Studies of Crystalline and Partially Crystalline Structure using PDF Methods: An Overview

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Rutherford Appleton Laboratory

2nd UK-China Joint Workshop on Neutron Scattering
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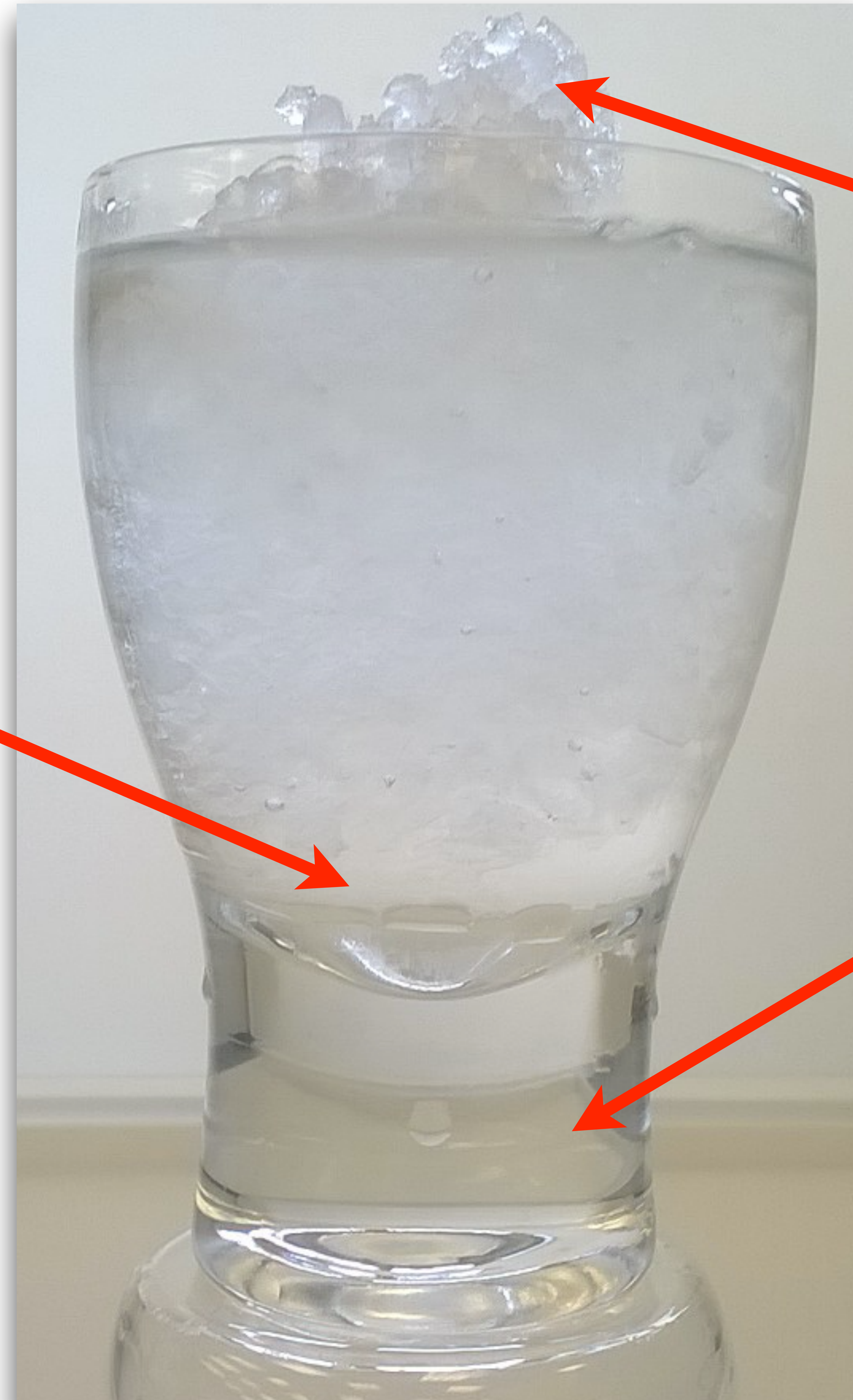
Science & Technology Facilities Council ISIS

