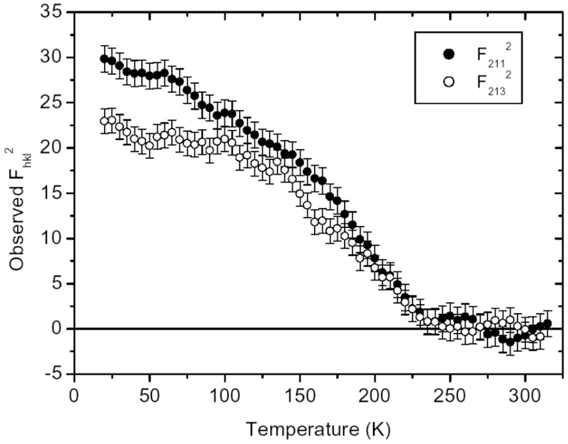
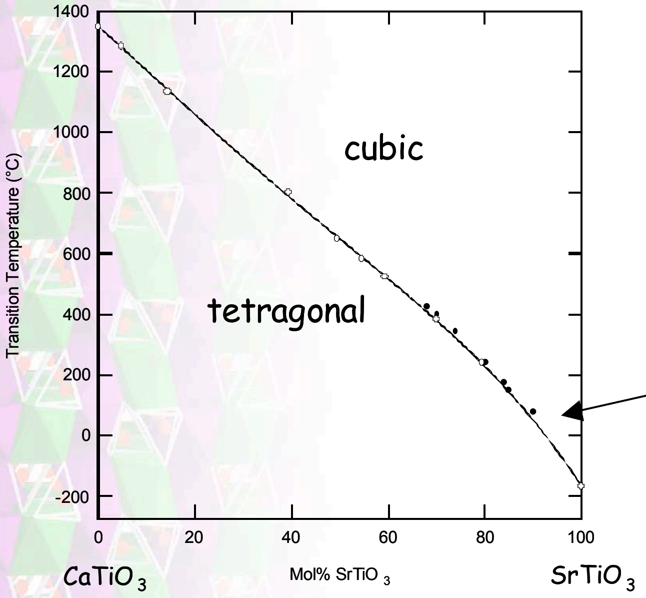


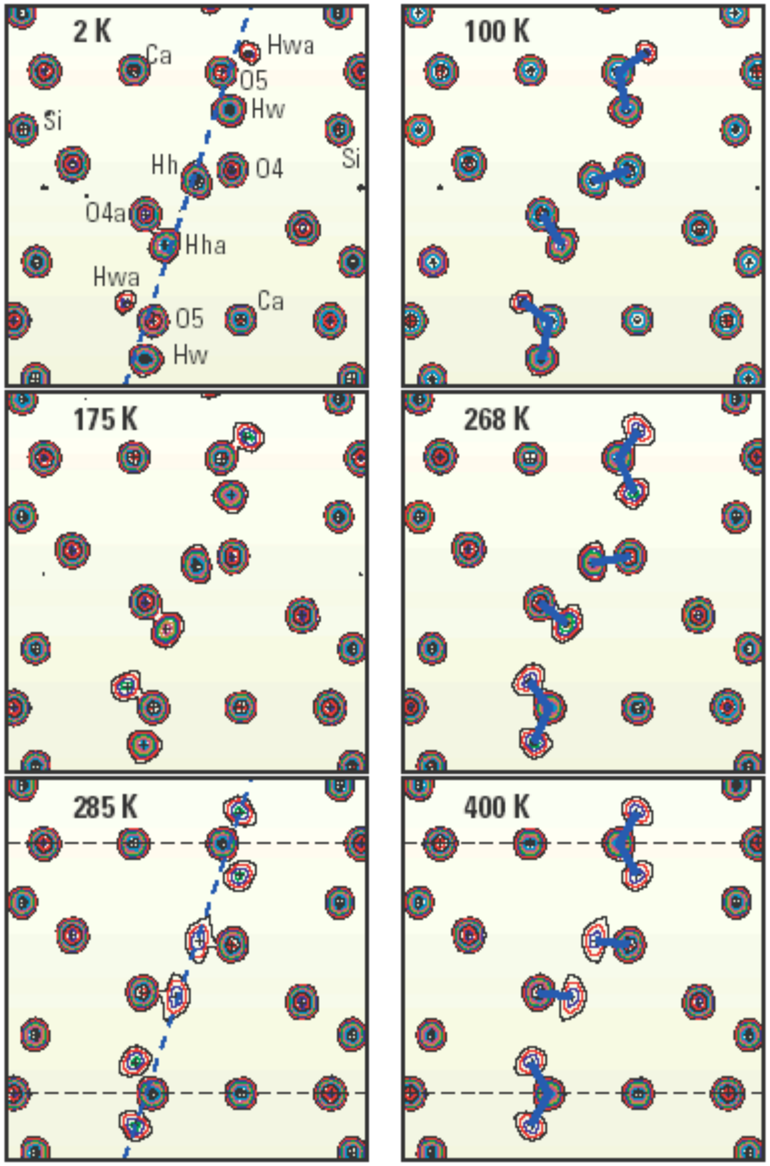
$$= \quad \Delta G = \frac{1}{2}A(T - T_c)Q^2 + \frac{1}{4}BQ^4 + \frac{1}{6}CQ^6 + \ldots.$$

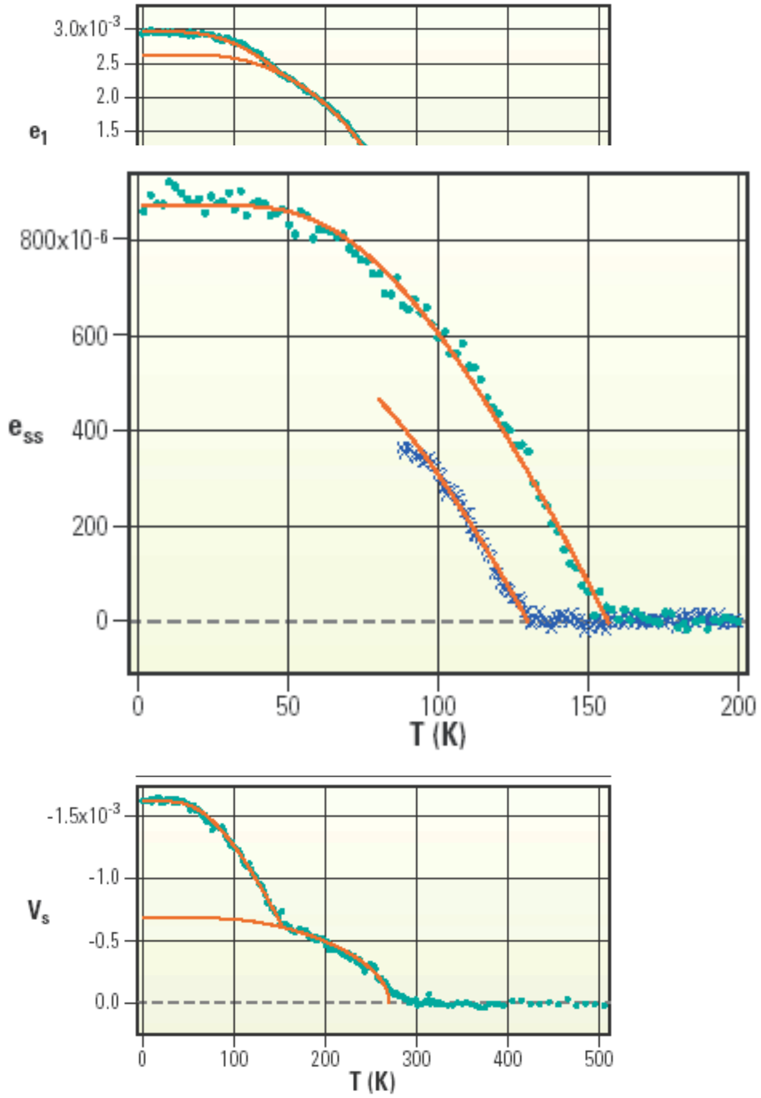


Explains curvature near $SrTiO_3$ end-member

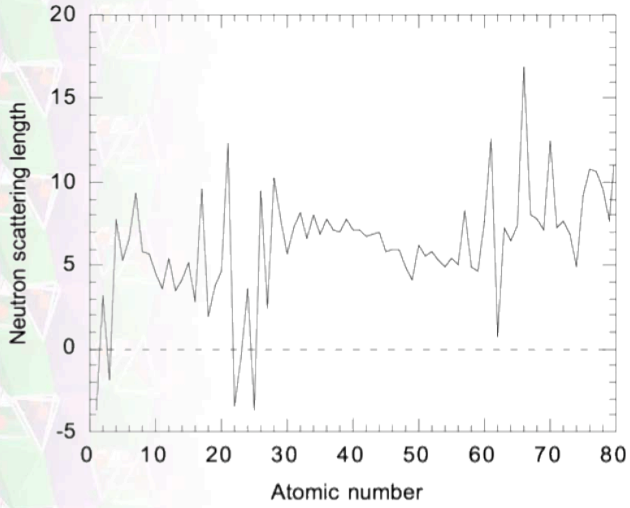
HRPD study: structure of lawsonite at low T

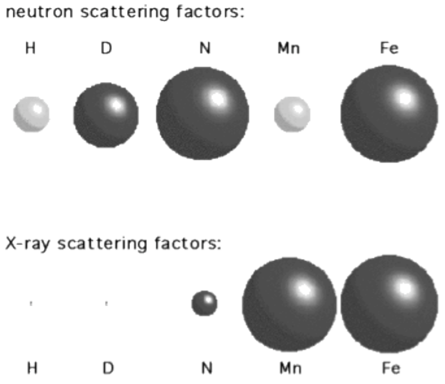
(Meyer et al. (2001) Am Min 86: 566)

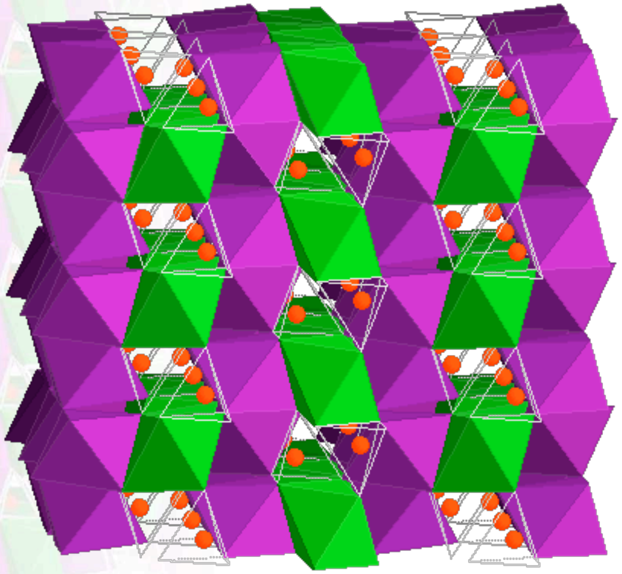




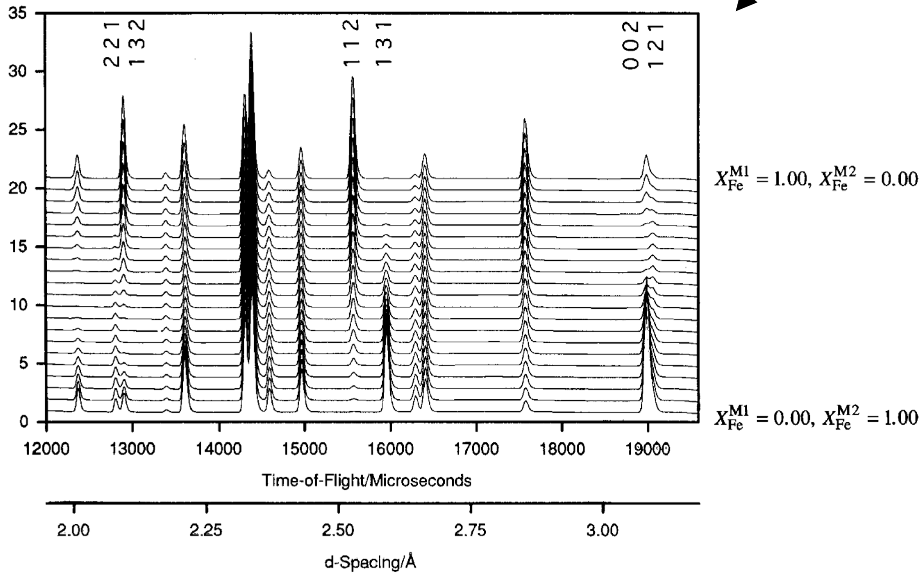
Neutrons to study order-disorder phase transitions







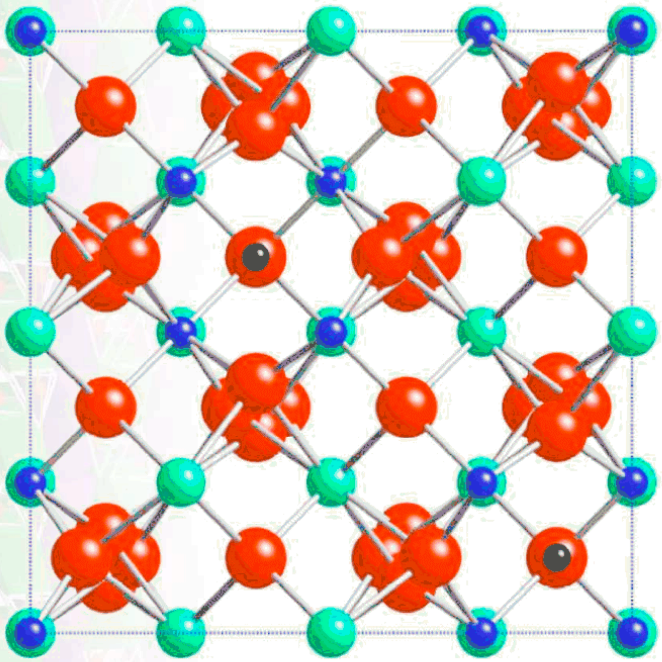
Simulated powder patterns as a function of degree of order in Fe-Mn olivine



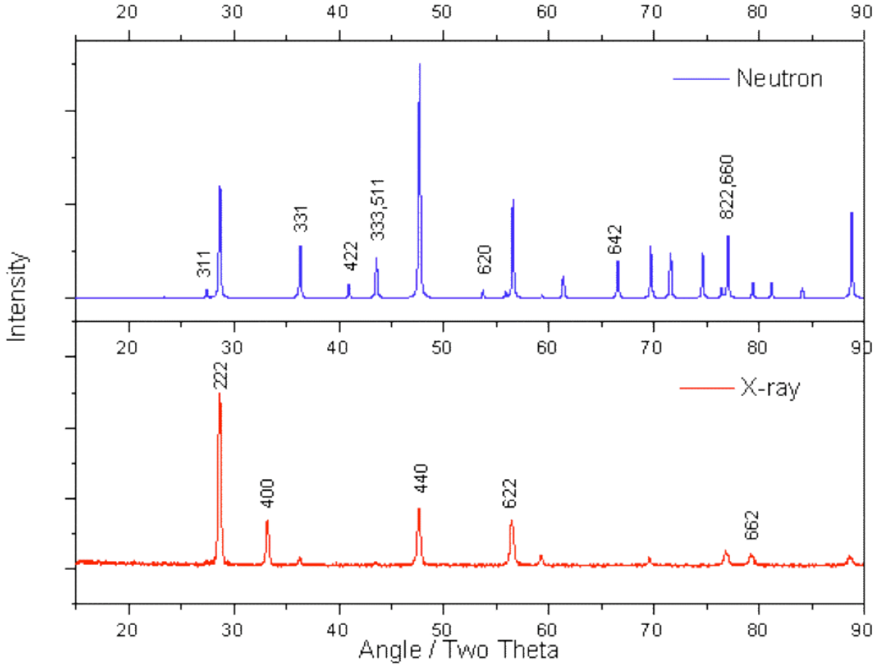
Neutrons to study cation and anion site occupancies: pyrochlores

Harvey et al. (2006) J Mat Chem 166: 4665
Harvey et al. (2005) J Solid State Chem 178:800

Related to fluorite, with ordered anion vacancies. Potential host for immobilisation of Pu.