Structural Disorder in a Glass

Structural Disorder in a Glass



Crystalline

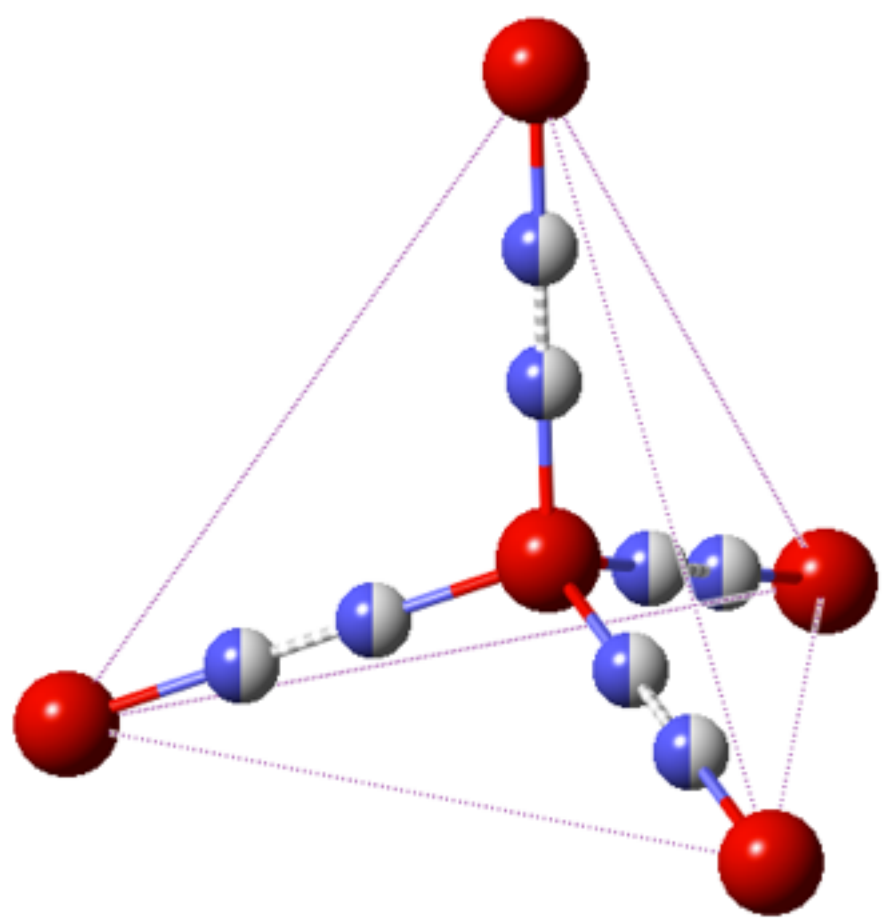
Liquid

Amorphous

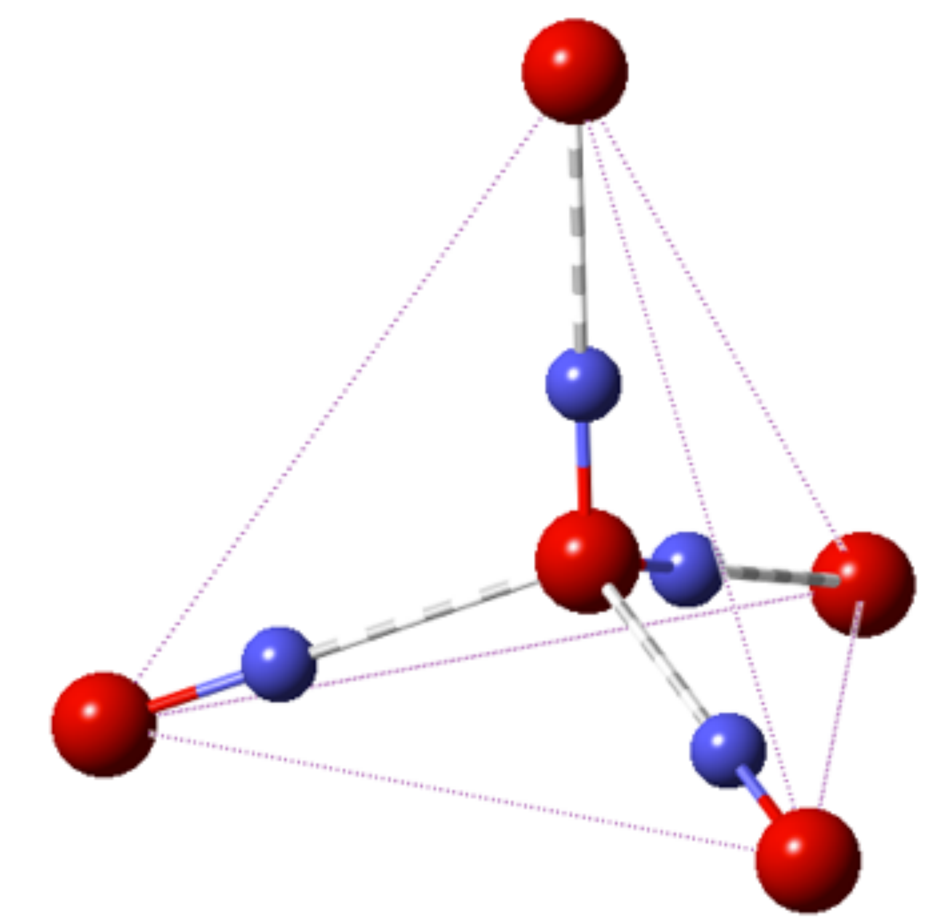
Ice 1h and Hypothetical Square Ice

Correlated Disorder

Ice Ih *average* structure



An Ice Ih *local* arrangement



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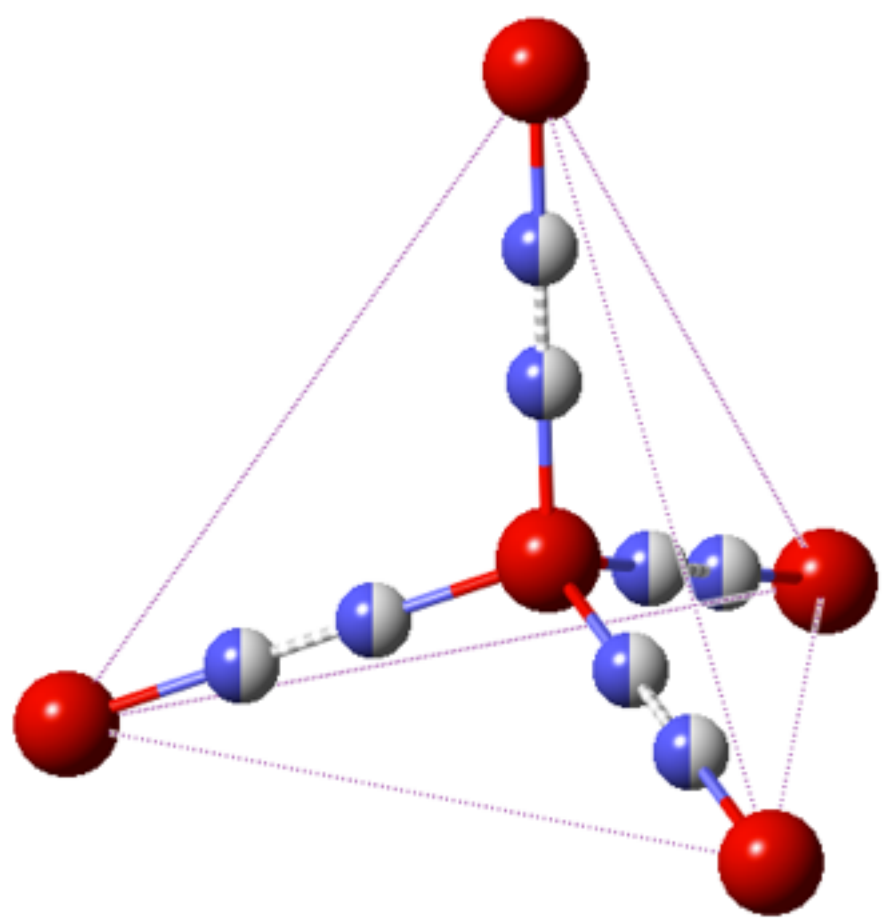

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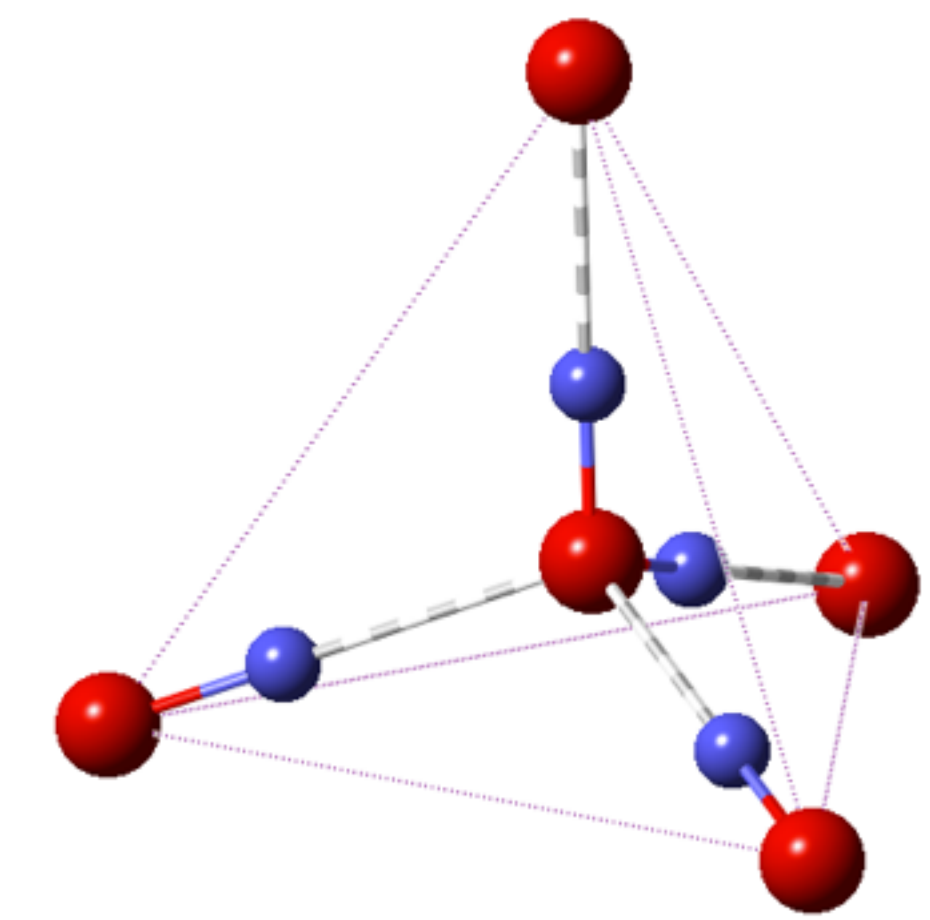
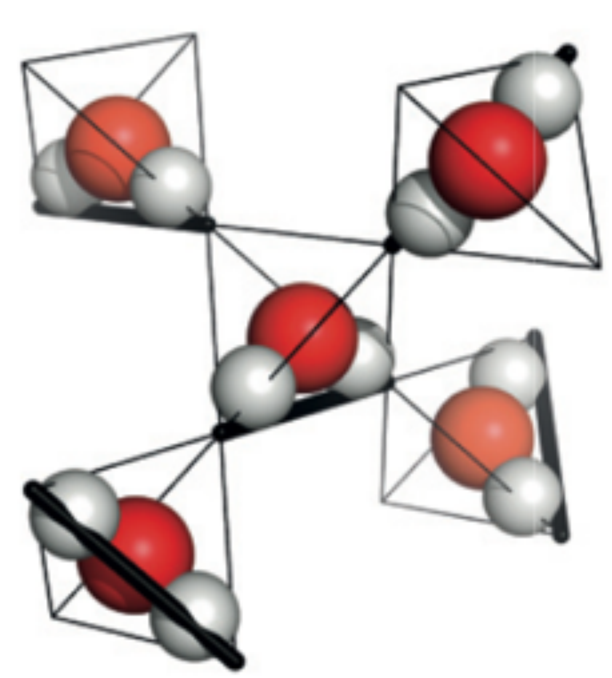
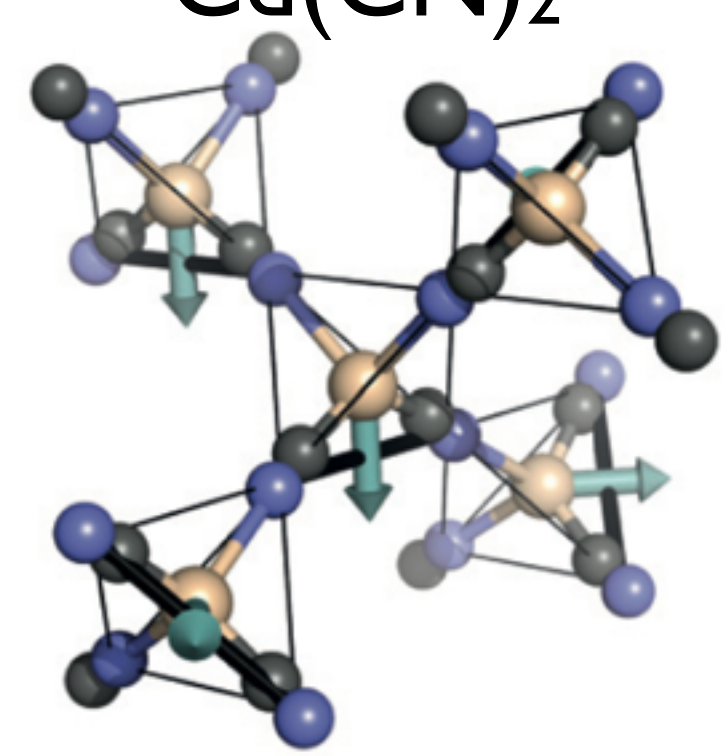