$La_2Zr_2O_7$ pyrochlore: neutrons provide essential information on oxygen order/disorder, and to higher scattering vectors



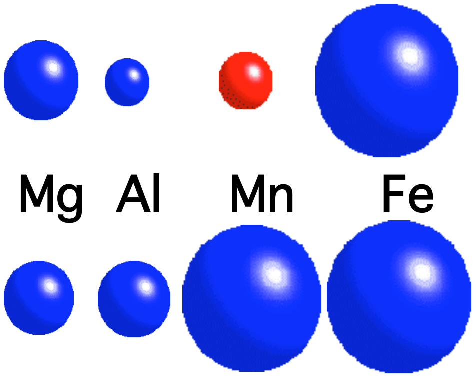
Order-disorder in spinel

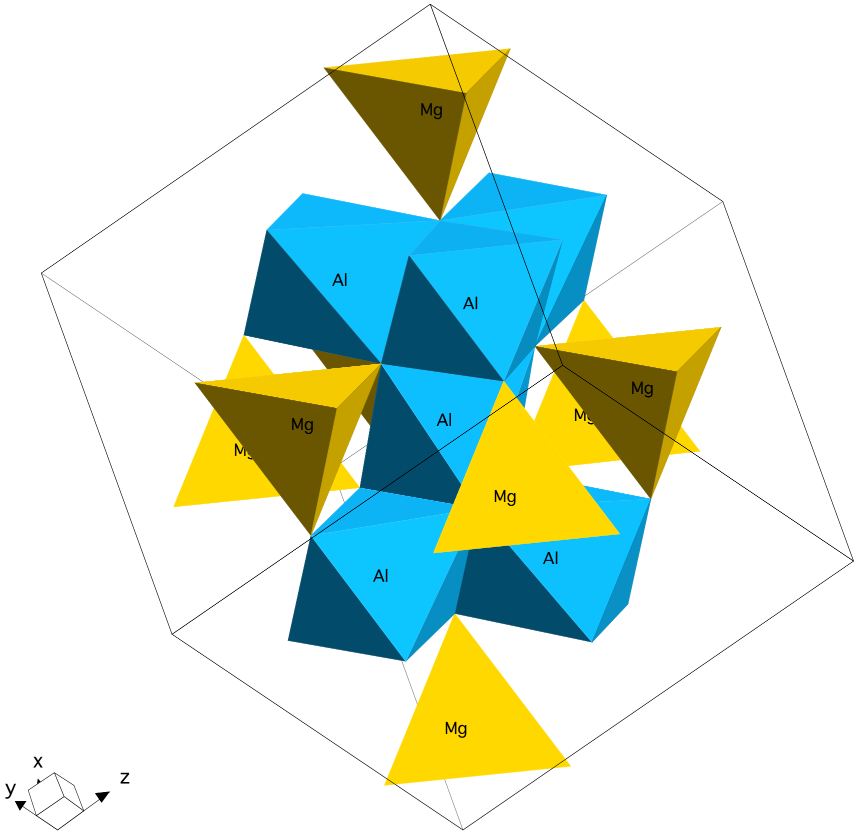
Spinel: AB_2O_4

e.g. $MgAl_2O_4$
normal A[4] 2 x B[6]
e.g. Mg_2TiO_4
inverse B[4] B[6]A[6]

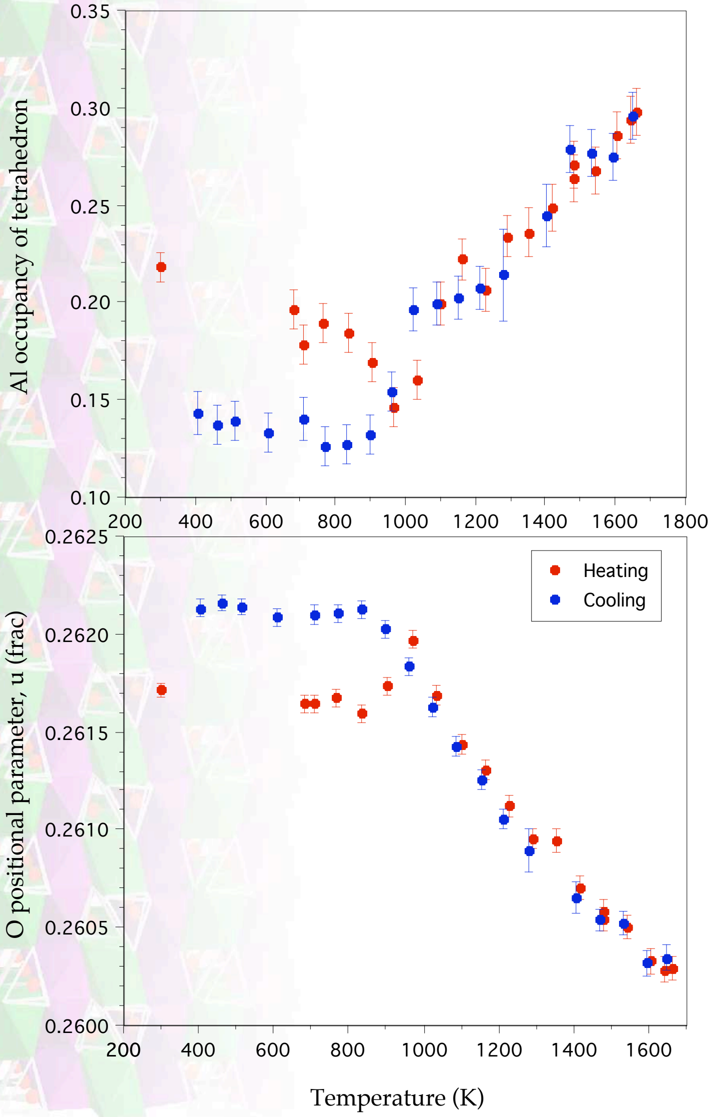
Neutron scattering lengths

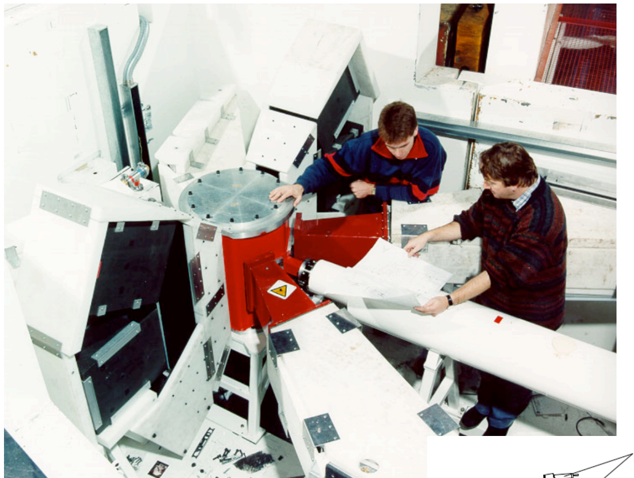
X-ray scattering factors

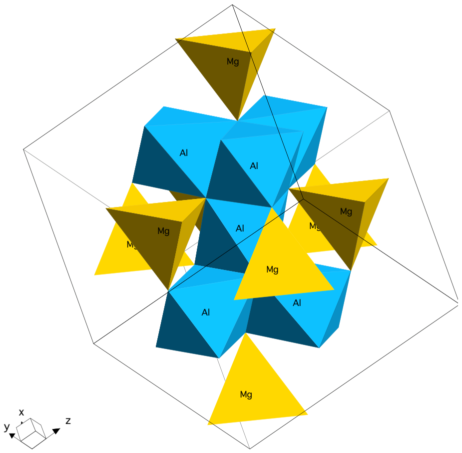


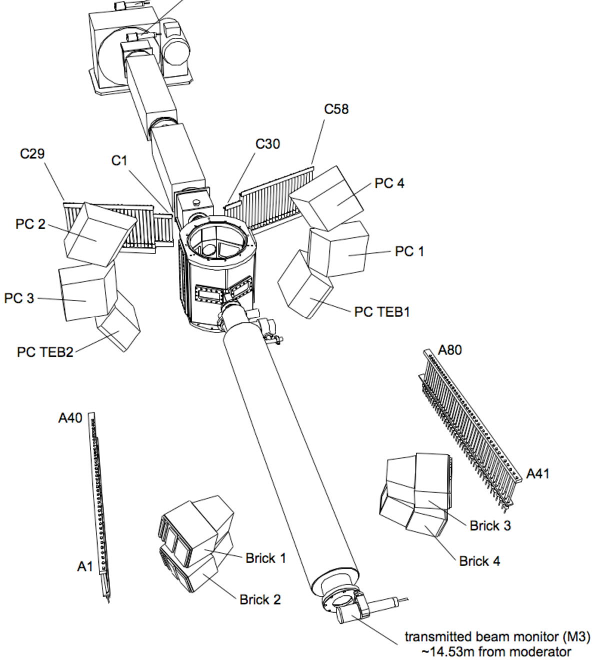


Order-disorder in spinel: occupancies from neutron powder diffraction

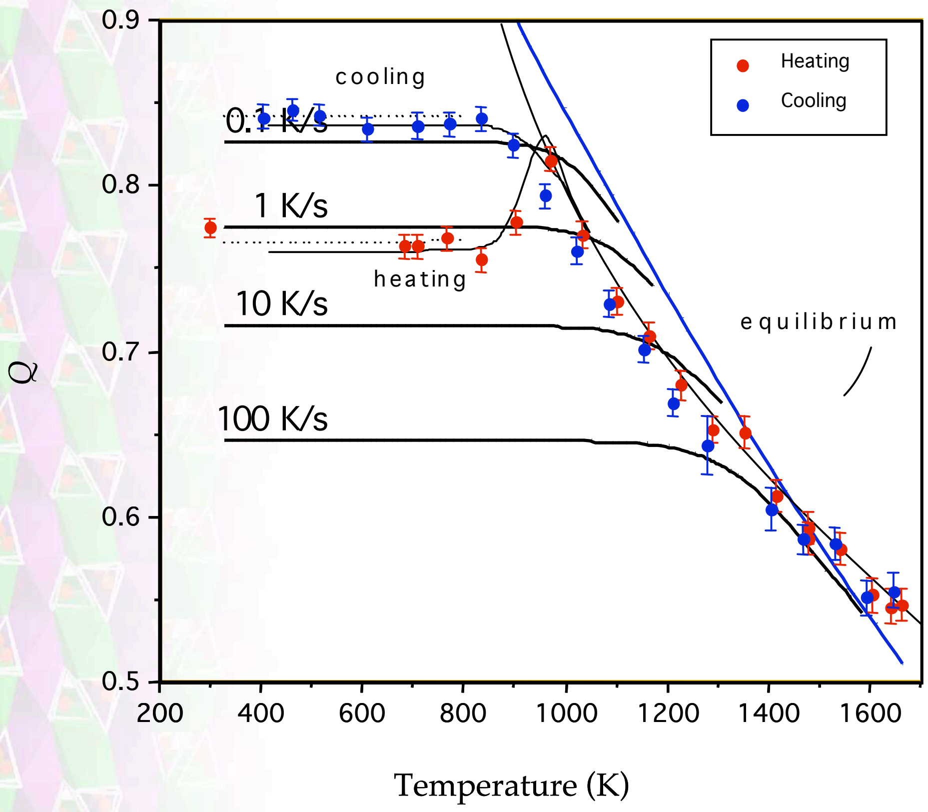








Order-disorder in spinel: occupancies from neutron powder diffraction



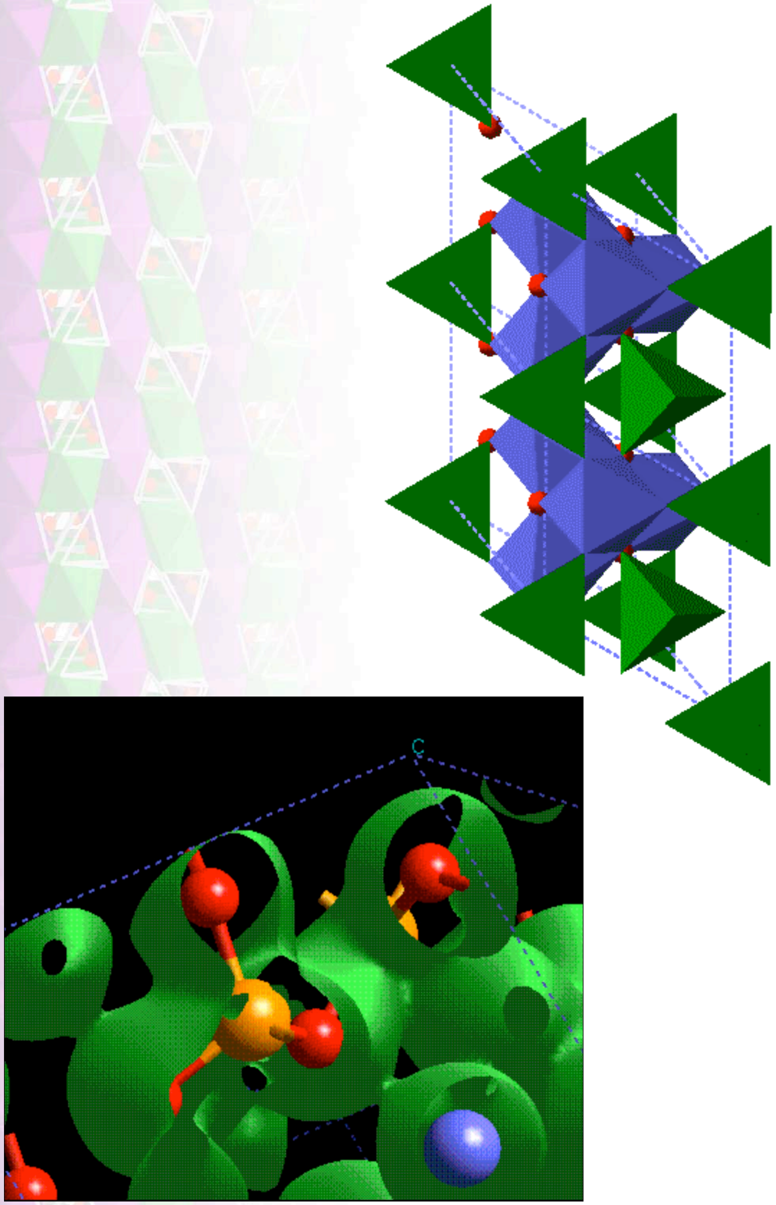
free energy difference between fully disordered distribution of metal cations and the equilibrium distribution is:

$$\Delta G = -hQ + \frac{a}{2}(T - T_C)Q^2 + \frac{b}{4}Q^4$$

lower-temperature kinetically-controlled *Q-T-t* pathways are defined by the Ginzburg-Landau equation:

$$\frac{dQ}{dt} = -\frac{\gamma \exp(-\Delta G^* / RT)}{2RT}\frac{\partial G}{\partial Q}$$

Modelling disorder: using spinel



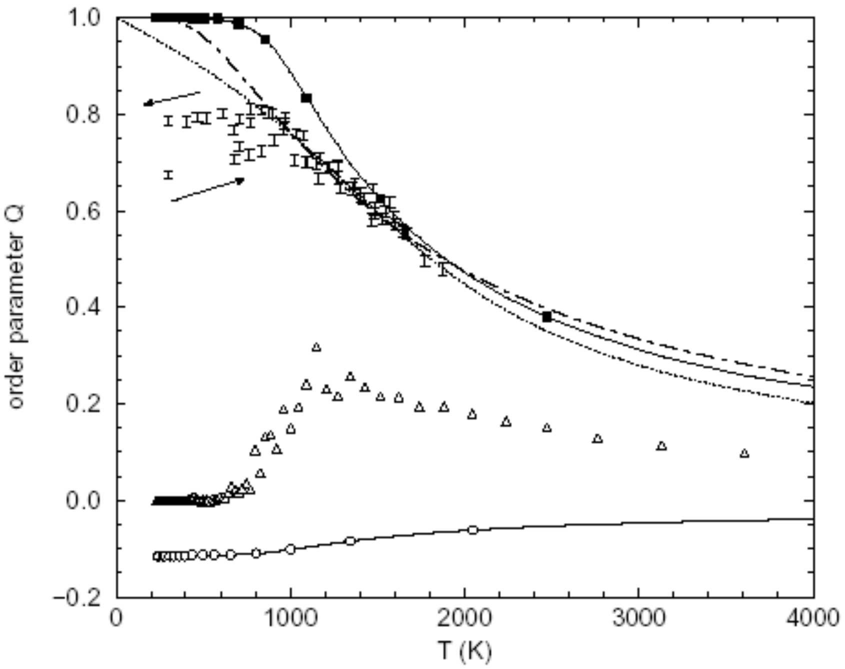
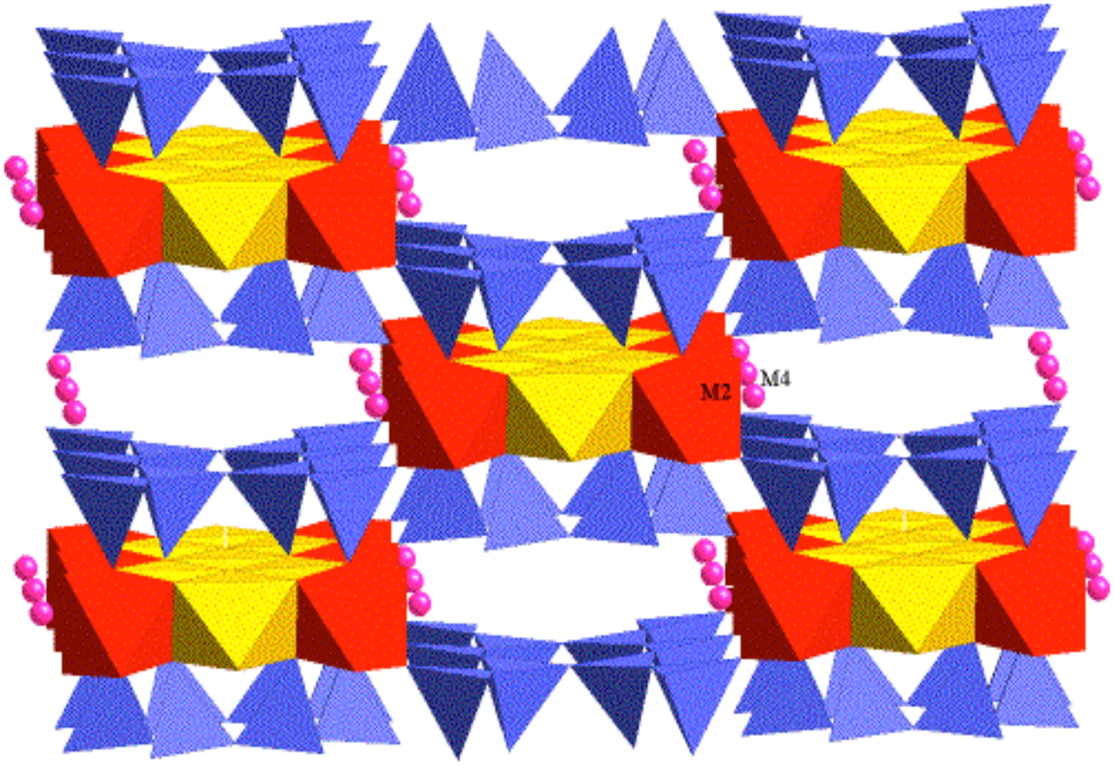


Figure 3. Results of Monte Carlo simulations, compared to results of three neutron scattering experiments and fits of analytic models to experimental data [1]. The order parameter Q is shown as ■, the energy of ordering as ○, and the susceptibility $(\langle Q^2\rangle - \langle Q\rangle^2)/T$ is amplified and shown as △. The experimental values of Q were fitted by Redfern *et al* [1] to a Landau model (⋯⋯) and the model of O'Neill and Navrotsky (— · —) [7]. The experimental data cover both heating and cooling, as indicated by arrows, and are kinetically limited below 1000 K.