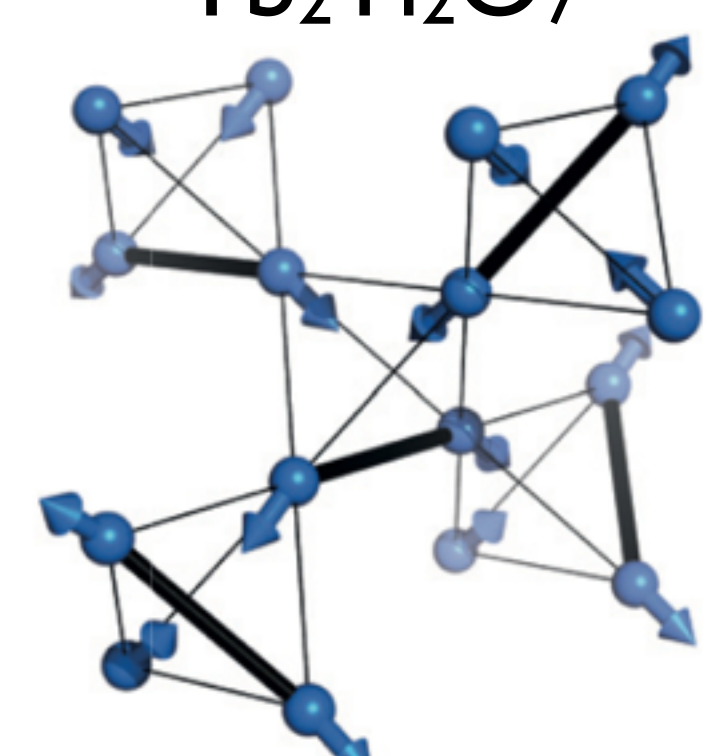
Cubic Ice, H_2O



Charge Ice, $Cd(CN)_2$



Spin Ice, $Yb_2Ti_2O_7$



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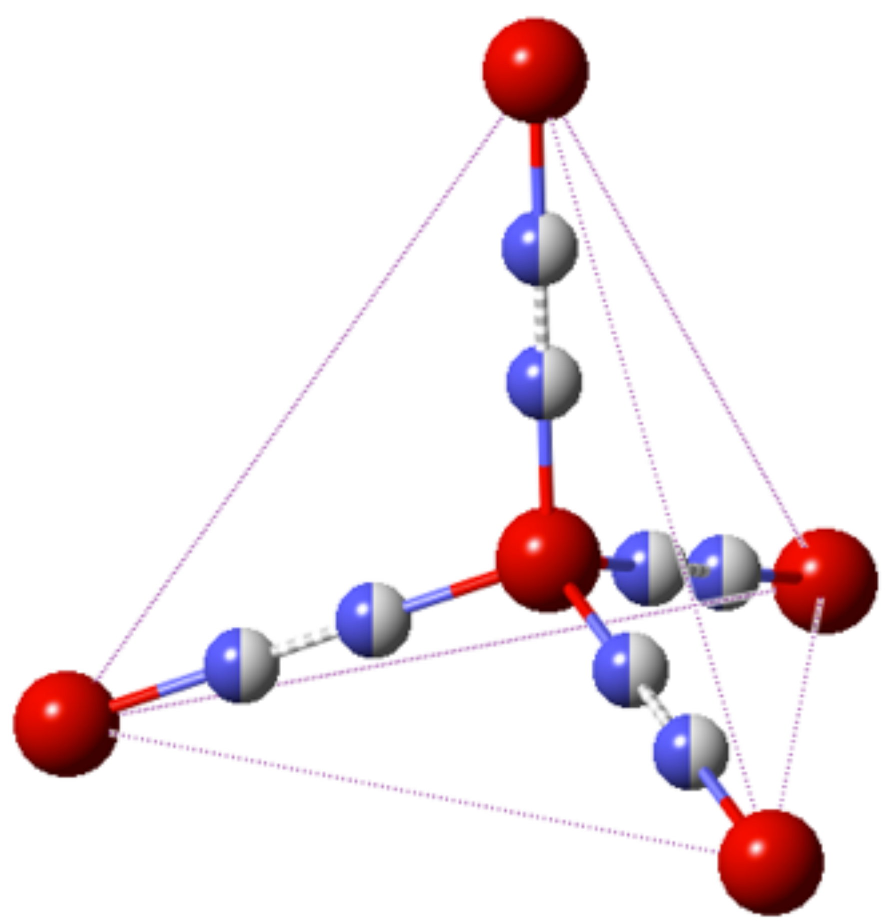
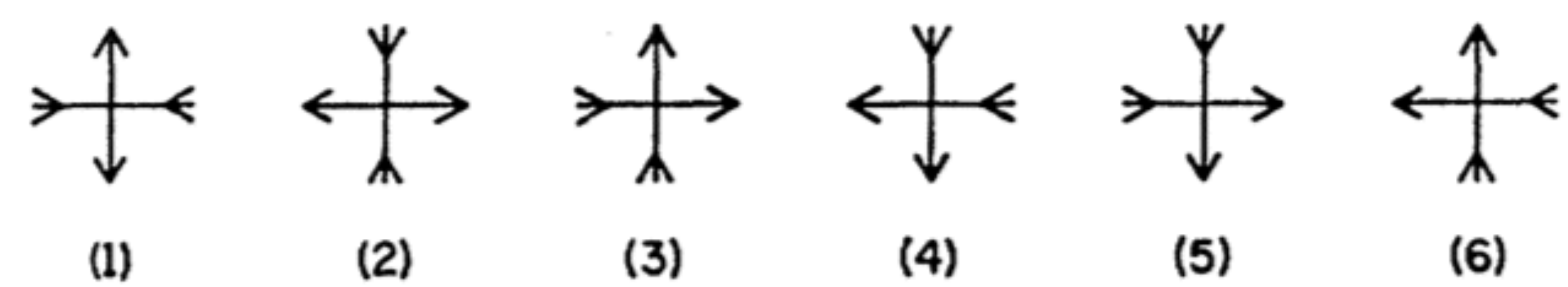
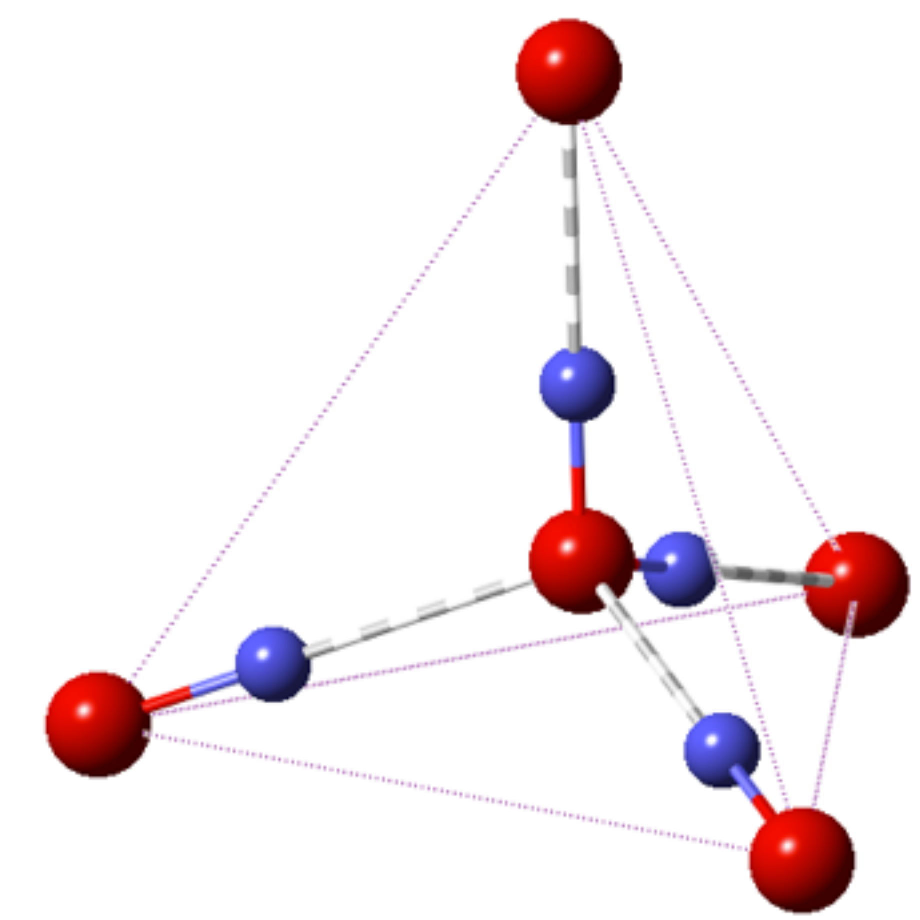


"2-in, 2-out" model



E H Lieb, *Phys Rev* **162** (1967) 162

An Ice Ih *local* arrangement



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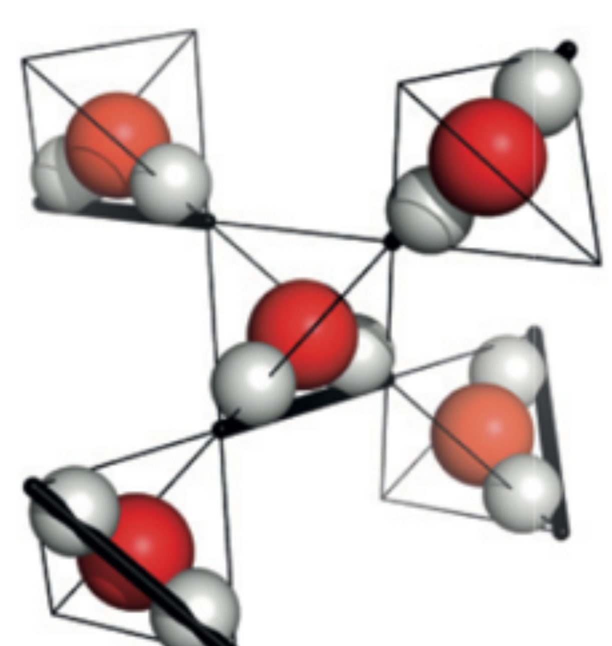

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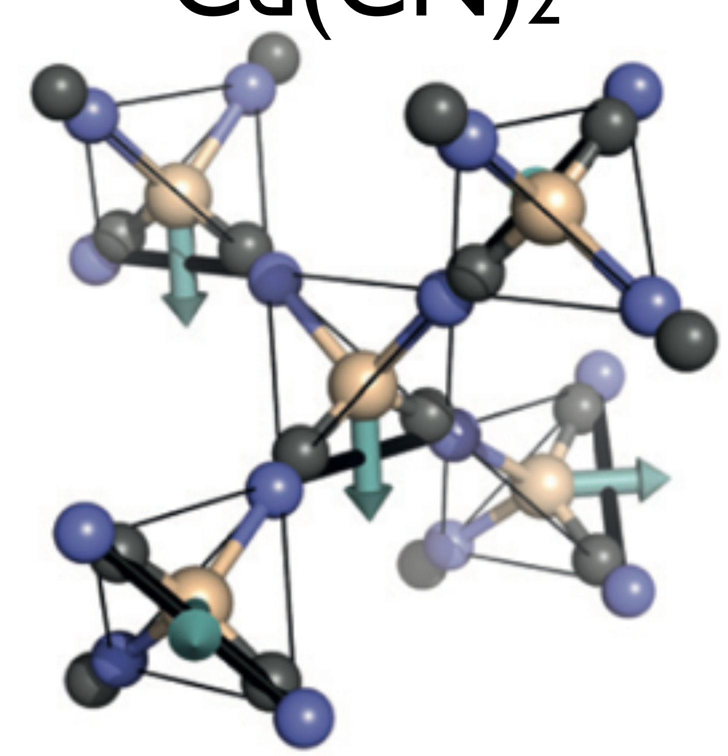