M4-M(1,2,3) order-disorder in Fe-free cummingtonite

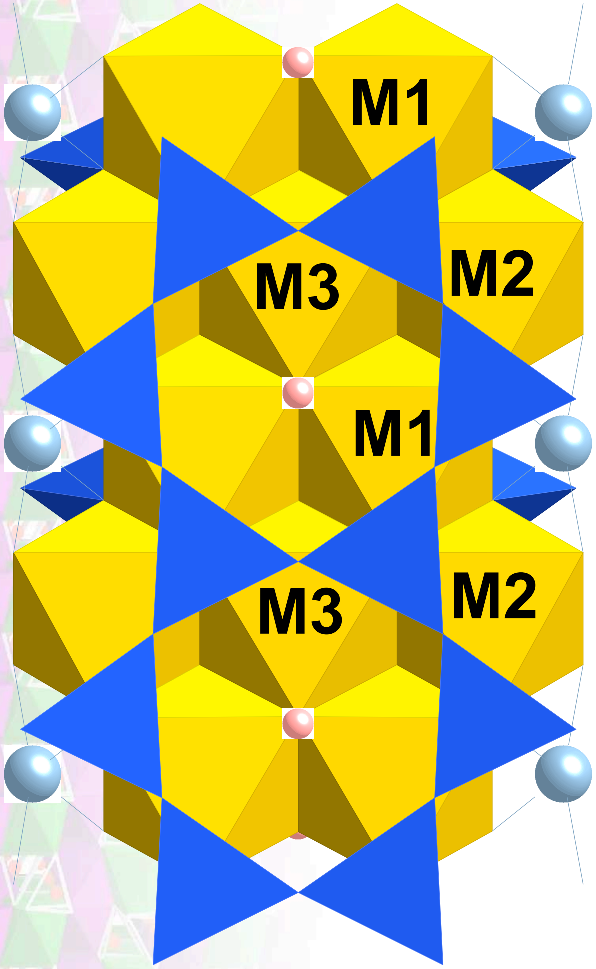


$(Na_{0.065}Ca_{0.205})_2Mg_{5.32}Mn_{1.14}[Si_8O_{22}](OH)_2$

$P2_1/m$ at room temperature, transforming to $C2/m$ at higher T

Reece et al. (2002) Phys Chem Minerals 29:562

M4-M(1,2,3) order-disorder in Fe-free cummingtonite

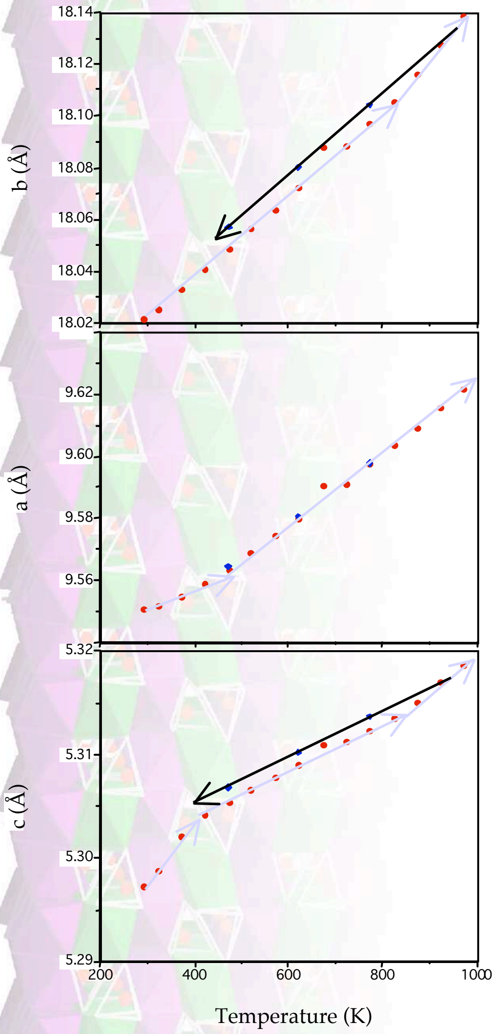


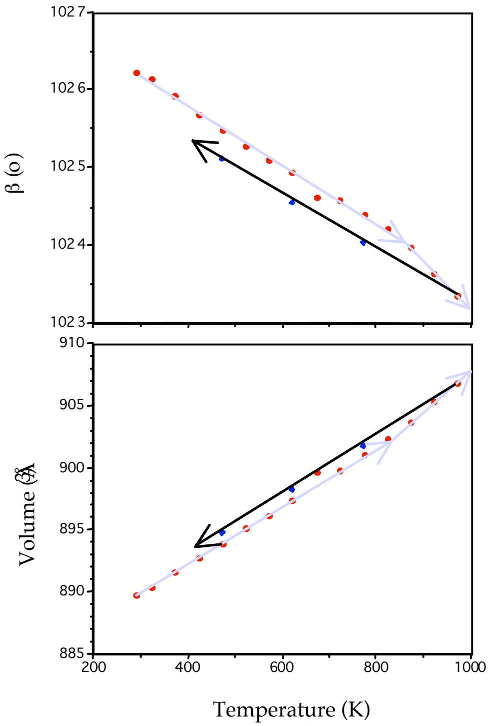
- How does Mn partition over the M sites? What are the equilibrium ordered states in amphiboles at temperatures greater than 500 °C, and can they be applied in geothermometry?

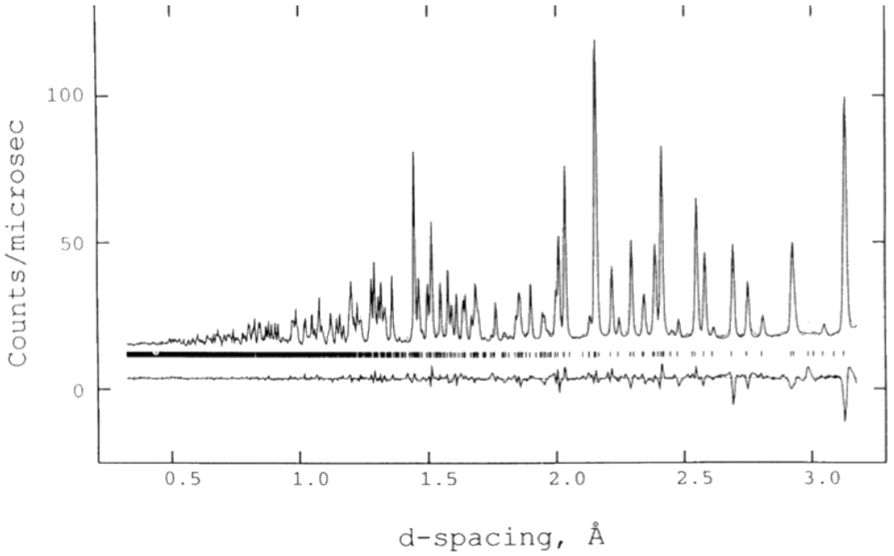
- What is the time-scale of ordering on cooling: does it occur during anneal and quench experiments, and can it be applied as a geospeedometer?

Approach: Structures and direct occupancies from high-T neutron powder diffraction data of Mn-Mg cummingtonite from Talcville.

M4-M(1,2,3) order-disorder in Fe-free cummingtonite







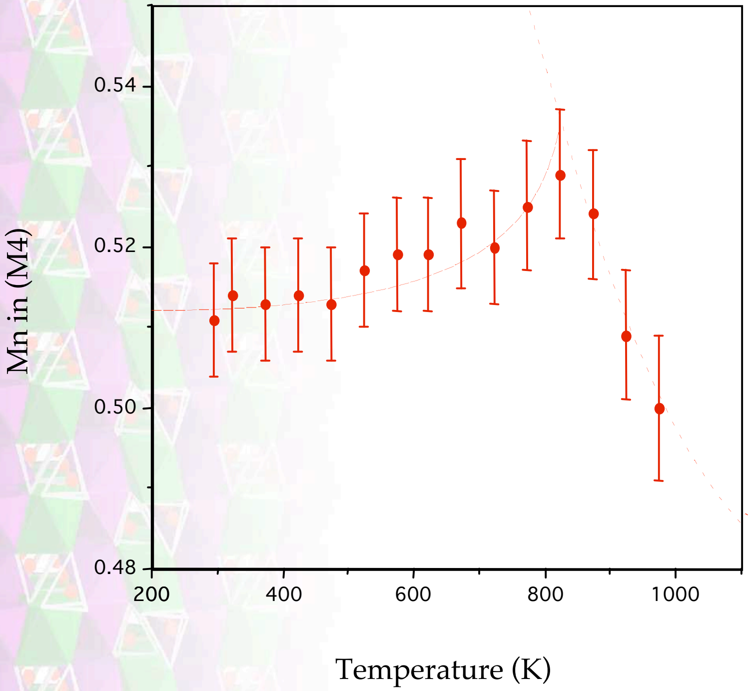
observed:

i) strains in +e1 » -e3 due to P21/m-C2/m transition,

ii) additional strains +e2, +e3 and -e5 resulting in a volume strain associated with M-site disordering.

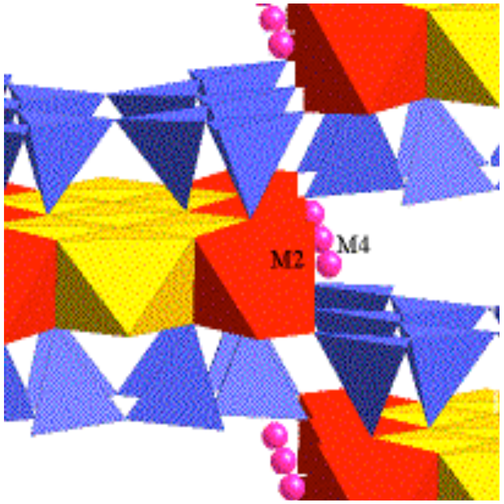
Reece et al. (2002) Phys Chem Minerals 29:562

M4-M(1,2,3) order-disorder in Fe-free cummingtonite



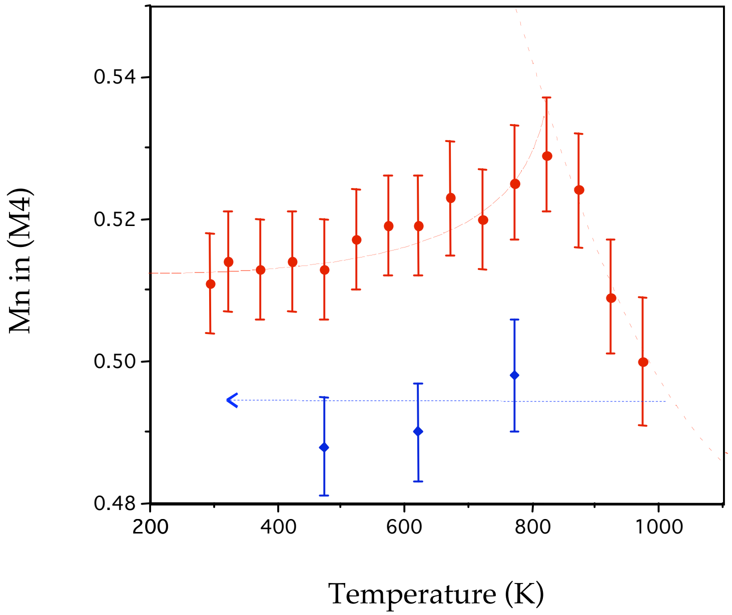
On heating, Mn in M4 increases initially (relaxation) before decreasing at temperatures above 800 K (disordering).

All changes are *very* small, however.



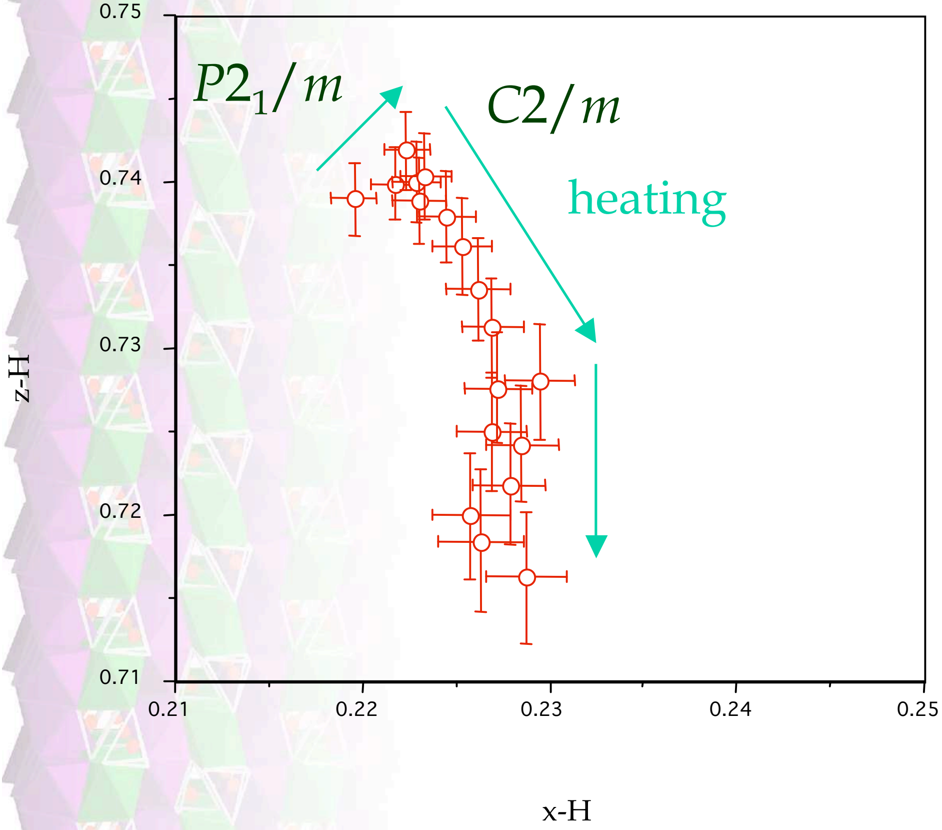
Since $K_D=[M_{123}*(1-M_4)]/[M_4*(1-M_{123})]$ and $\Delta G=-RT\ln K_D$ these data give and exchange energy of 21.5±0.7 kJ/mol
(cf. A value of 8.95 kJ/mol for Fe-Mg exchange given by Ghose, 1961)

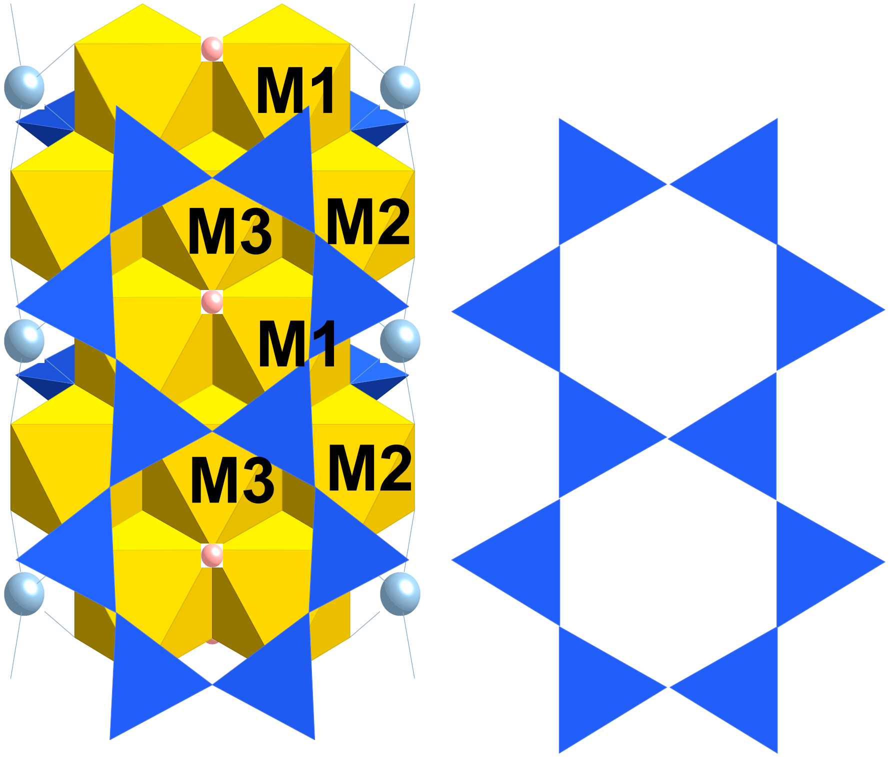
On cooling, the high-T disorder is frozen in.



M4-M(1,2,3) order-disorder in Fe-free cummingtonite

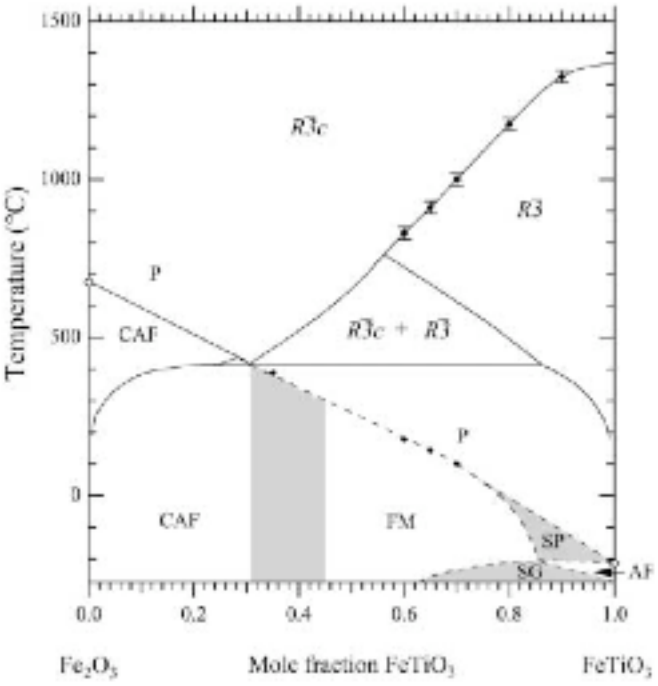
Neutron diffraction also provides sensitive information on the position of the hydrogen within the structure: it is affected more by the $P2_1/m$-$C2/m$ transition than by the disordering process. This is a reflection of the rotation-translation coupling at this transition.

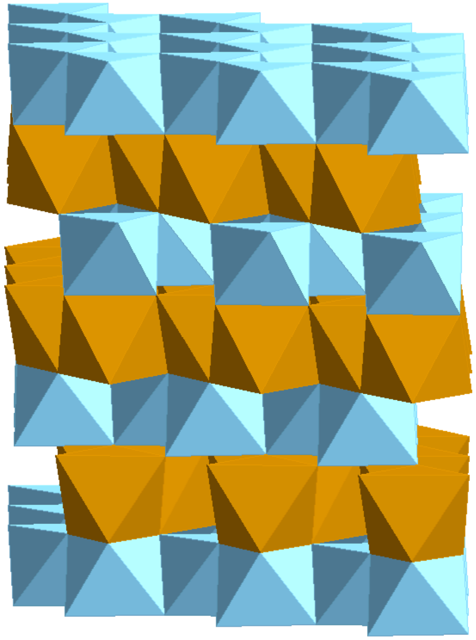




Reece et al. (2002) Phys Chem Minerals 29:562

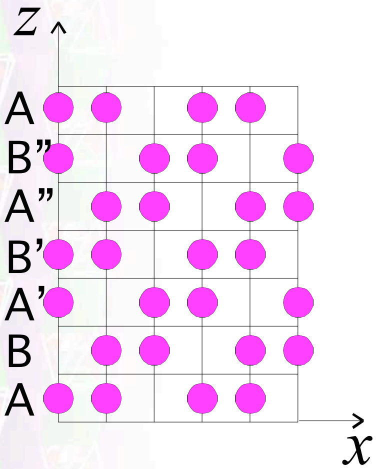
Convergent cation ordering, magnetic transitions and exsolution in ilmenite-hematite



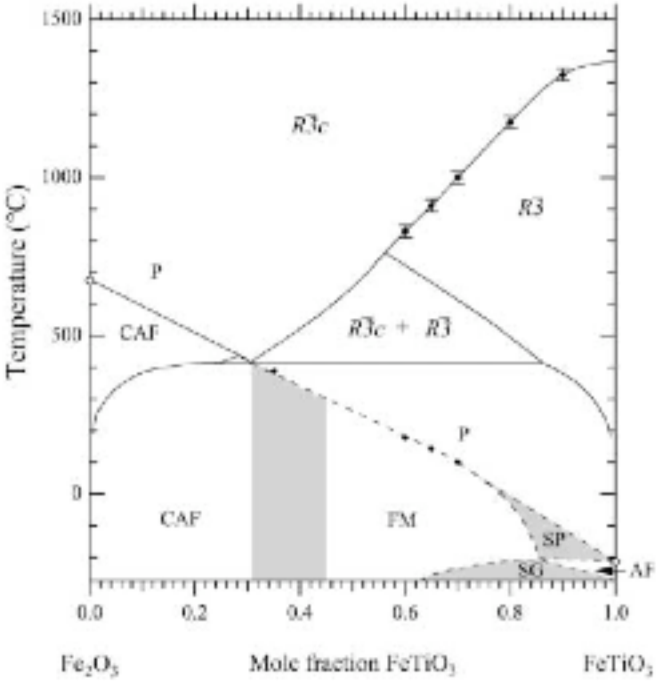


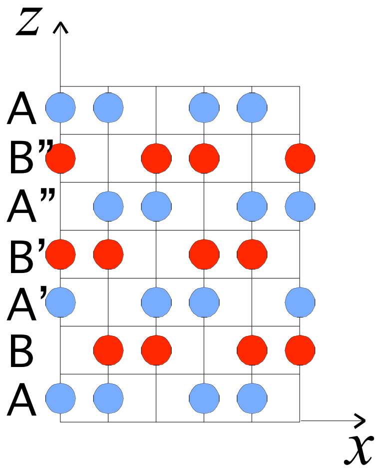
Harrison & Redfern (2001) Phys Chem Minerals 28: 399
Harrison et al. (2000) Am Min 85: 194, 1694.