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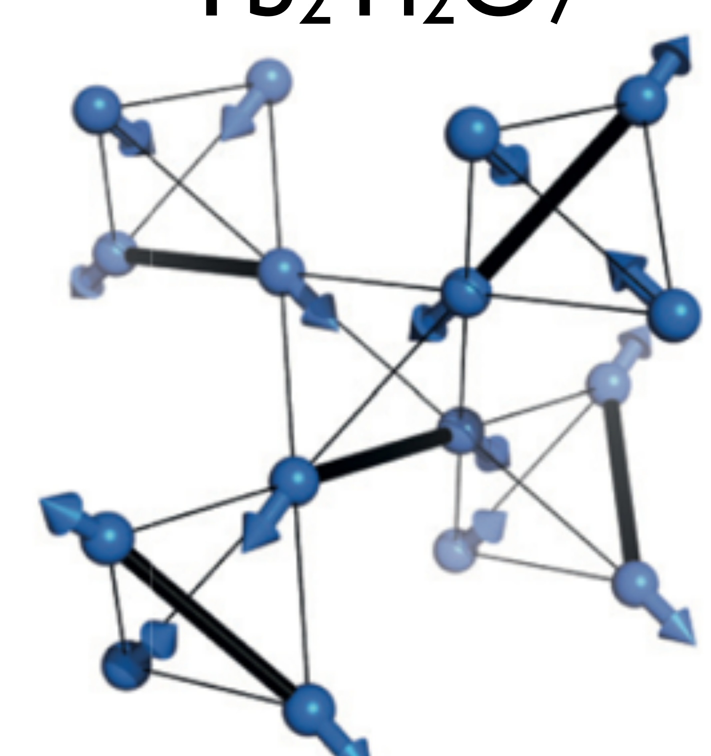
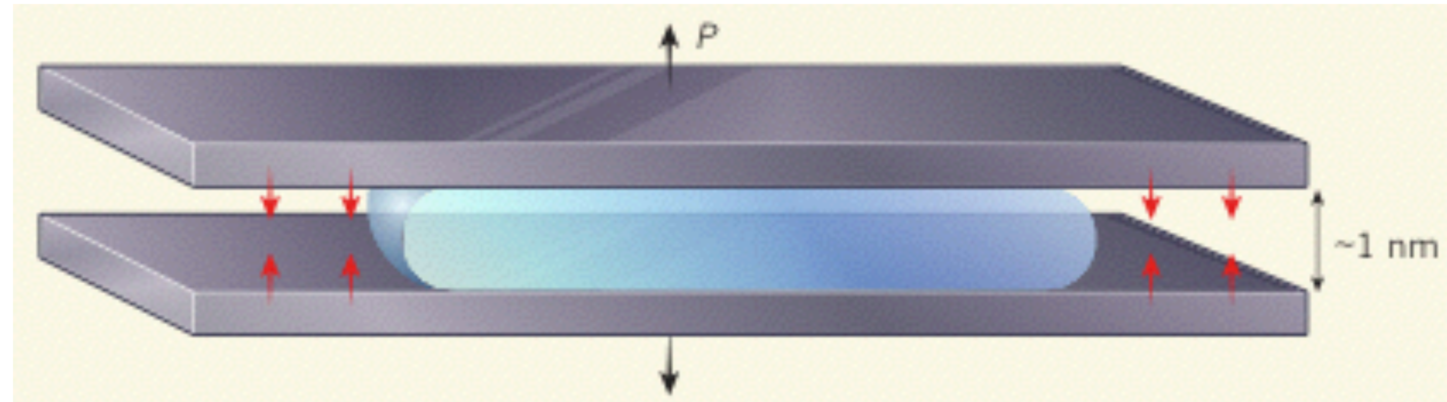
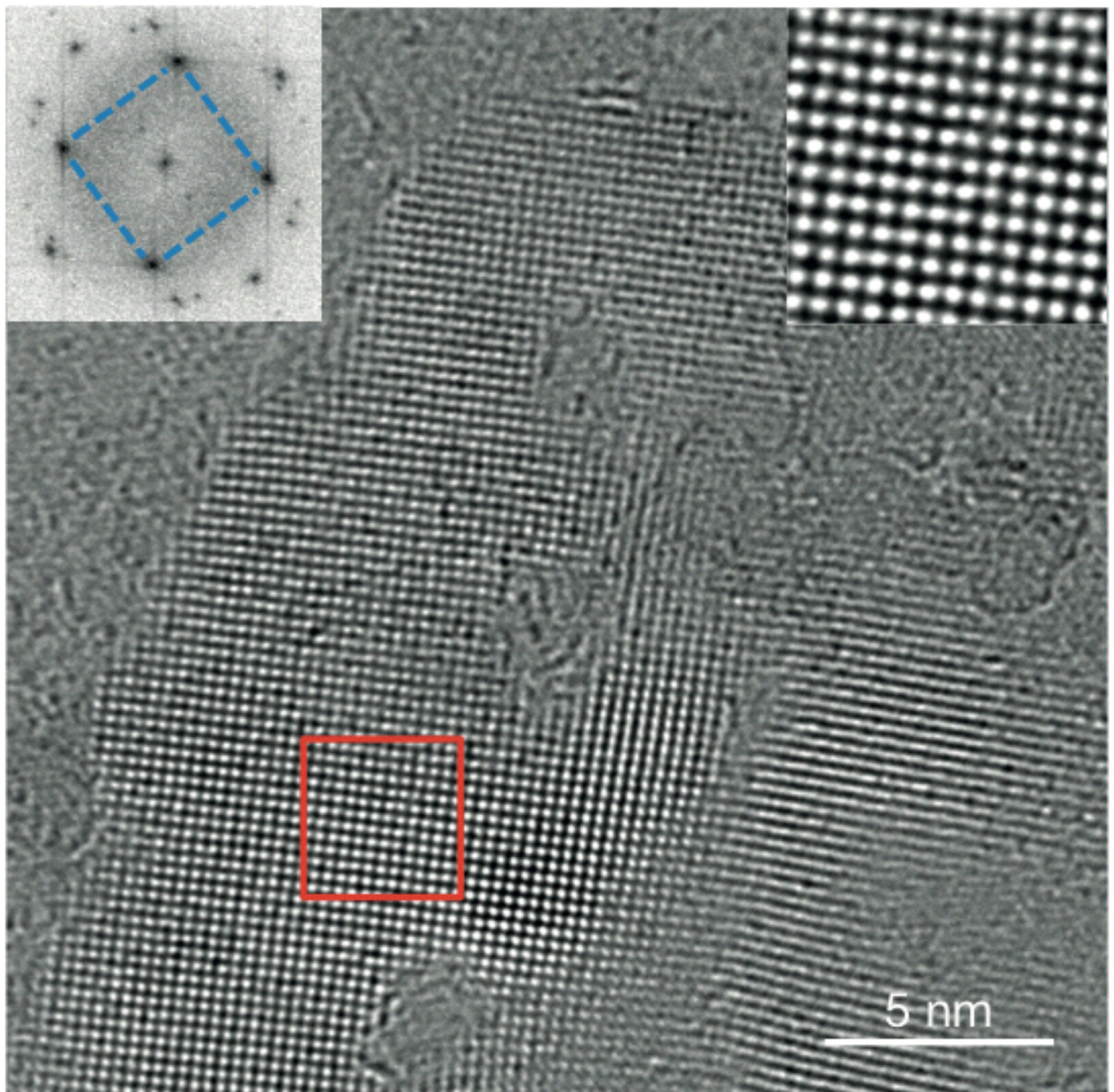
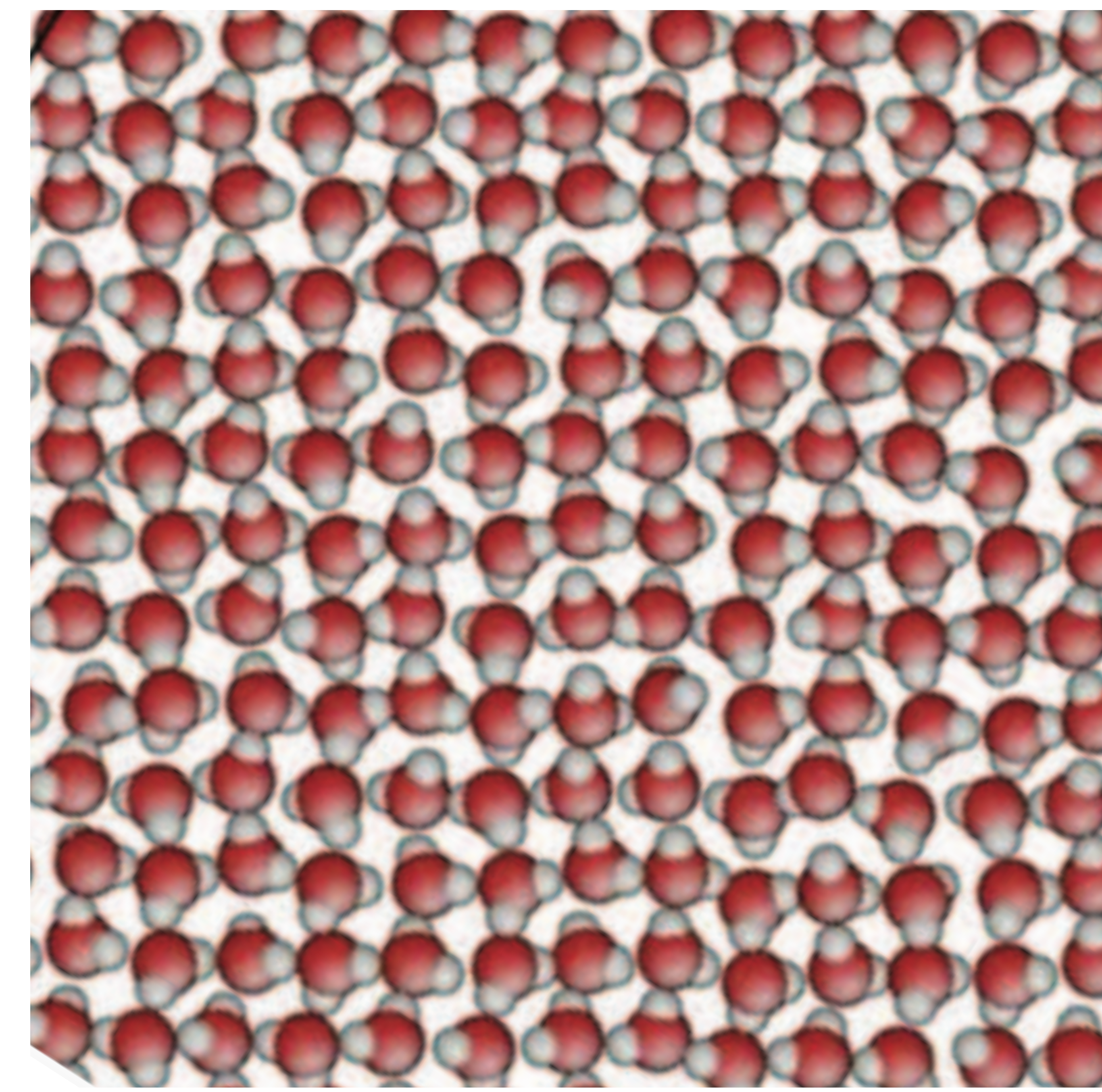