Cation ordering and exsolution in ilmenite-hematite

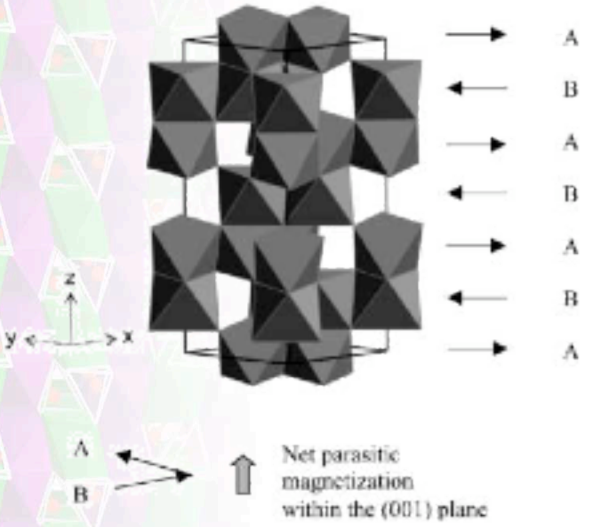


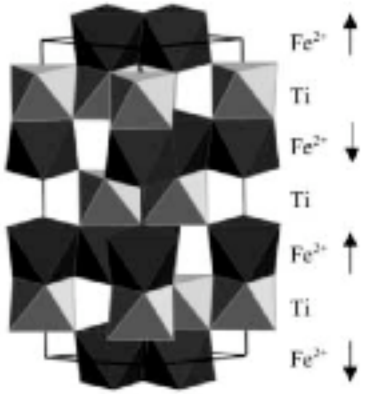
Hematite
(corundum structure)
R-3c





Ilmenite
Ti^{4+} ● Fe^{2+} ●
R-3





Harrison & Redfern (2001) Phys Chem Minerals 28: 399
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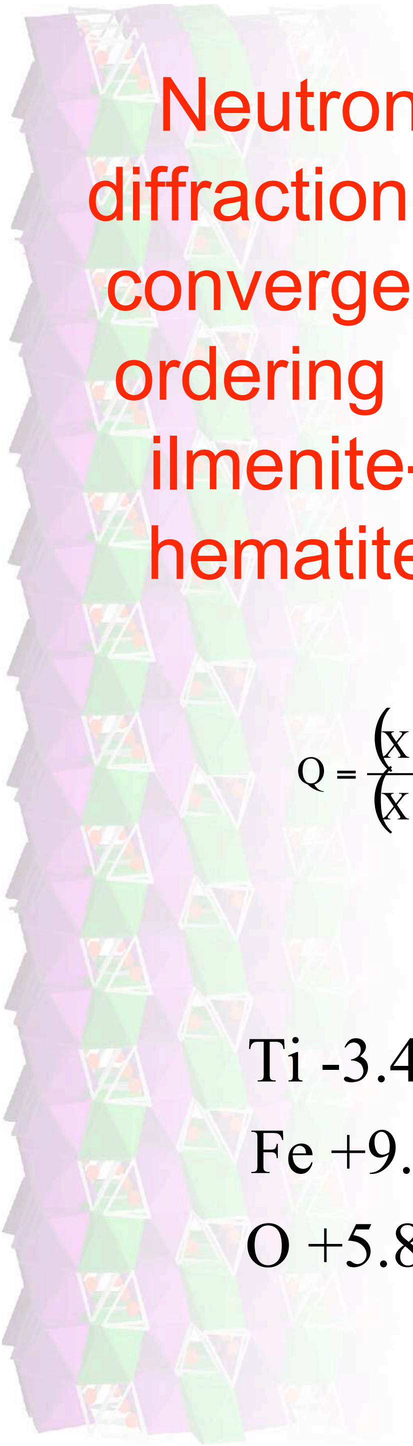
Neutron diffraction of convergent ordering in ilmenite-hematite



$$Q = \frac{\left(X_{Ti}^{B} - X_{Ti}^{A}\right)}{\left(X_{Ti}^{B} + X_{Ti}^{A}\right)}$$

Ti -3.438 fm

Fe +9.45 fm

O +5.803 fm

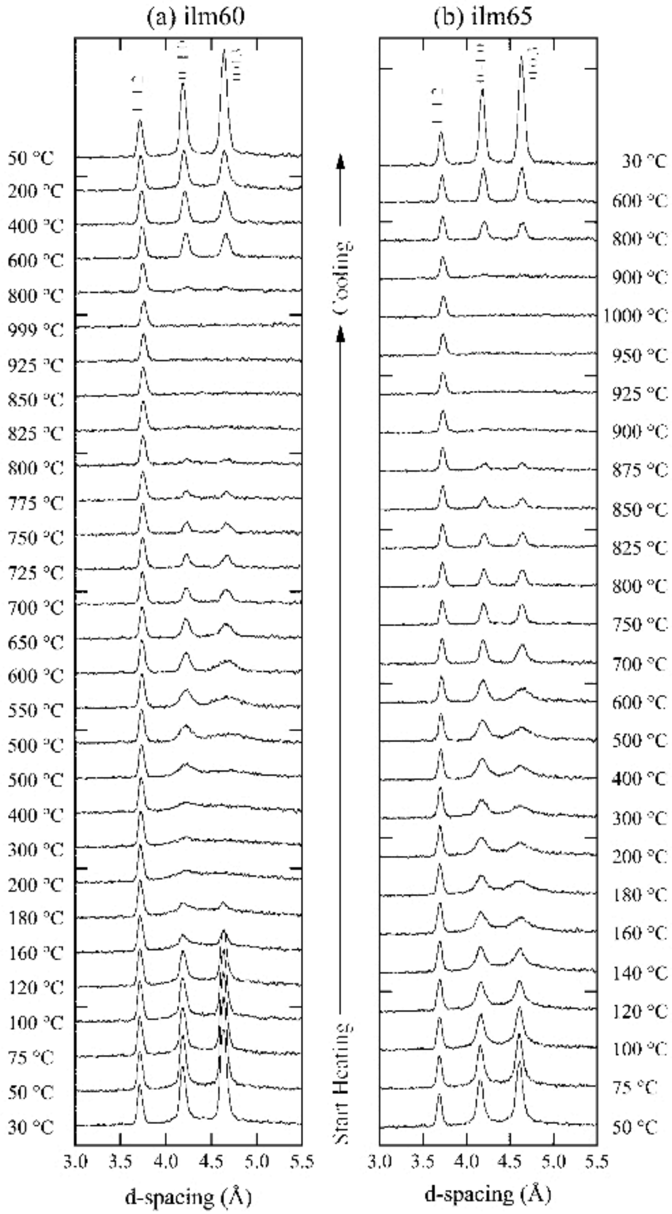
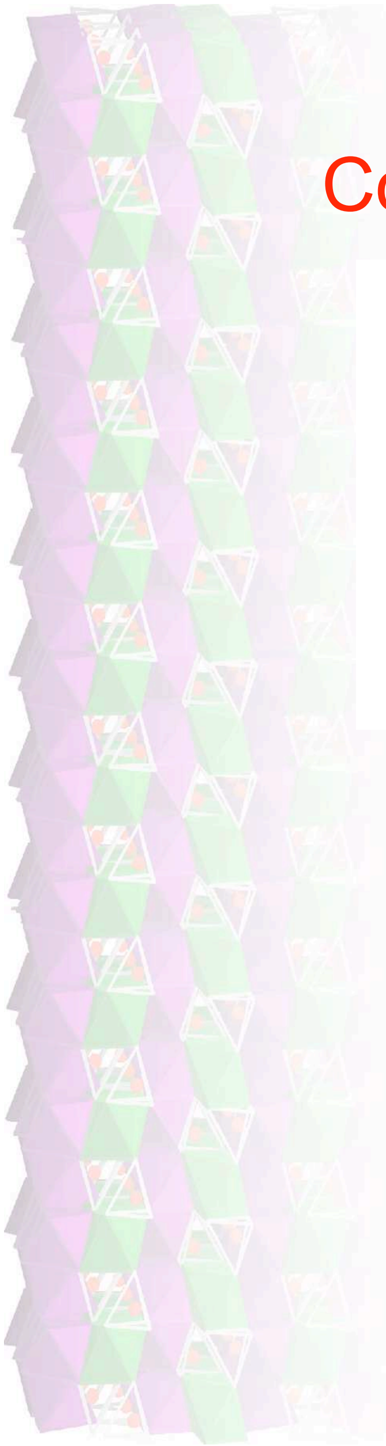


Fig. 3a, b Neutron diffraction profiles of the ($1\bar{1}2$) fundamental reflection ($d \approx 3.7$ Å) and the ($0\bar{1}1$) and (003) superlattice reflections ($d \approx 4.2$ Å and $d \approx 4.6$ Å, respectively), as a function of temperature for **a** ilm60 and **b** ilm65

Time of flight data collected on a very simple neutron powder diffractometer (ROTAX)

Harrison & Redfern (2001) Phys Chem Minerals 28: 399

Harrison et al. (2000) Am Min 85: 194, 1694.



Convergent ordering in ilmenite-hematite

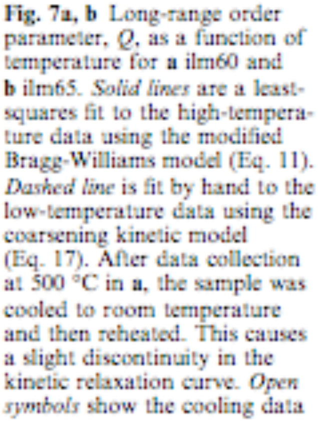
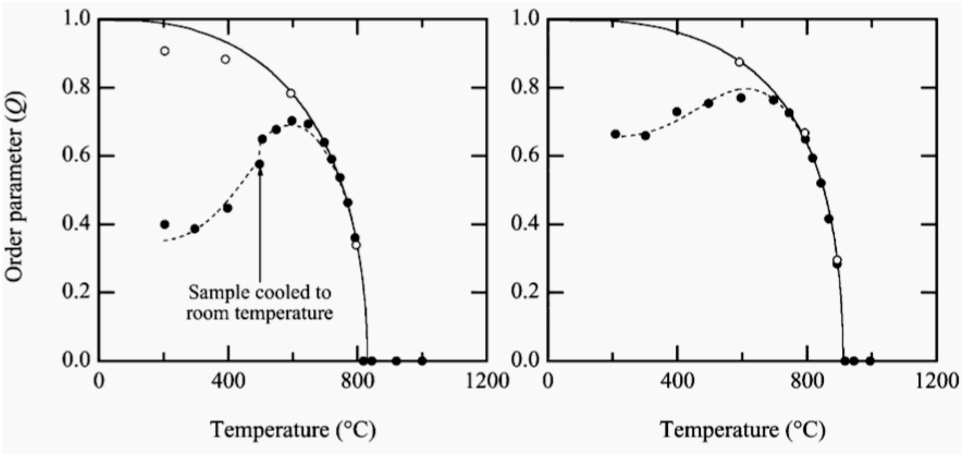
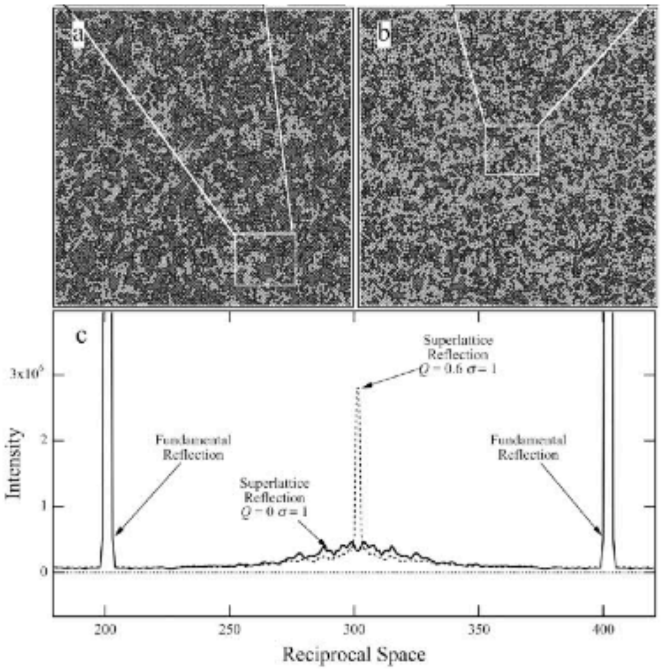


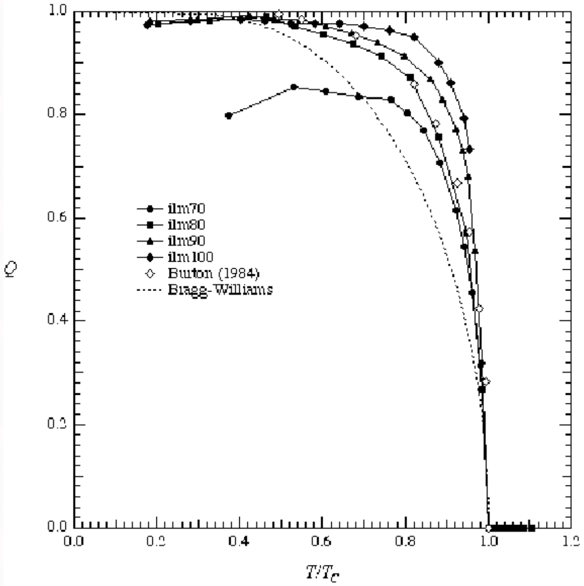
Fig. 7a, b Long-range order parameter, *Q*, as a function of temperature for **a** ilm60 and **b** ilm65. *Solid lines* are a least-squares fit to the high-temperature data using the modified Bragg-Williams model (Eq. 11). *Dashed line* is fit by hand to the low-temperature data using the coarsening kinetic model (Eq. 17). After data collection at 500 °C in **a**, the sample was cooled to room temperature and then reheated. This causes a slight discontinuity in the kinetic relaxation curve. *Open symbols* show the cooling data

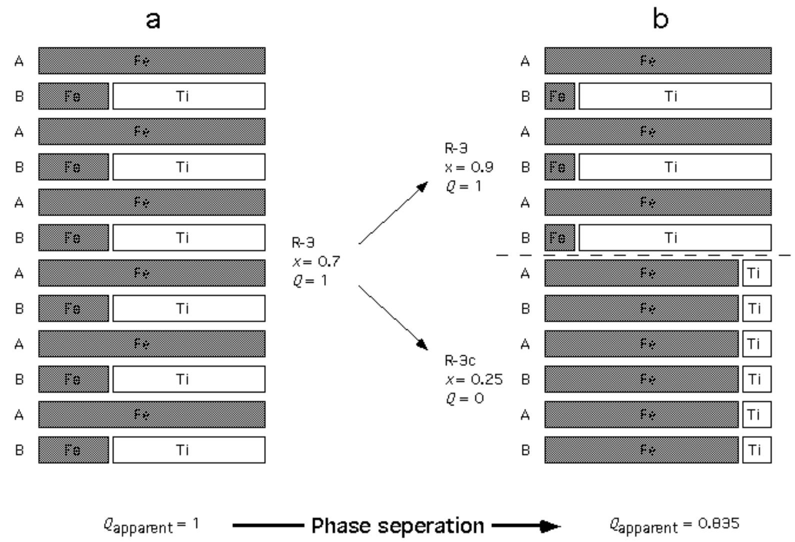


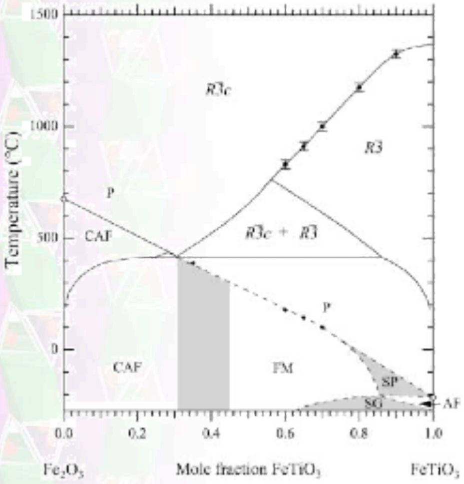


$$Q = \frac{\left(X_{Ti}^{B} - X_{Ti}^{A}\right)}{\left(X_{Ti}^{B} + X_{Ti}^{A}\right)}$$

Why is ilm70 less ordered at lower T than ilm 80-100? incipient phase separation



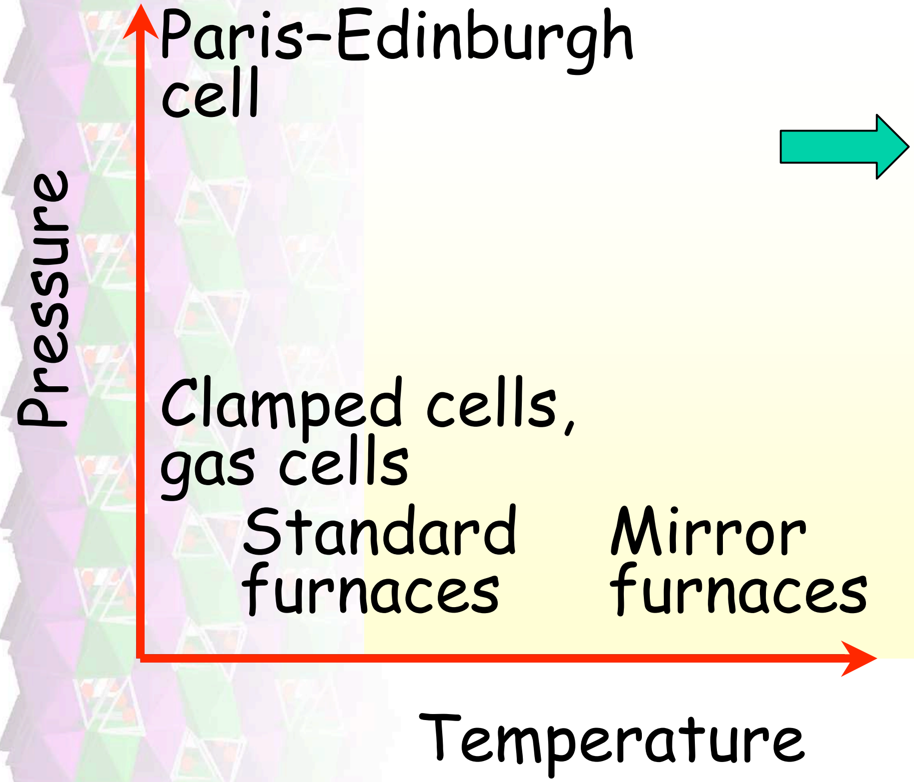




- Neutron powder diffraction is very sensitive to Fe-Ti distributions
- Magnetic ordering contributions give a measure of the magnetic structure
- Discrepancies can be attributed to allied effects: exsolution
- Data have been employed in macroscopic thermodynamic and microscopic statistical mechanical modelling

Harrison & Redfern (2001) Phys Chem Minerals 28: 399
Harrison et al. (2000) Am Min 85: 194, 1694.

What is the influence of P? Developing experiments at P & T


Paris-Edinburgh cell

Clamped cells, gas cells

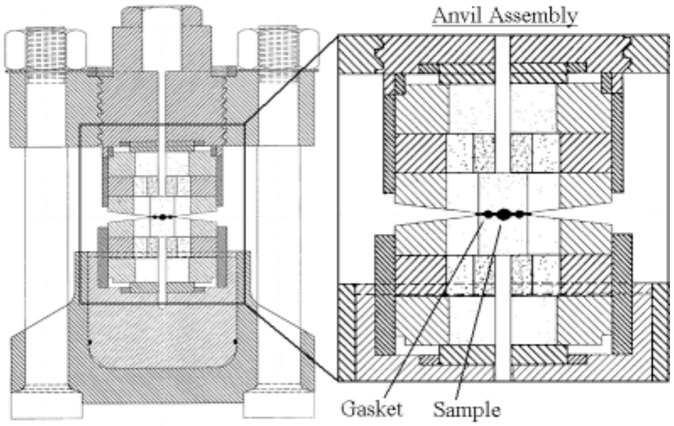
Standard furnaces

Mirror furnaces

Pressure

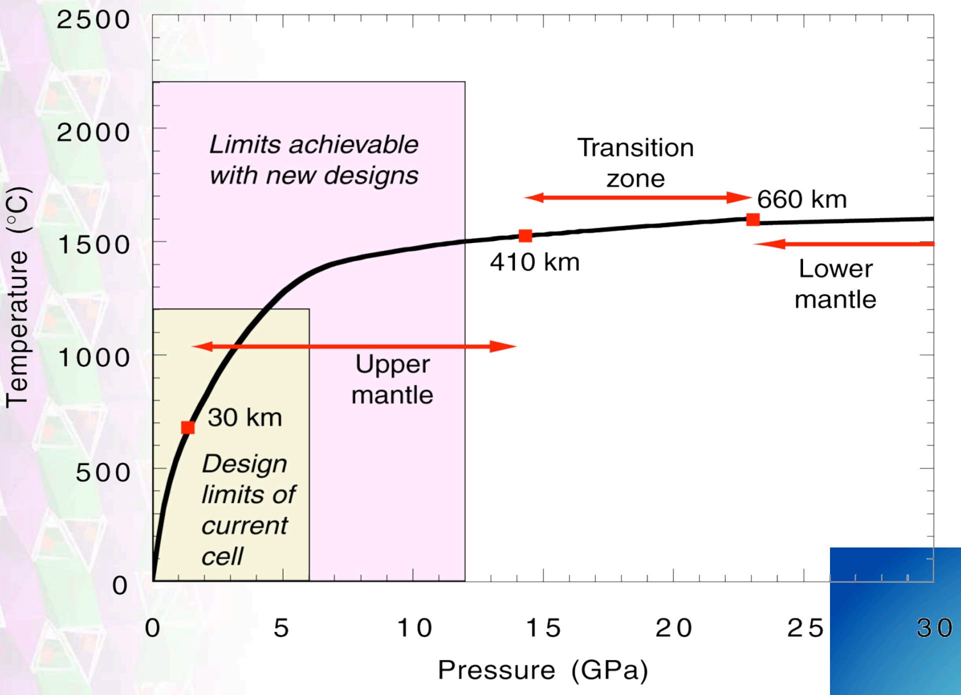
Temperature

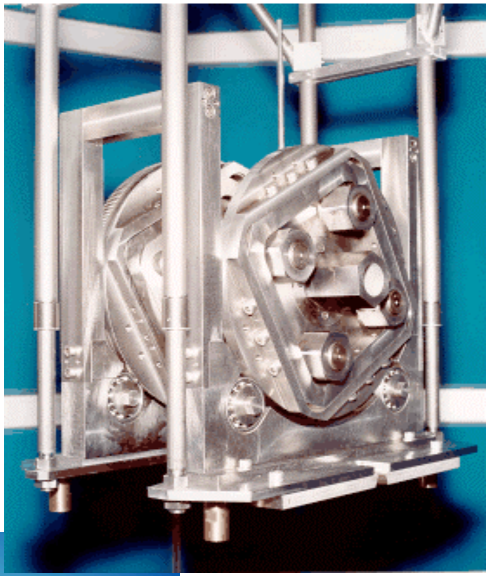
Project to develop internal heating of Paris-Edinburgh cell

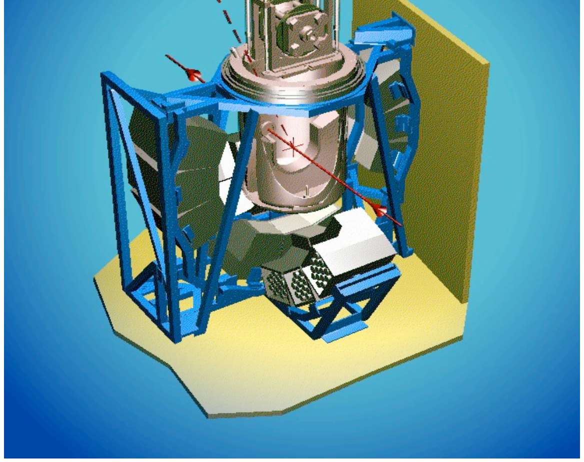


- portable (50kg, 30cm cube) 200 tonne loading frame
- toroidal gasket and cupped anvils
- < 100 mm^3 of sample

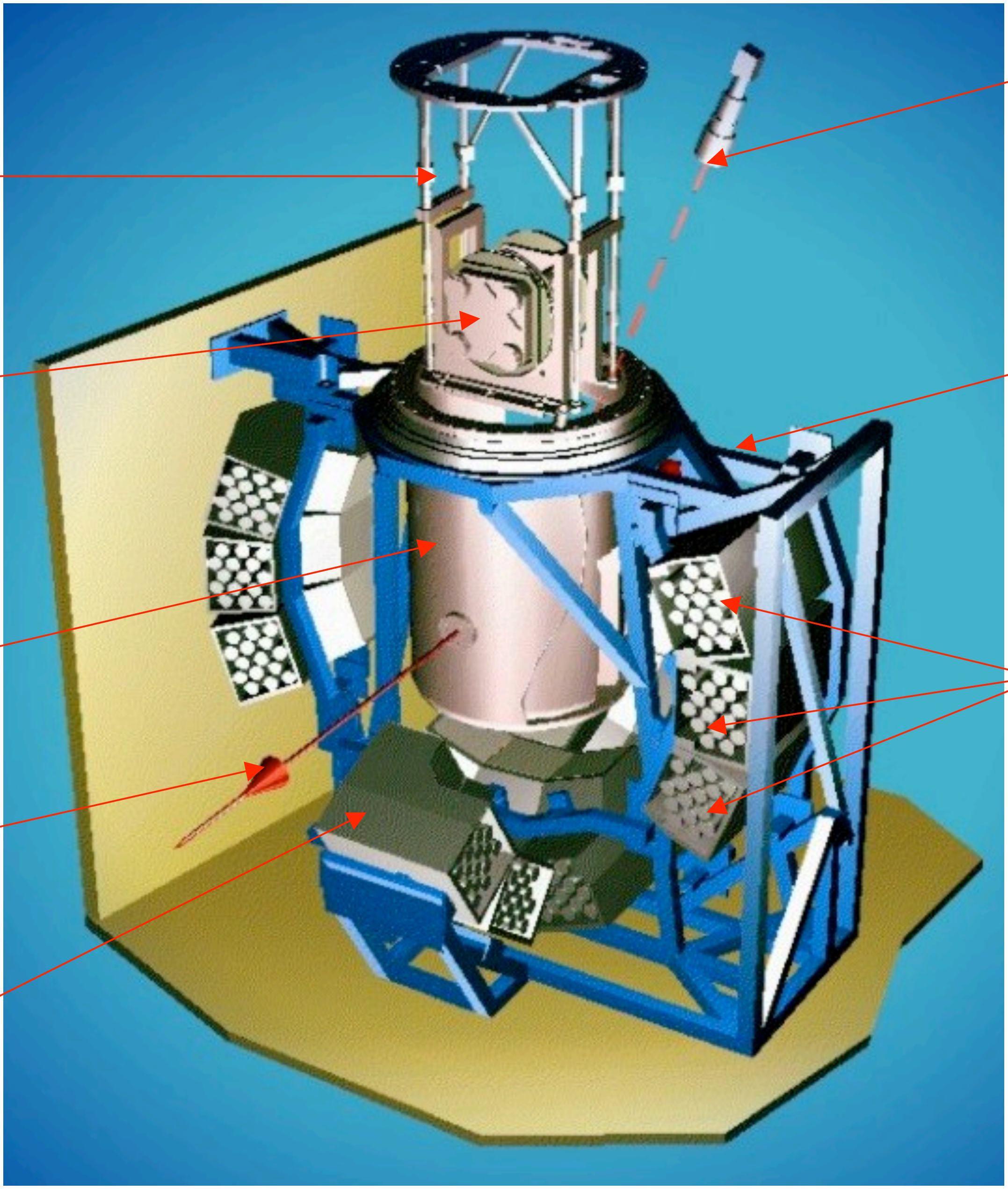
The high-P/T cell at ISIS







The PEARL high pressure facility at ISIS



sample camera

supporting frame

Paris-Edinburgh cell

beam in

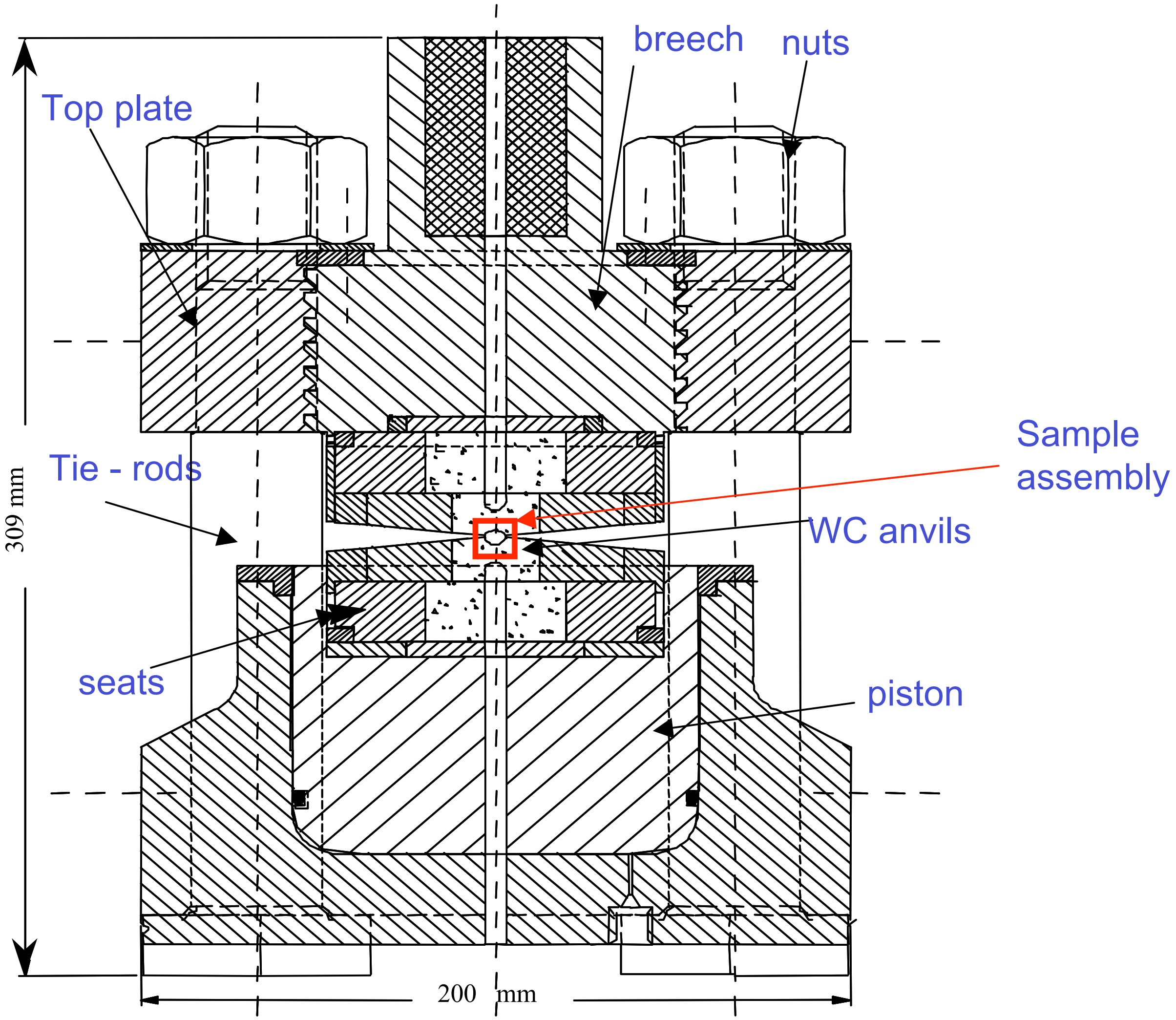
tank

transverse detector bank

beam out

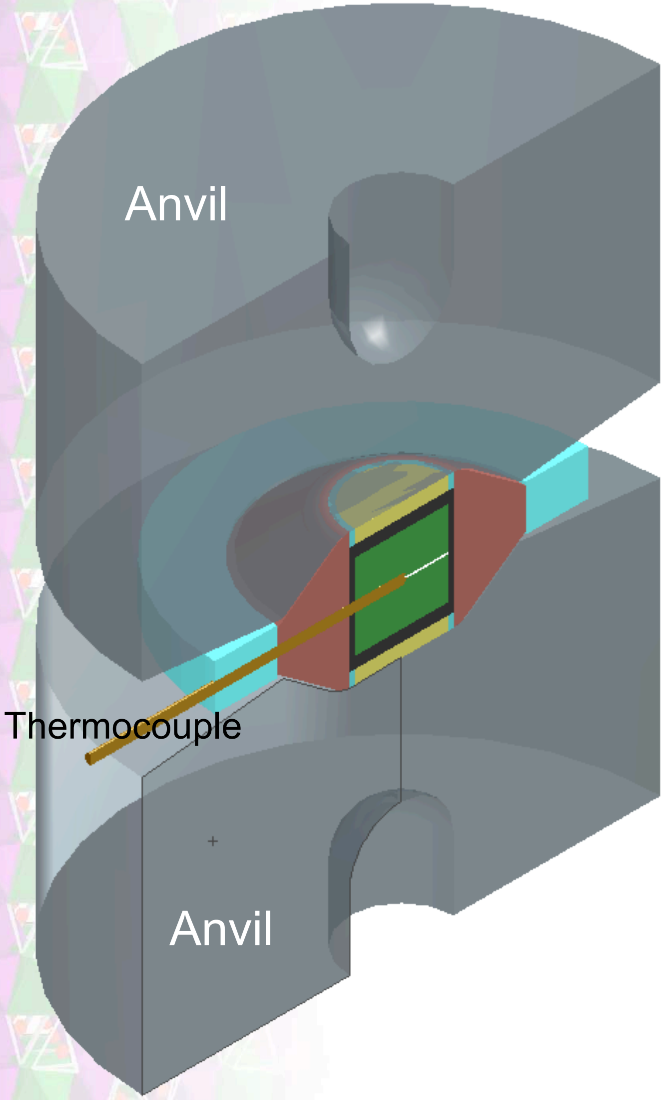
longitudinal detector bank

Paris-Edinburgh cell with internal micro-furnace for use with neutron resonance spectroscopy



University of Cambridge Department of Earth Sciences

An alternative to thermocouples?