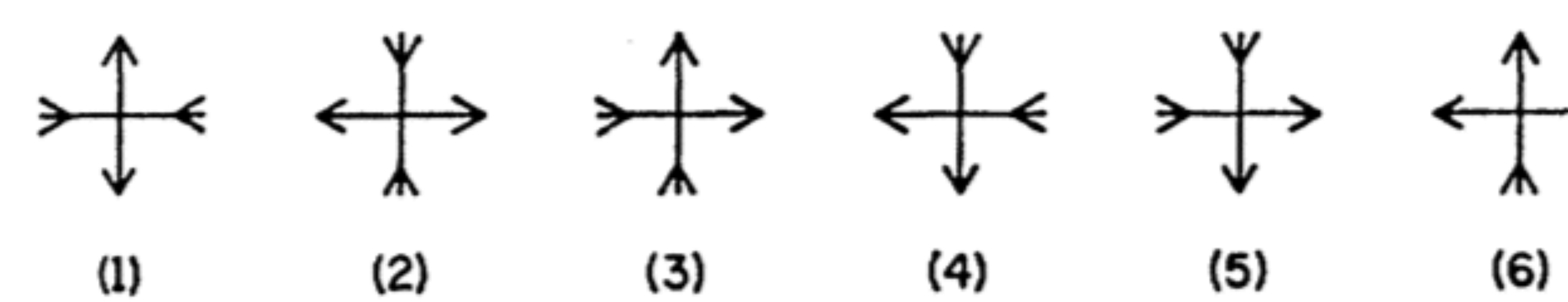
An Experimental Square Ice Graphene Sandwich



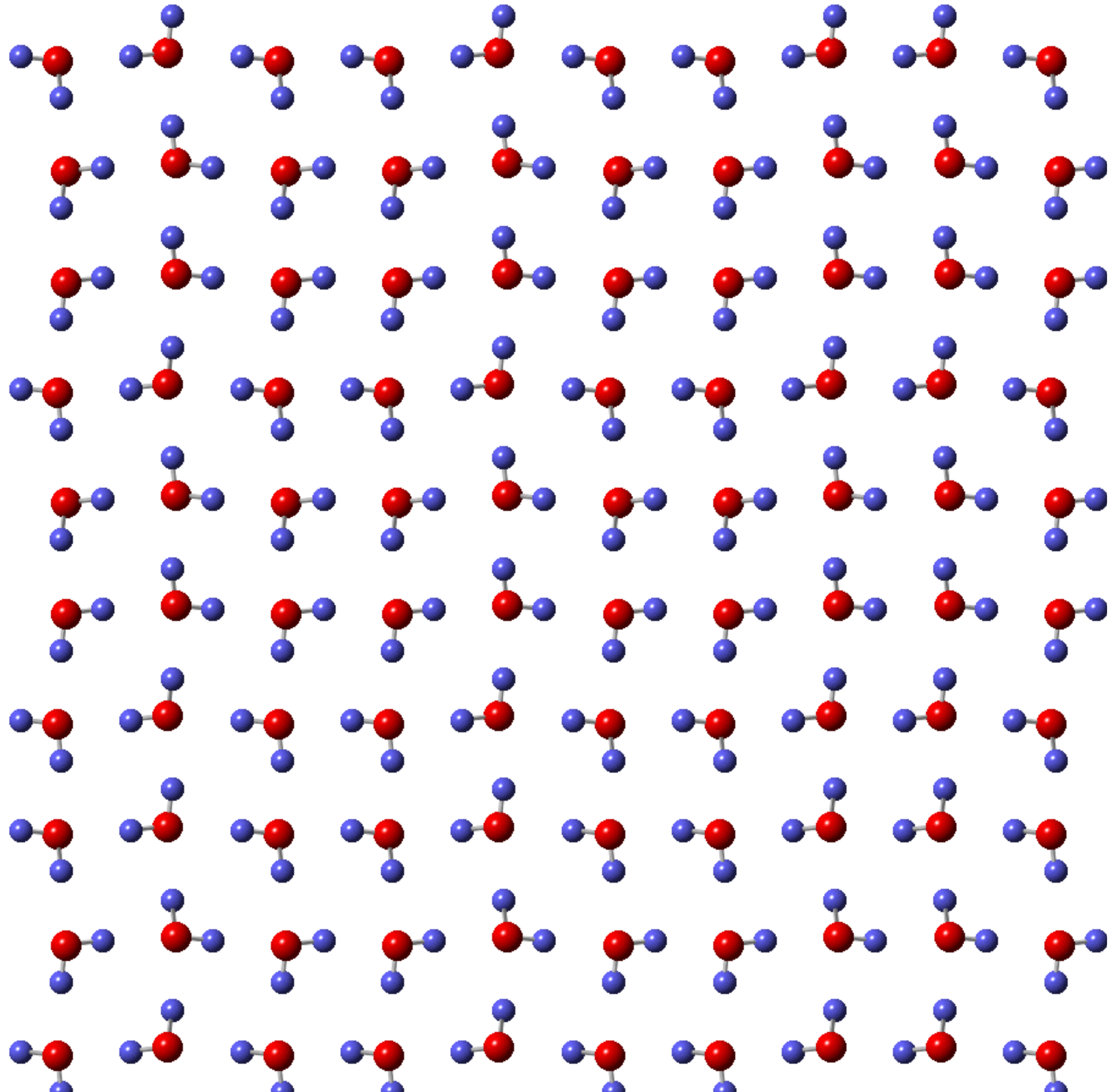
G Algara-Siller *et al*, *Nature* **519** (2015) 443

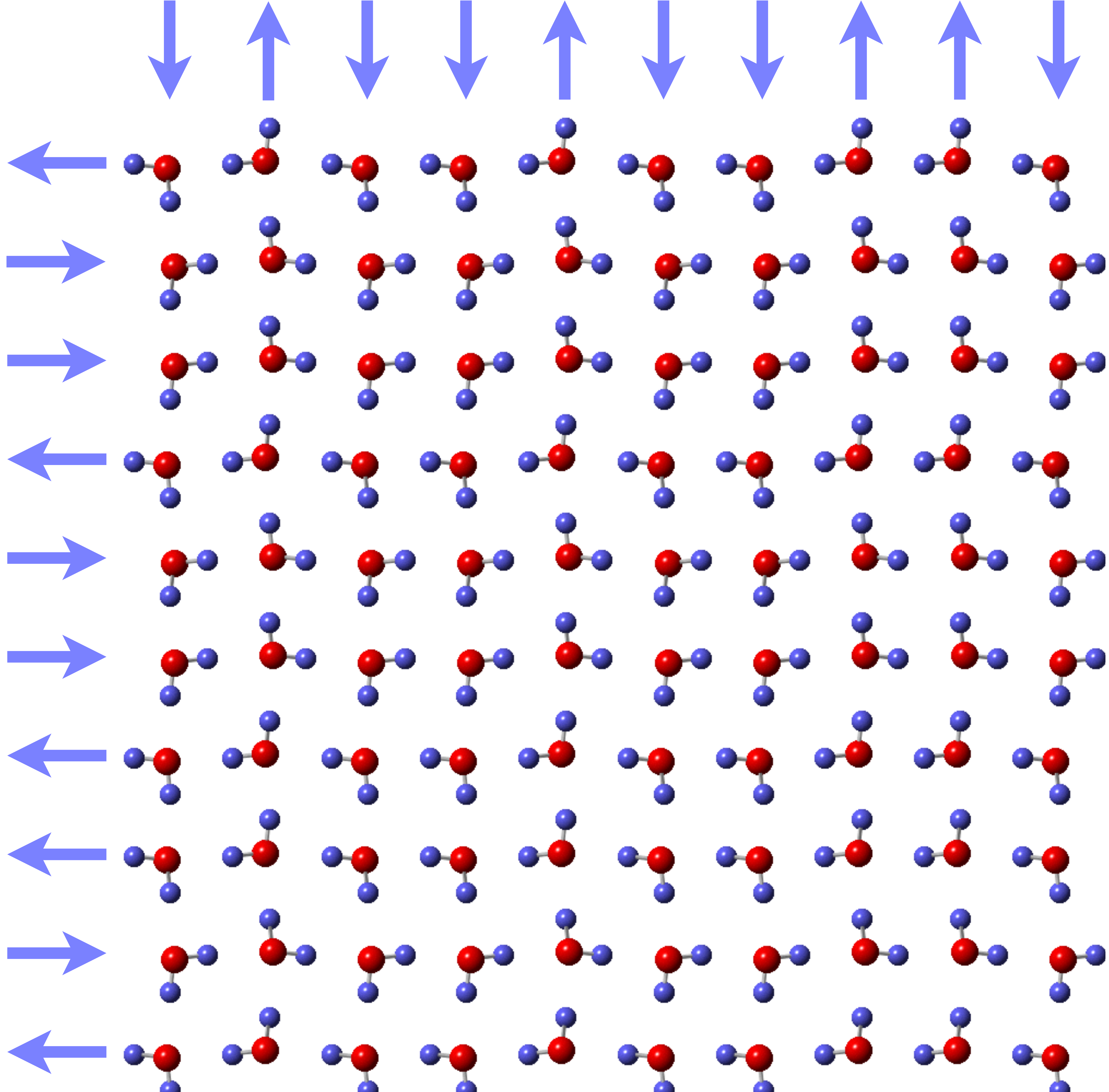


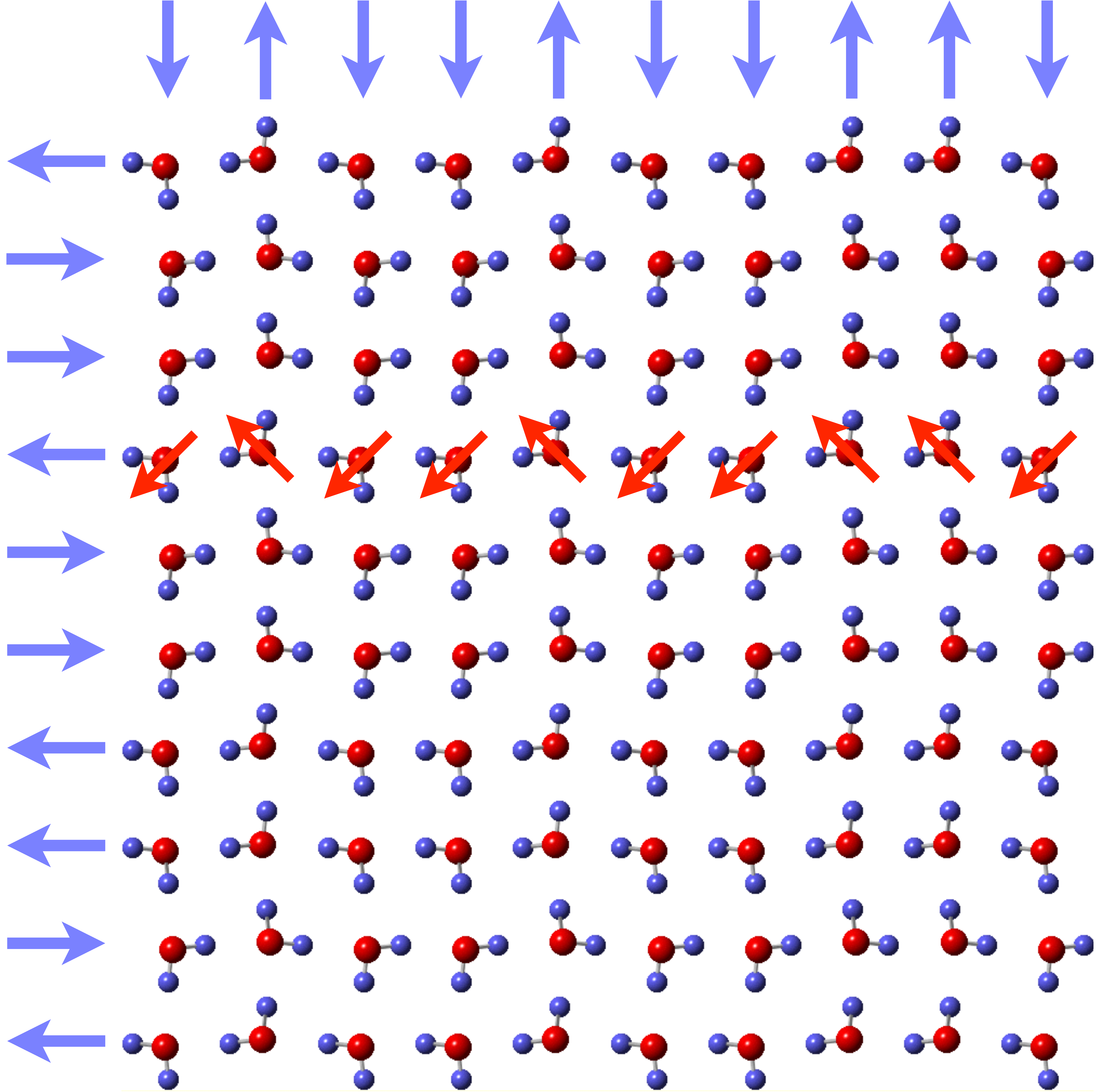


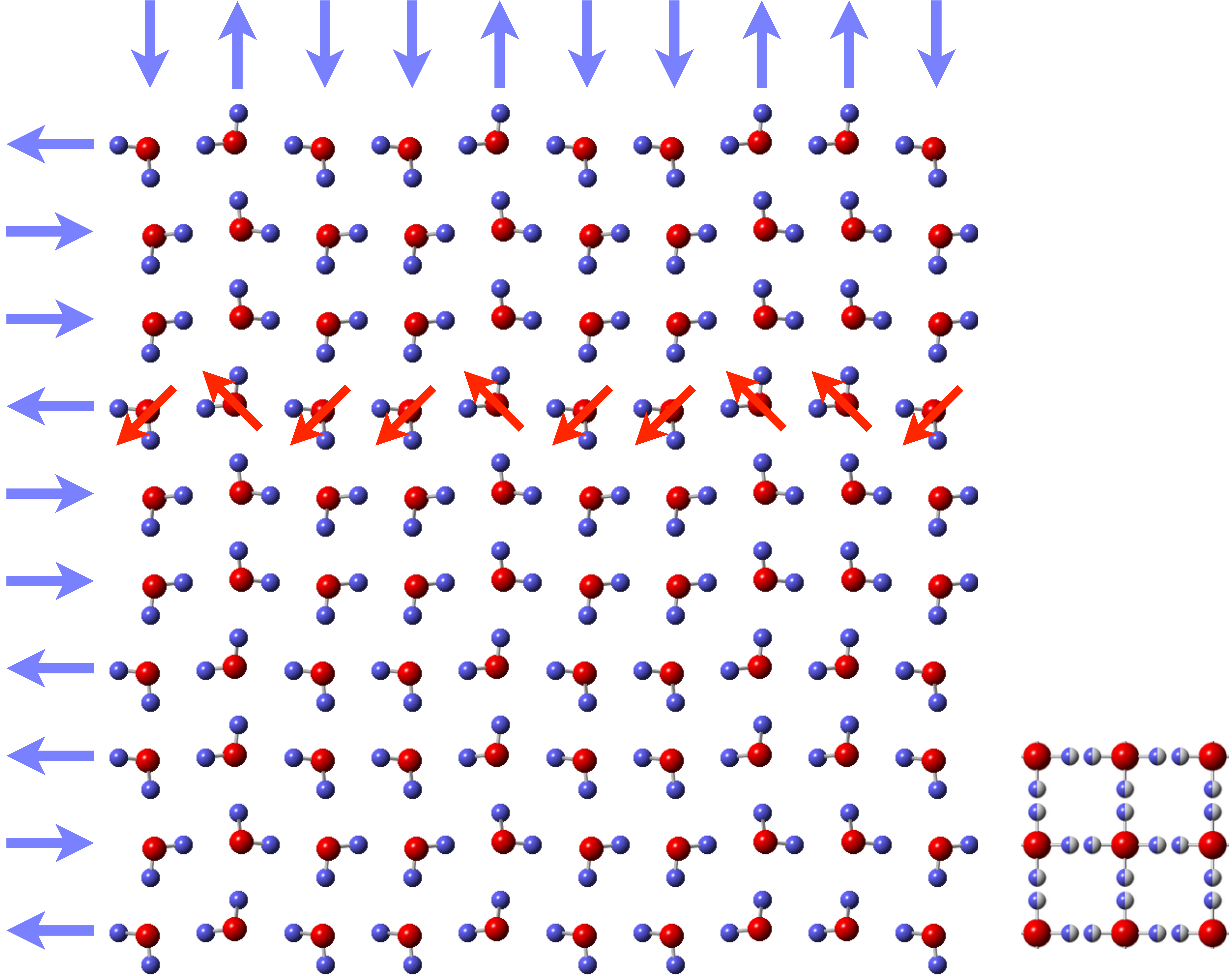


Square Ice

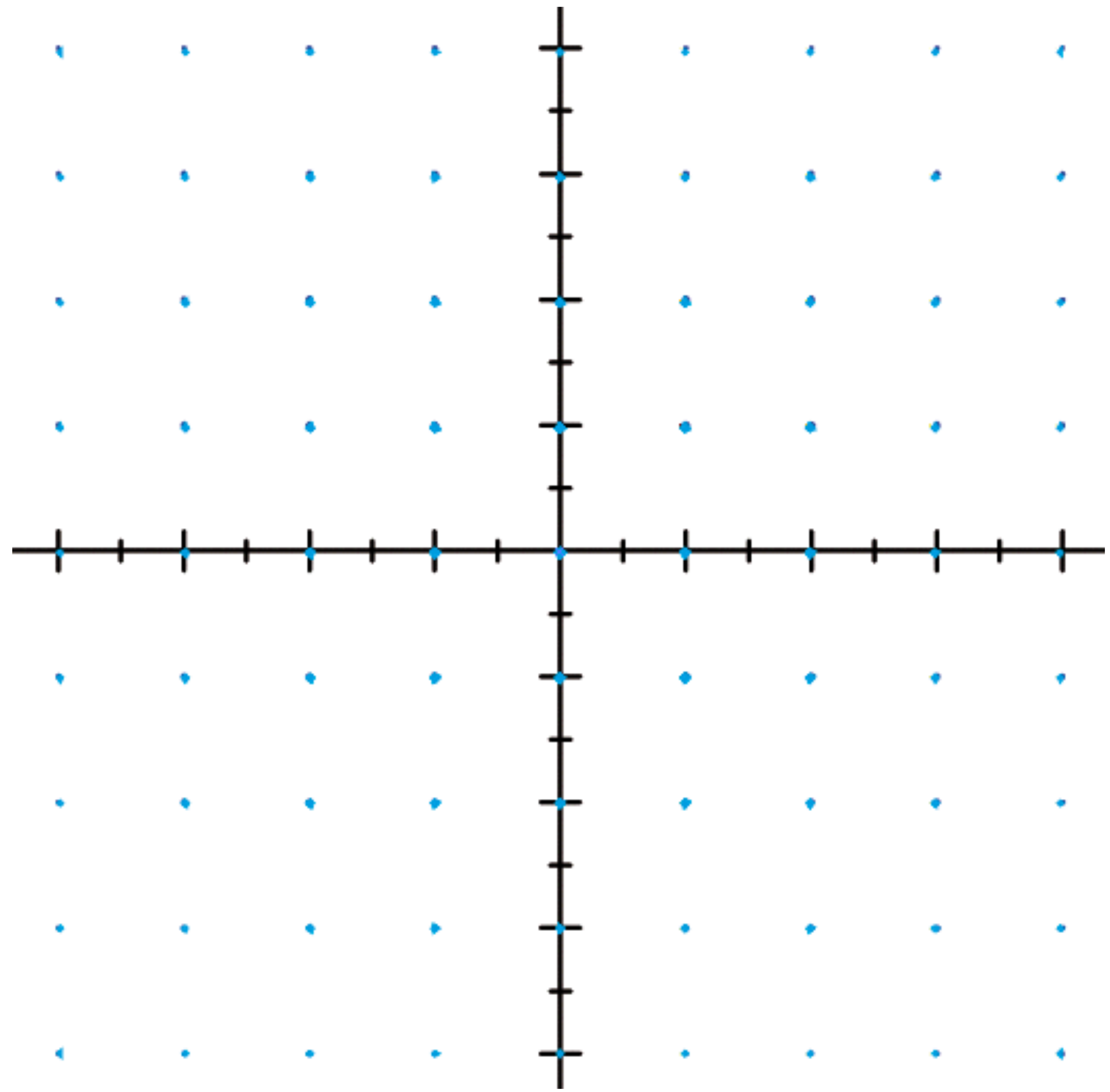