- Temperatures measured by neutron resonance spectroscopy
- Pressures determined by compressibility of MgO or NaCl

Can determine sample conditions in dependent of the measured thermocouple emf

Problem:
During experiments the thermocouple failed or withdrew from the sample

Solution:
New design for the sample assembly

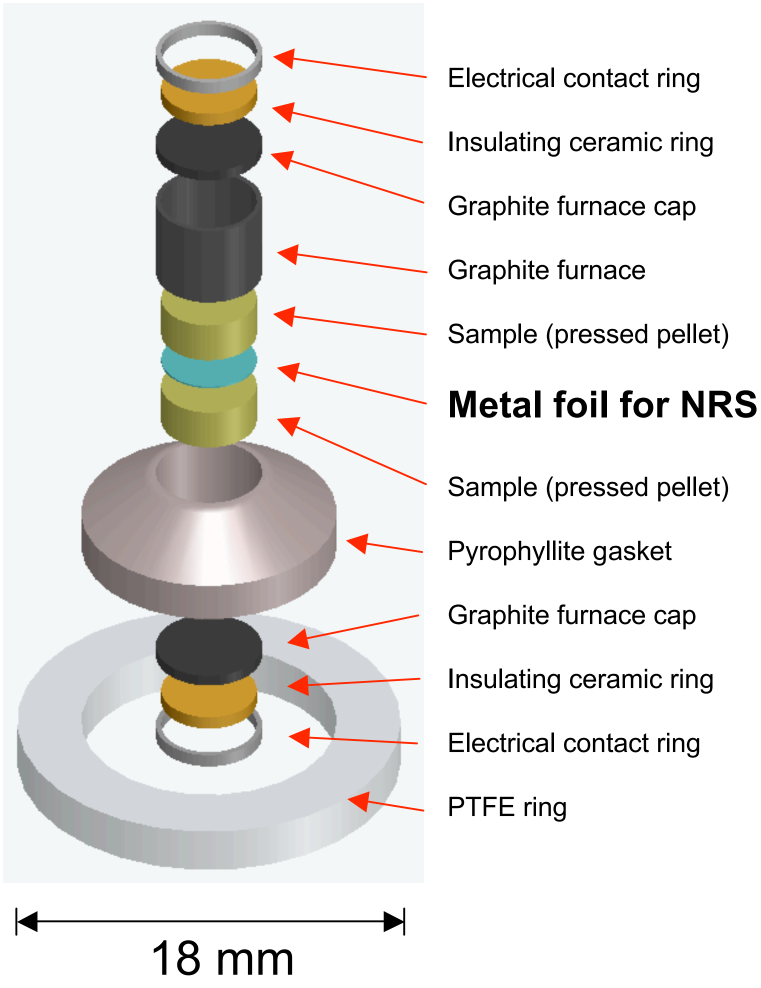
Temperature Measurement by NRS

Some difficulties with the use of thermocouples in high P/T experiments

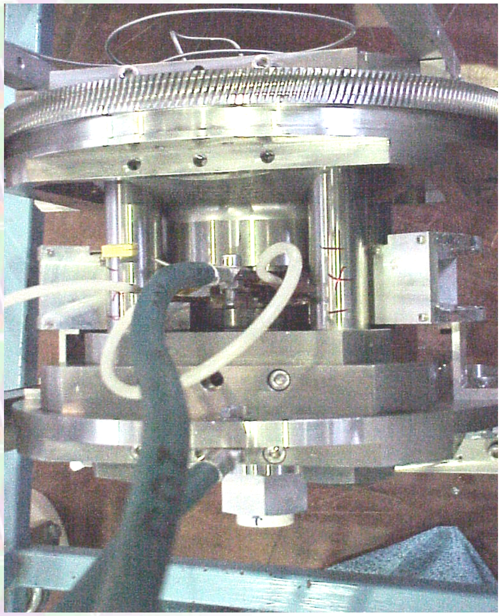
- Significant probability of thermocouple failure
- Compromises the structural integrity of the gasket
- Acts as a heat sink
- Uncertainty of Seebeck coefficients at high P

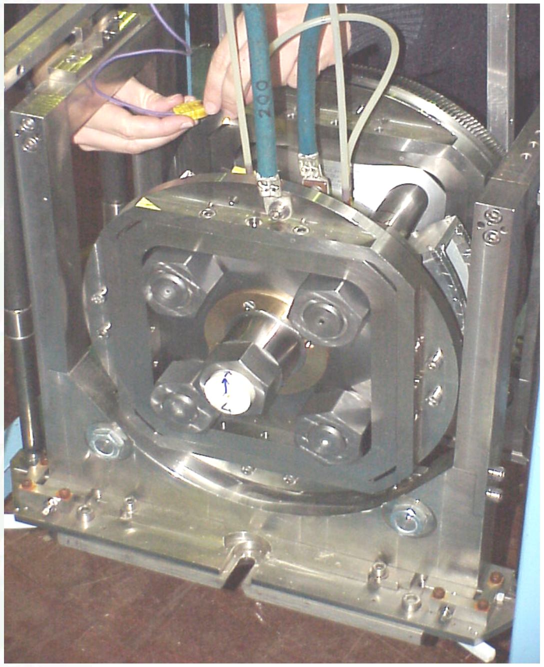
Solution:

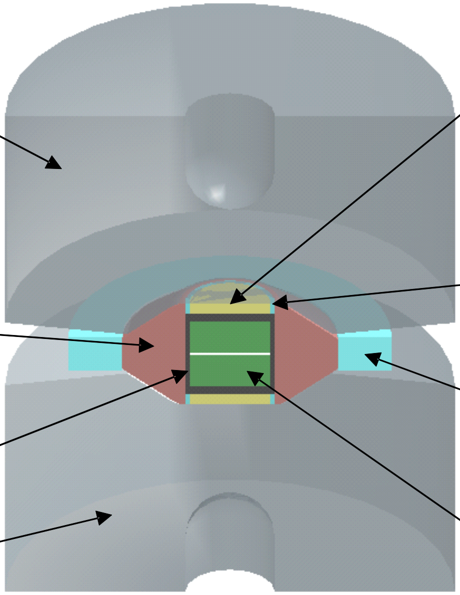
Use the thermally-induced Doppler broadening of neutron absorption resonances



Stone et al. (2005) J Appl Phys 98: 064905,
Stone et al. (2005) Nucl Inst Meth A, 547: 601
LeGodec et al (2001) Mineral Mag 65: 737







Anvil

Insulating
Ceramic disk

Electrical
contact ring

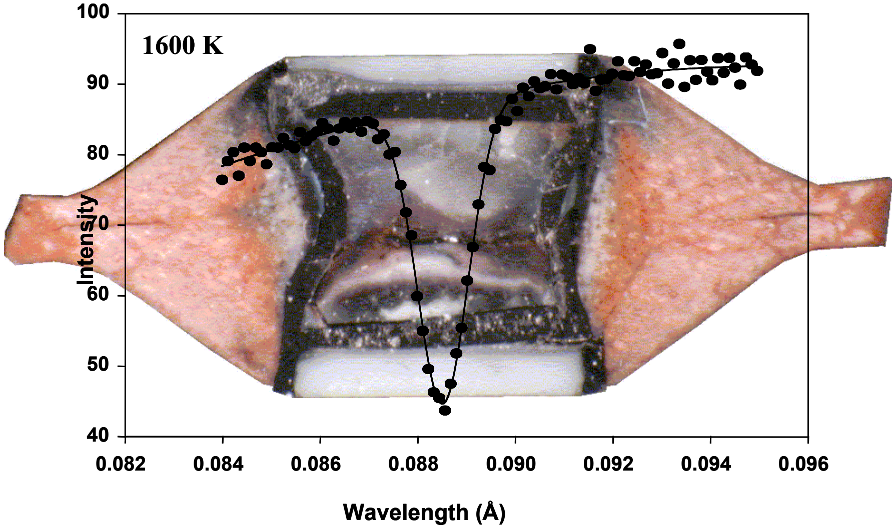
Ceramic
gasket

PTFE ring

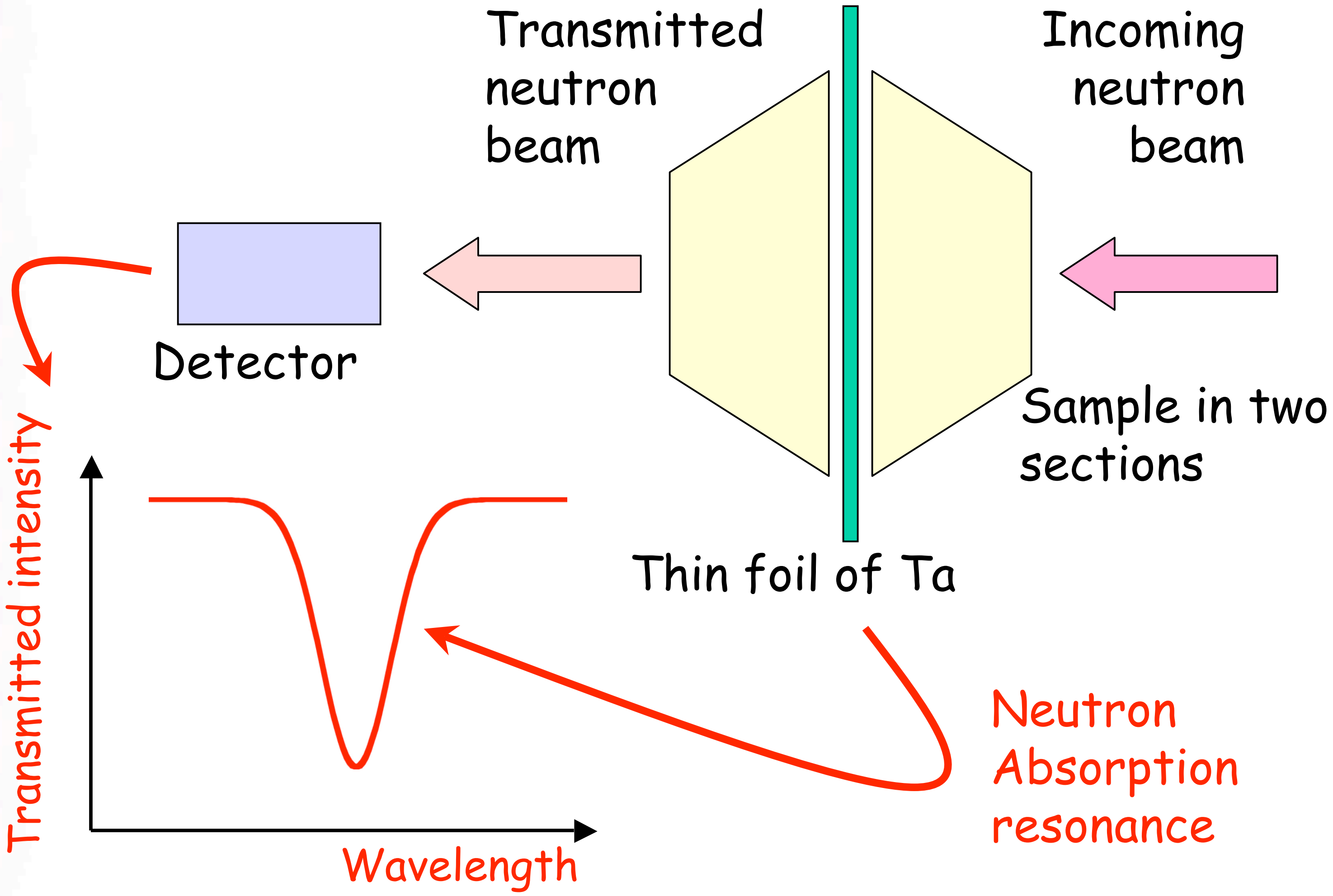
Cylindrical
furnace

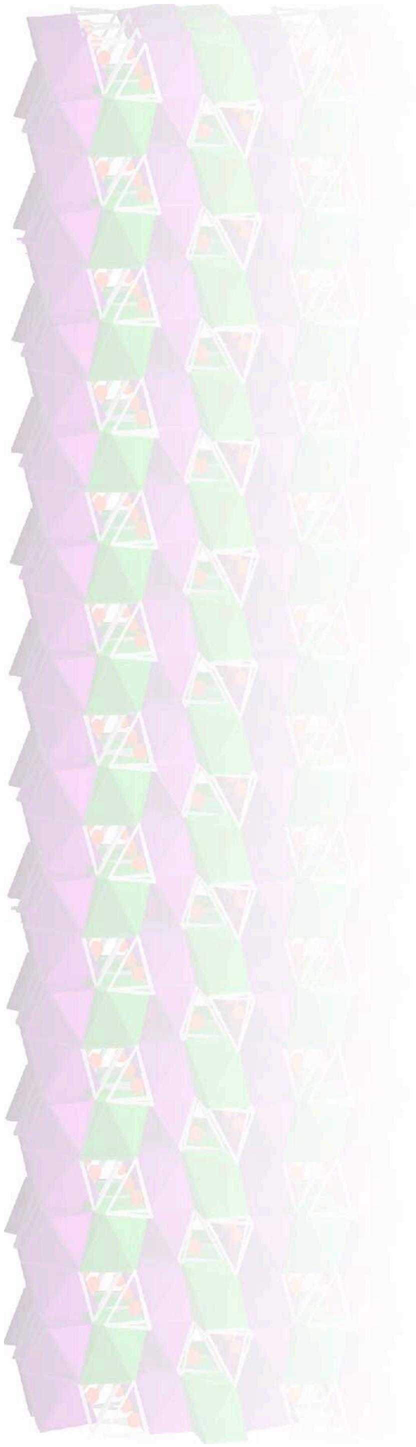
Anvil

Sample

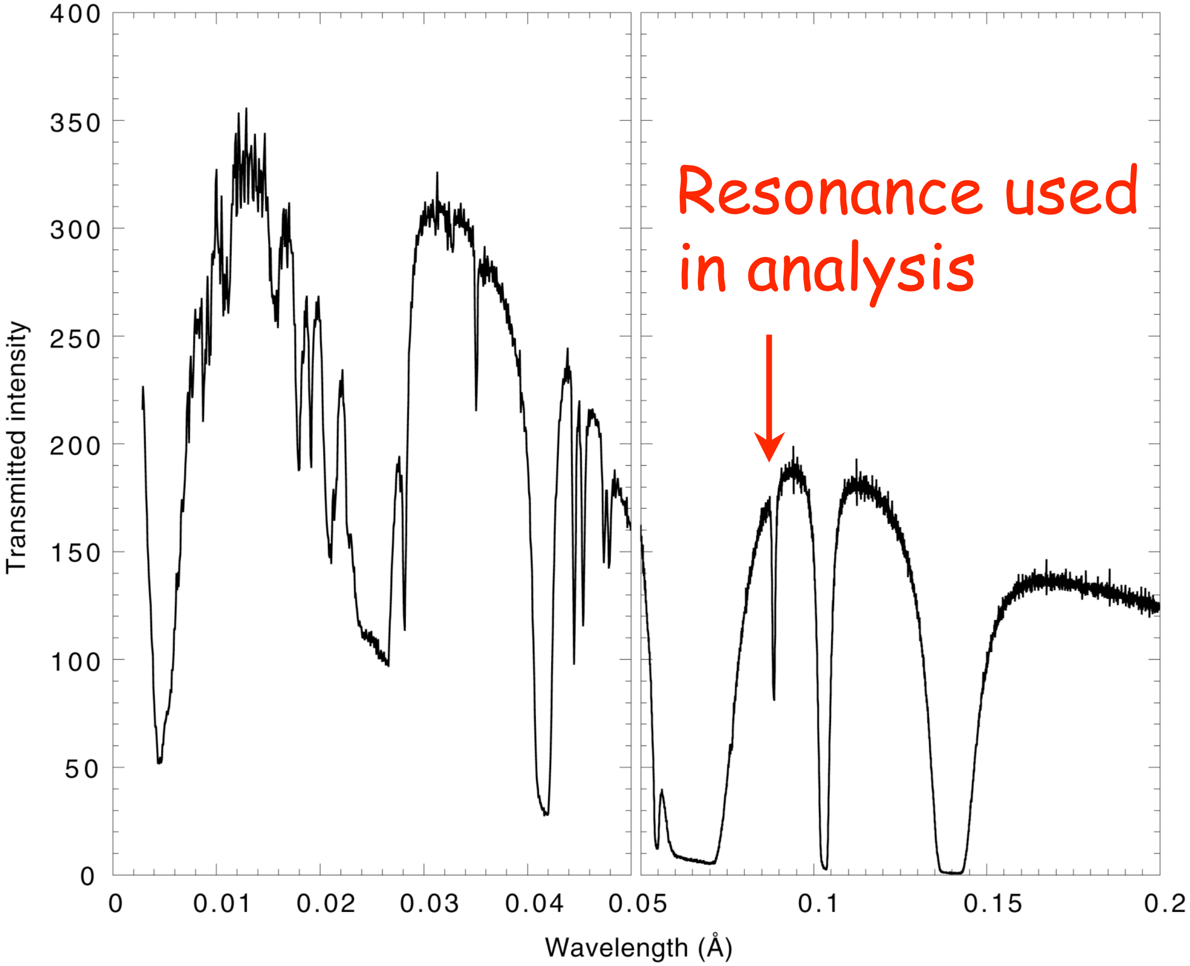


Temperature measurement by radiography



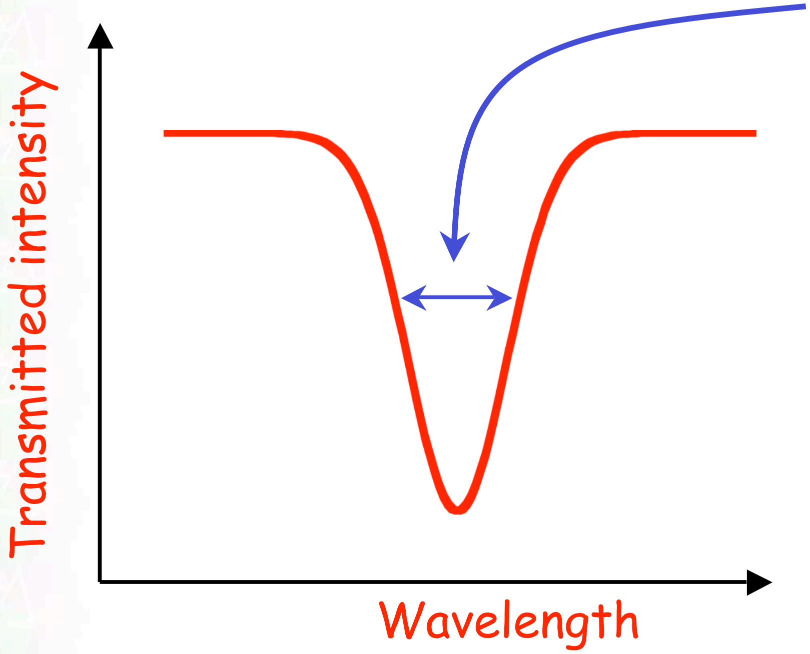


Transmission spectrum



Resonance used in analysis

Effect of temperature

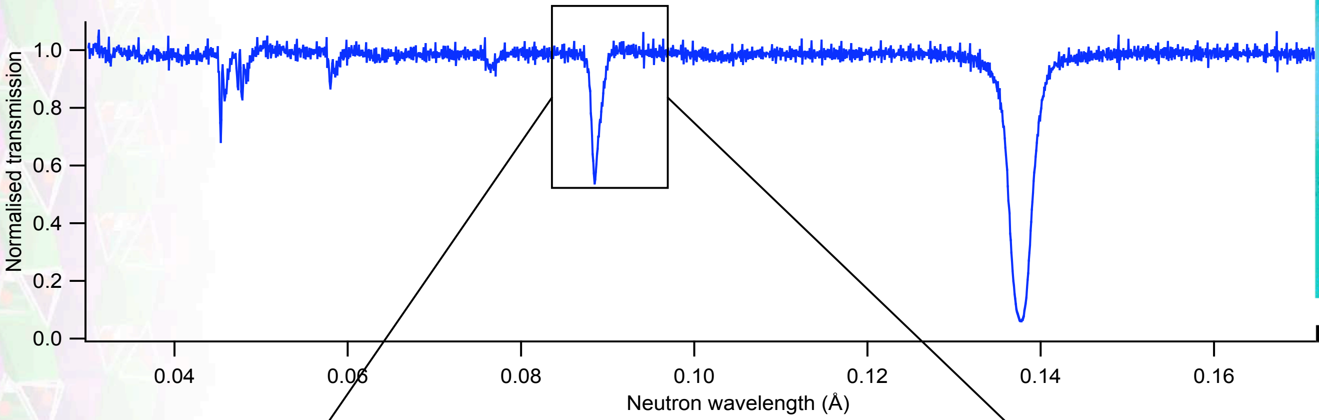


Width of resonance line increases with temperature due to Doppler effect

Width of resonance line can be used to calibrate temperature

Doppler Broadening of Absorption Resonances

Transmission spectrum from ^{181}Ta:



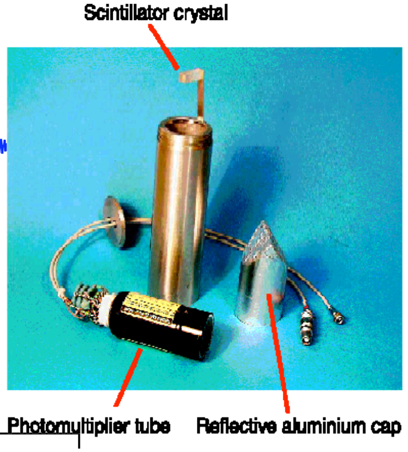
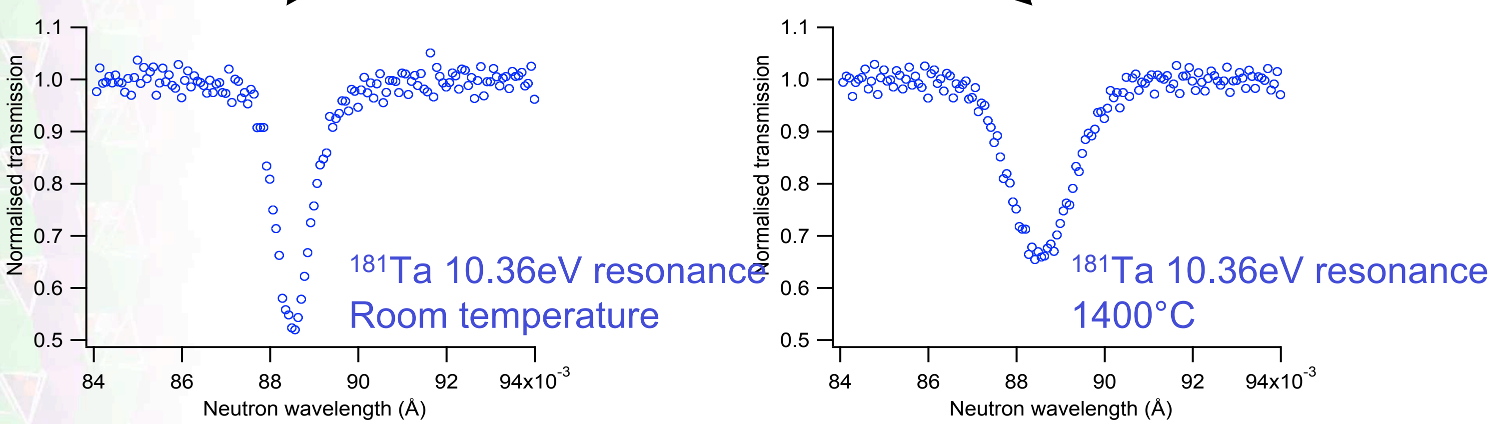


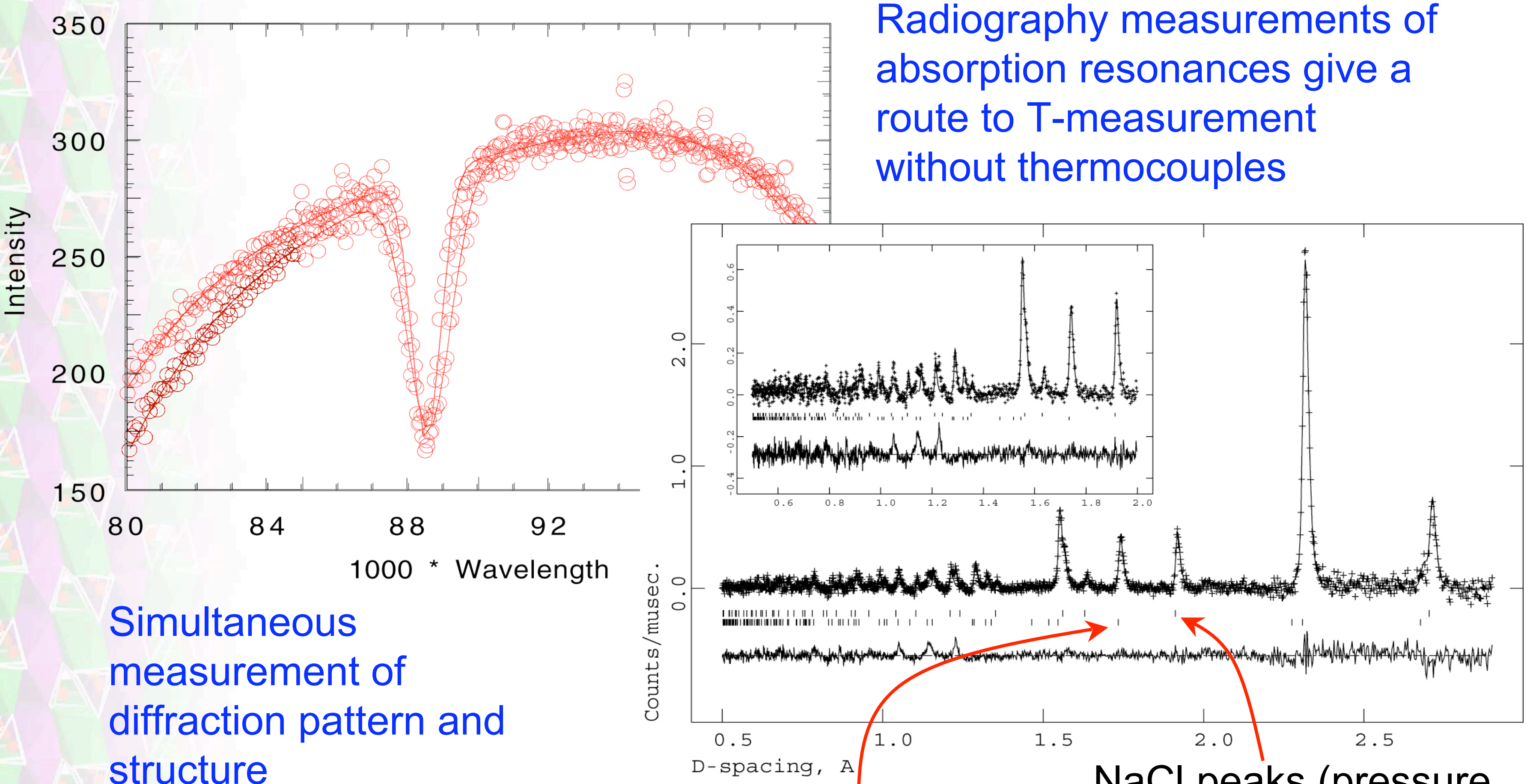
FIG. 3. Components of the neutron resonance monitor.



Stone et al. (2005) J Appl Phys 98: 064905,
Stone et al. (2005) Nucl Inst Meth A, 547: 601
LeGodec et al (2001) Mineral Mag 65: 737

Measurement of P, T, and stucture (including order-disorder)

Radiography measurements of absorption resonances give a route to T-measurement without thermocouples



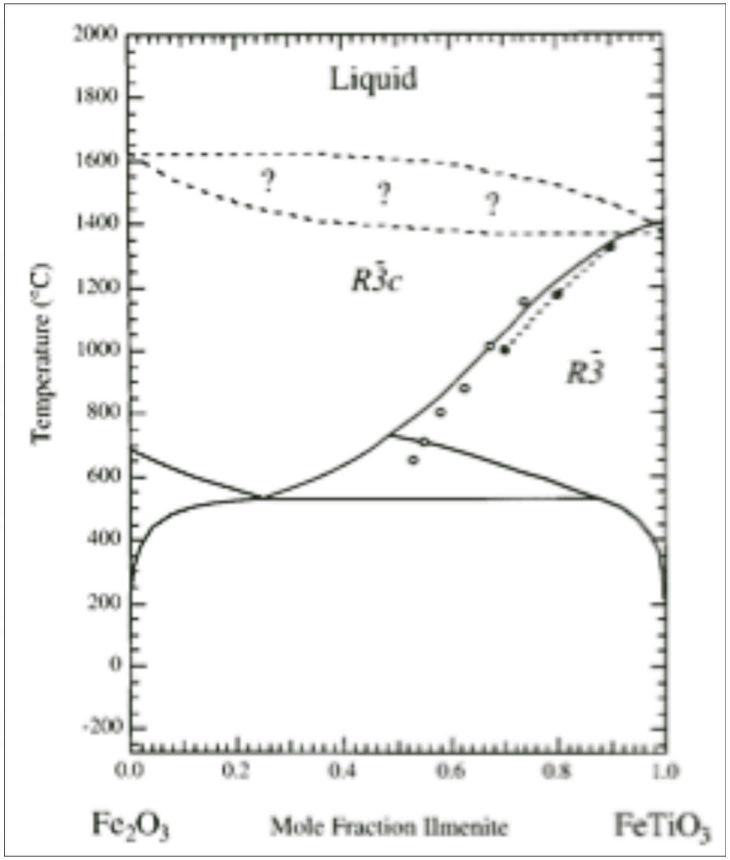
Simultaneous measurement of diffraction pattern and structure

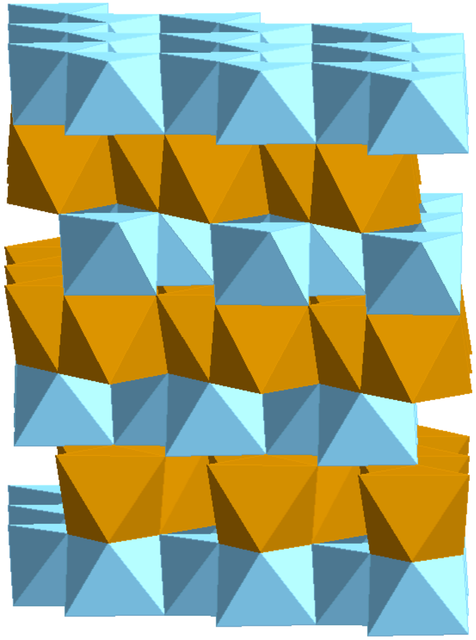
$Mg(OD)_2$ peaks

NaCl peaks (pressure calibrant)

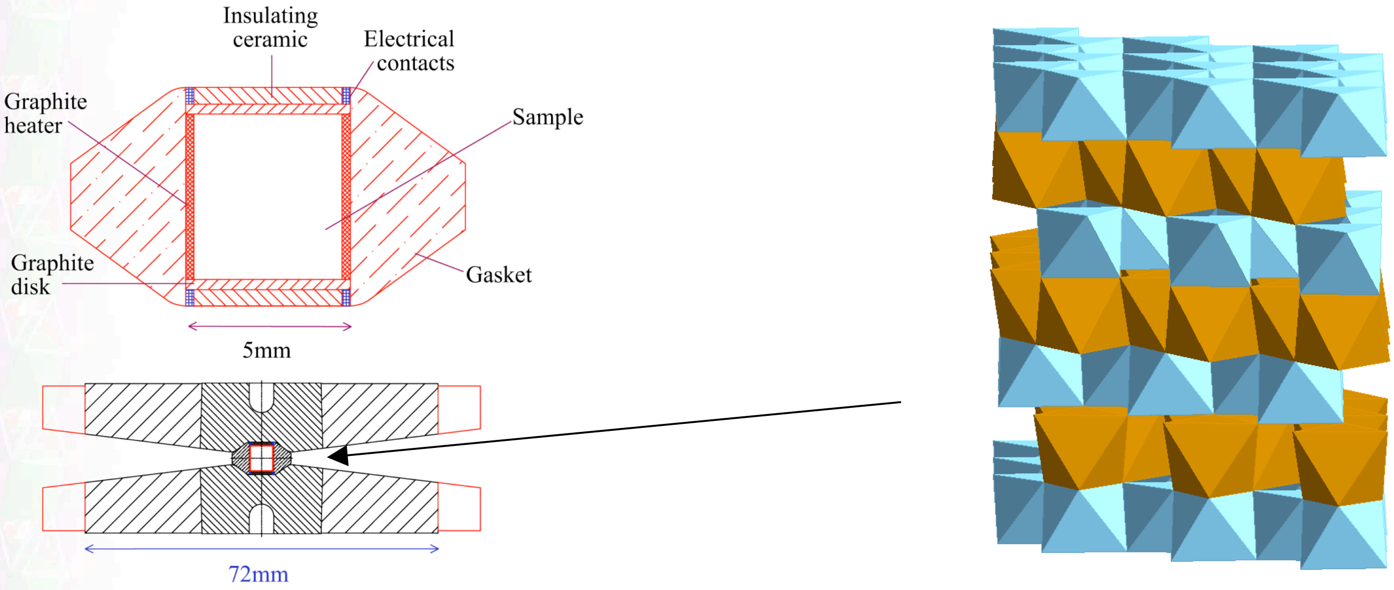
Pressure Dependence of Cation Order in ilmenite 65% - hematite 35%

Harrison, Stone & Redfern (2006) Phys Earth Planet Int 154: 266





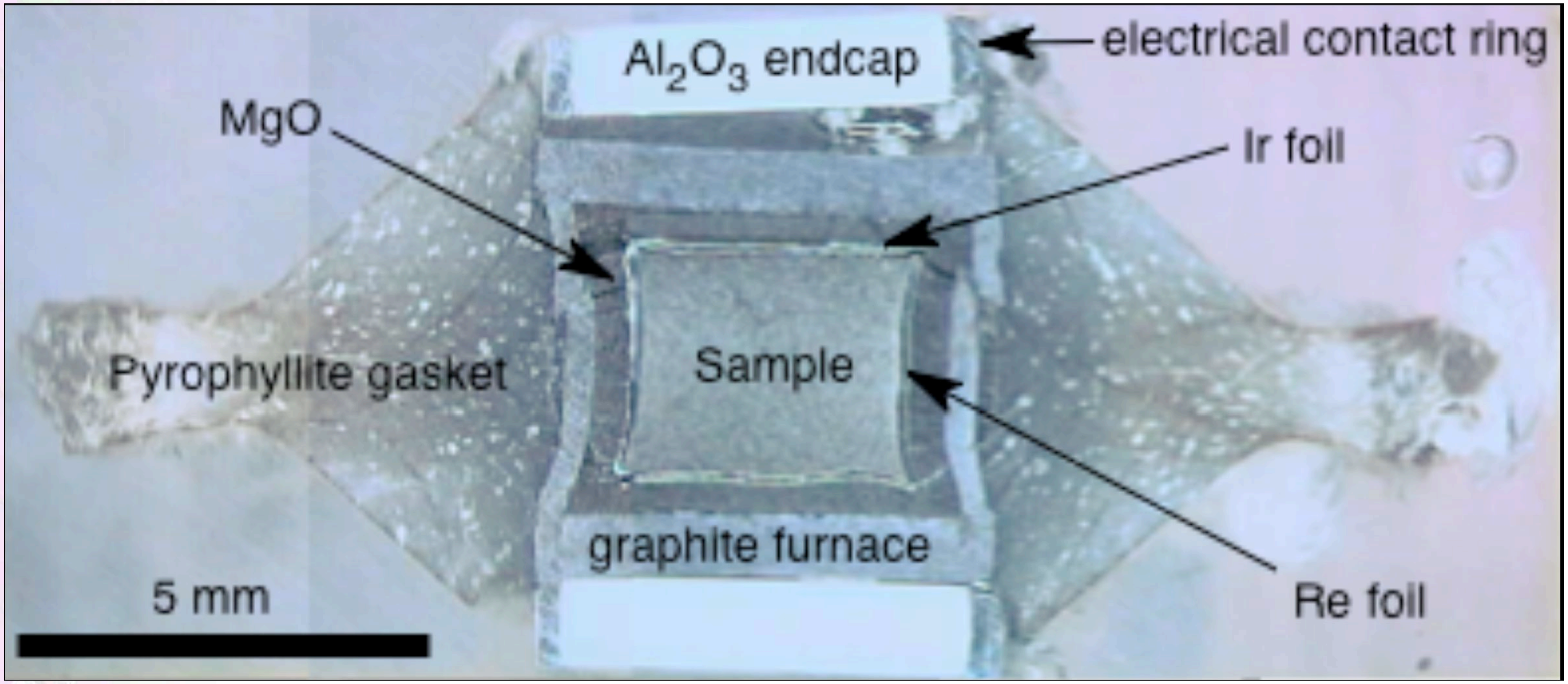
Influence of P on high T order-disorder in ilmenite



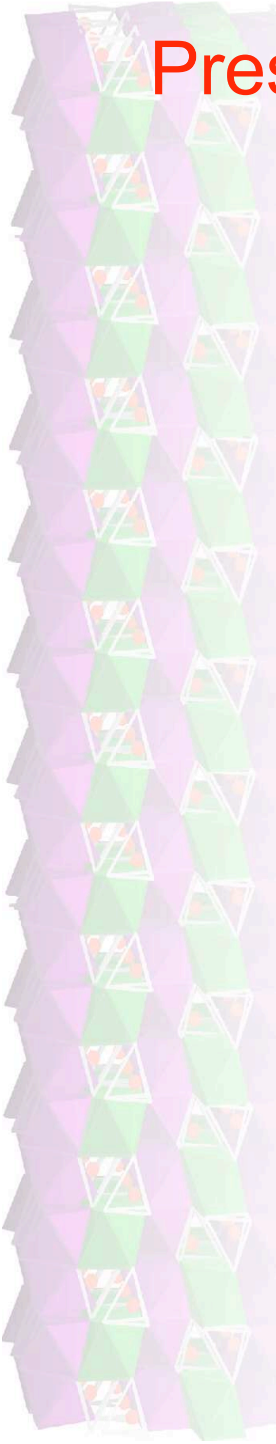
- Determine the pressure-dependence of high-T order-disorder in minerals

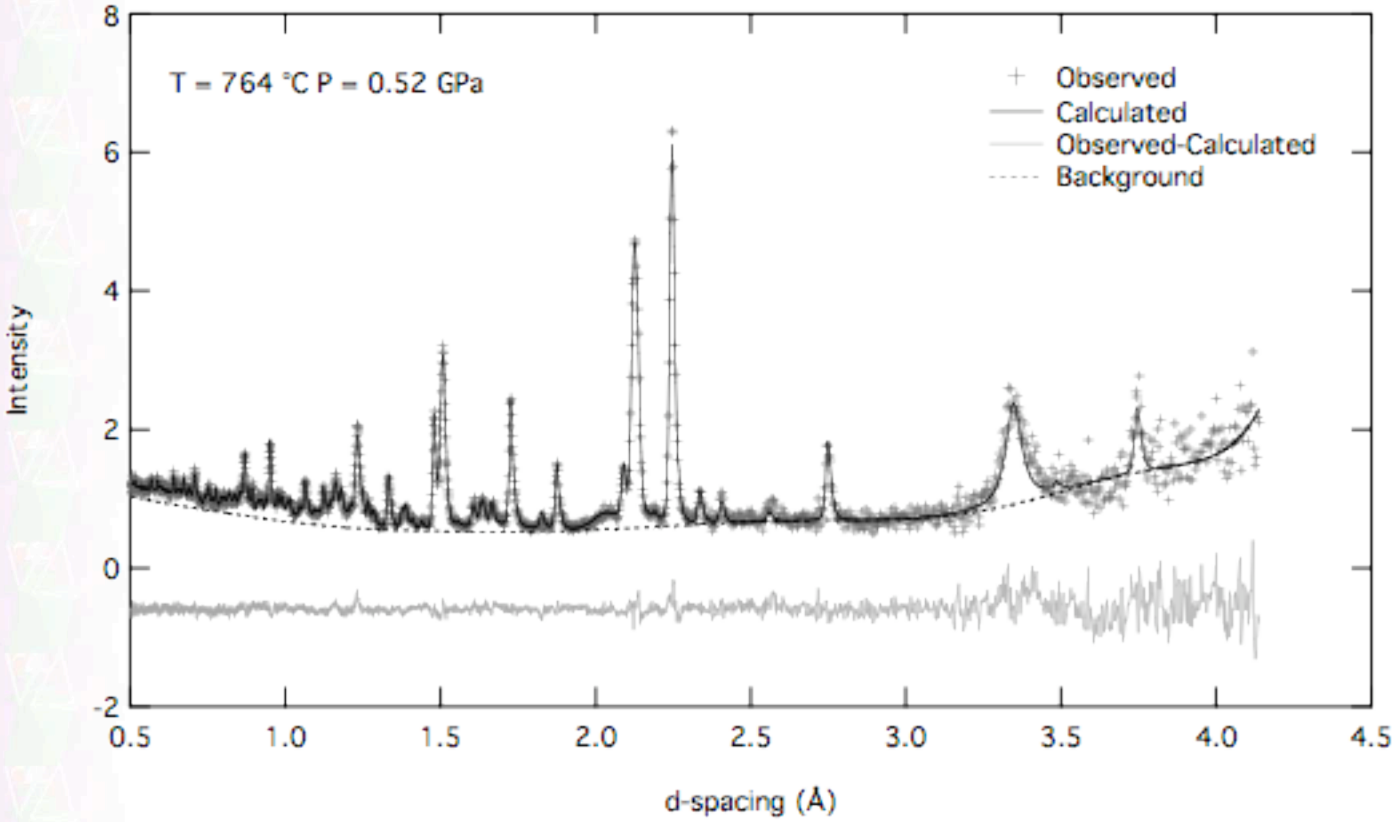
- Probe the pressure dependence of the equilibrium high-T order-disorder properties: first neutron measurements of these phenomena at real Earth interior conditions

Pressure Dependence of Cation Order in ilmenite 65% - hematite 35%

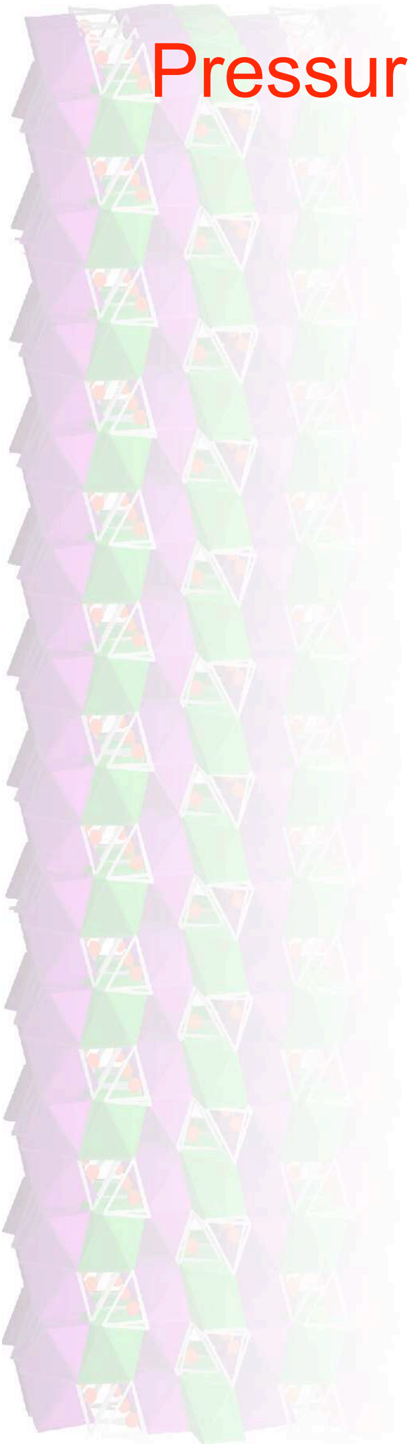


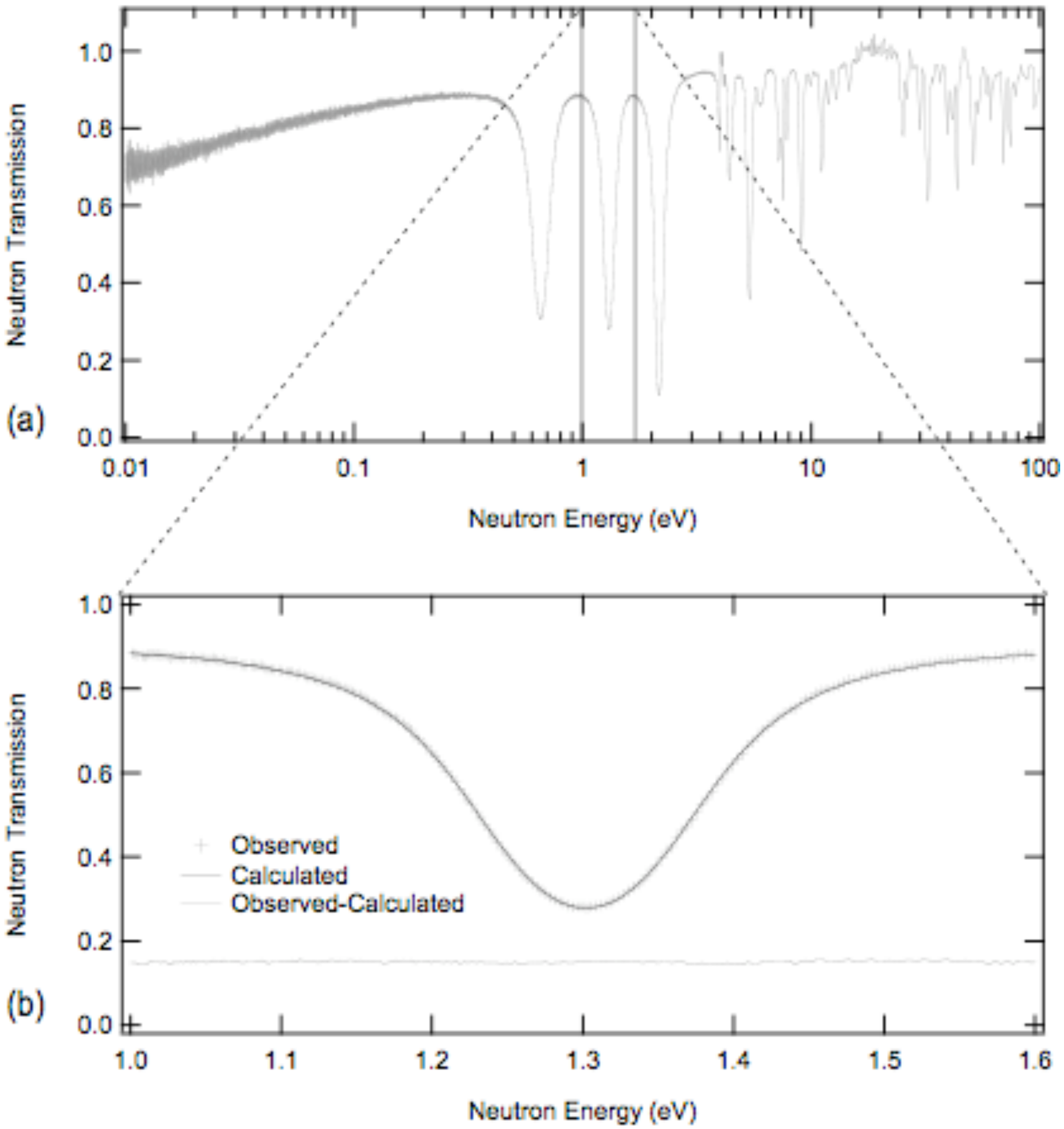
Pressure Dependence of Cation Order in ilmenite 65% - hematite 35%



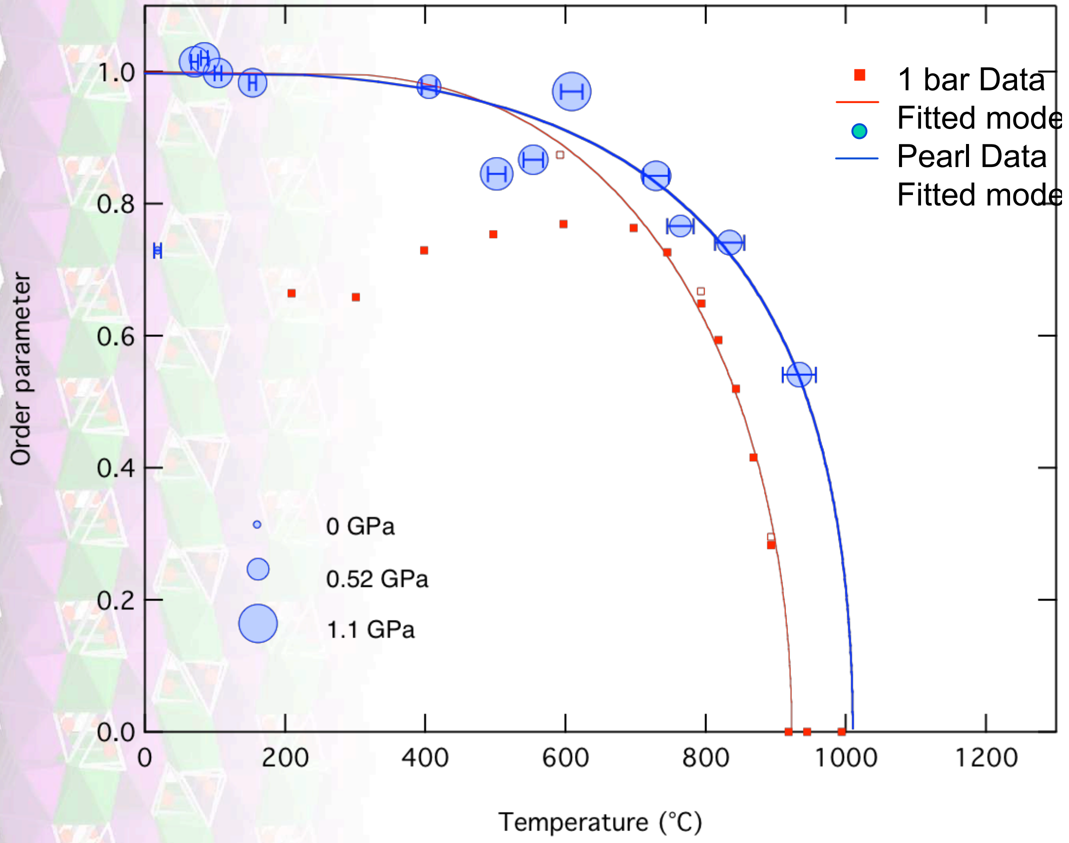


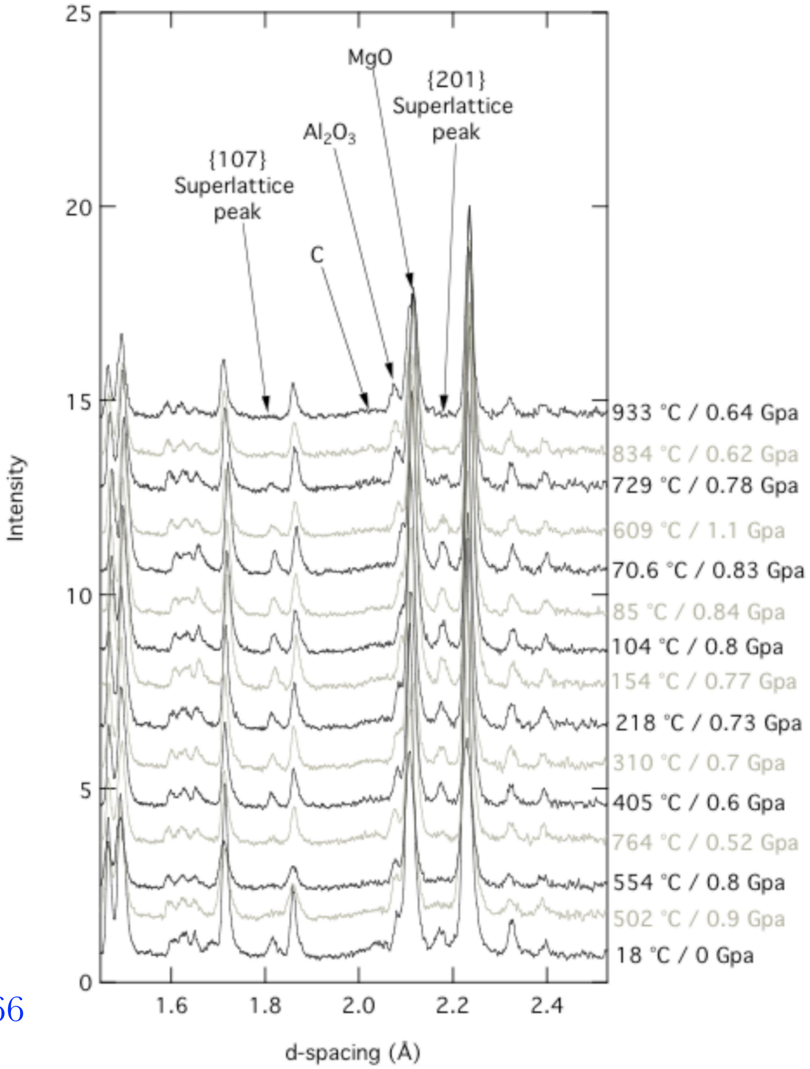
Pressure Dependence of Cation Order in ilmenite 65% - hematite 35%





Pressure Dependence of Cation Order in ilmenite 65% - hematite 35%





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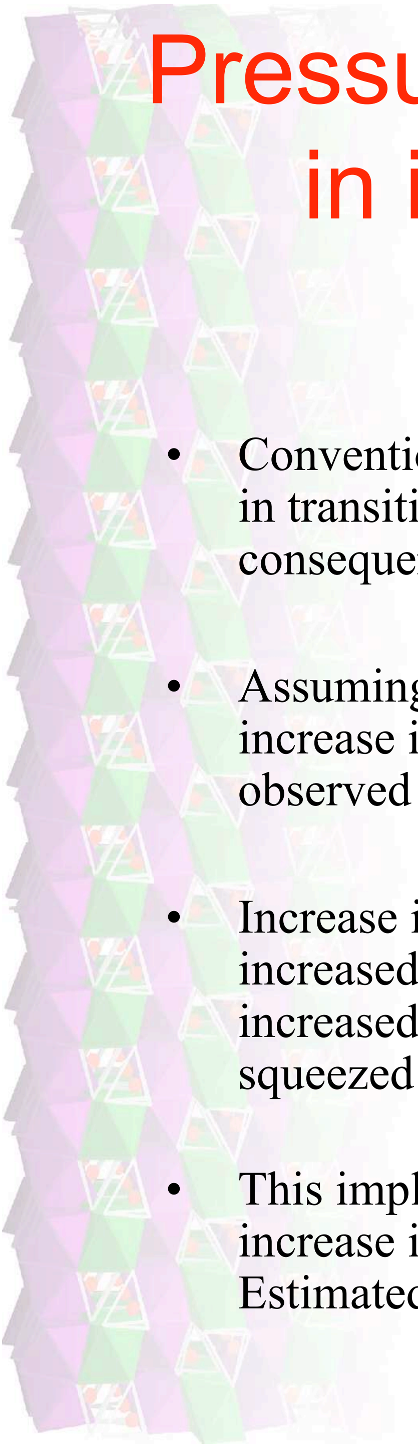
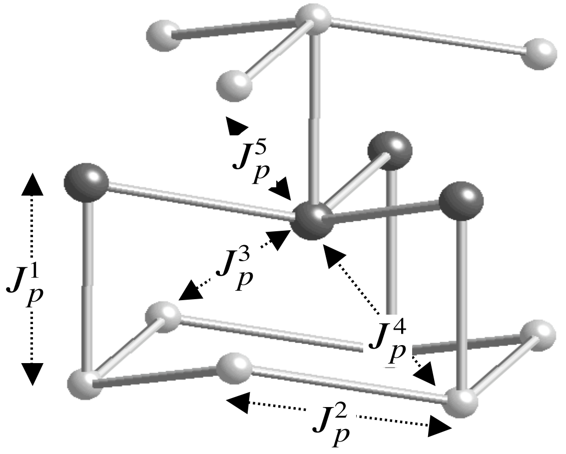
Pressure Dependence of Cation Order in ilmenite 65% - hematite 35%





- Conventional wisdom states that the increase in transition temperature with pressure is a consequence of a negative volume strain
- Assuming a 1% volume strain, the calculated increase in T_c is only 35°C at 0.6 GPa (note: observed strain is <<1%)
- Increase in T_c must therefore come from increased internal energy of ordering, i.e. increased cation interaction as structure is squeezed
- This implies that the miscibility gap would also increase in temperature with pressure. Estimated increase of up to 150 °C at 1 GPa