Square Ice X-ray Diffraction



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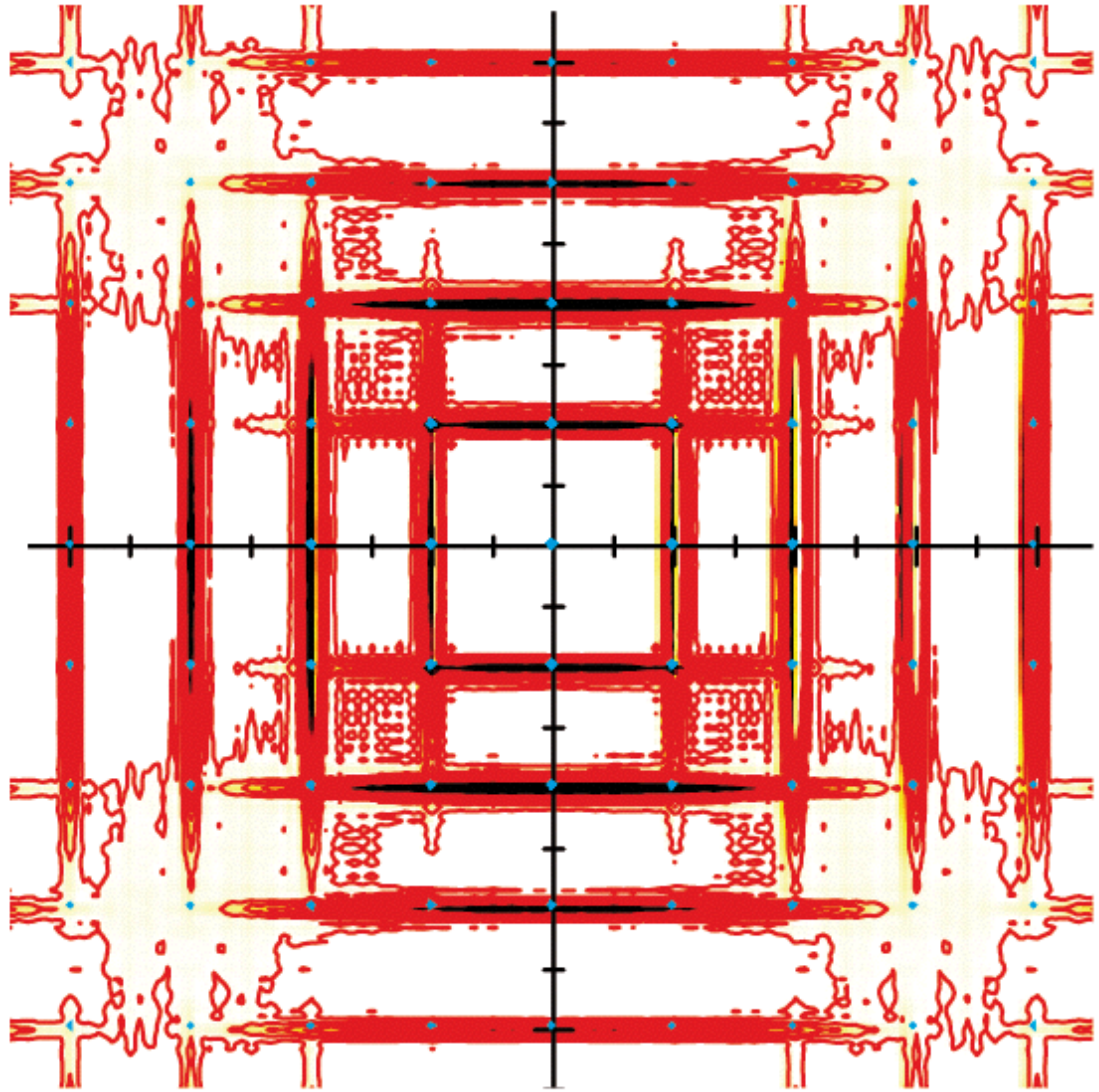

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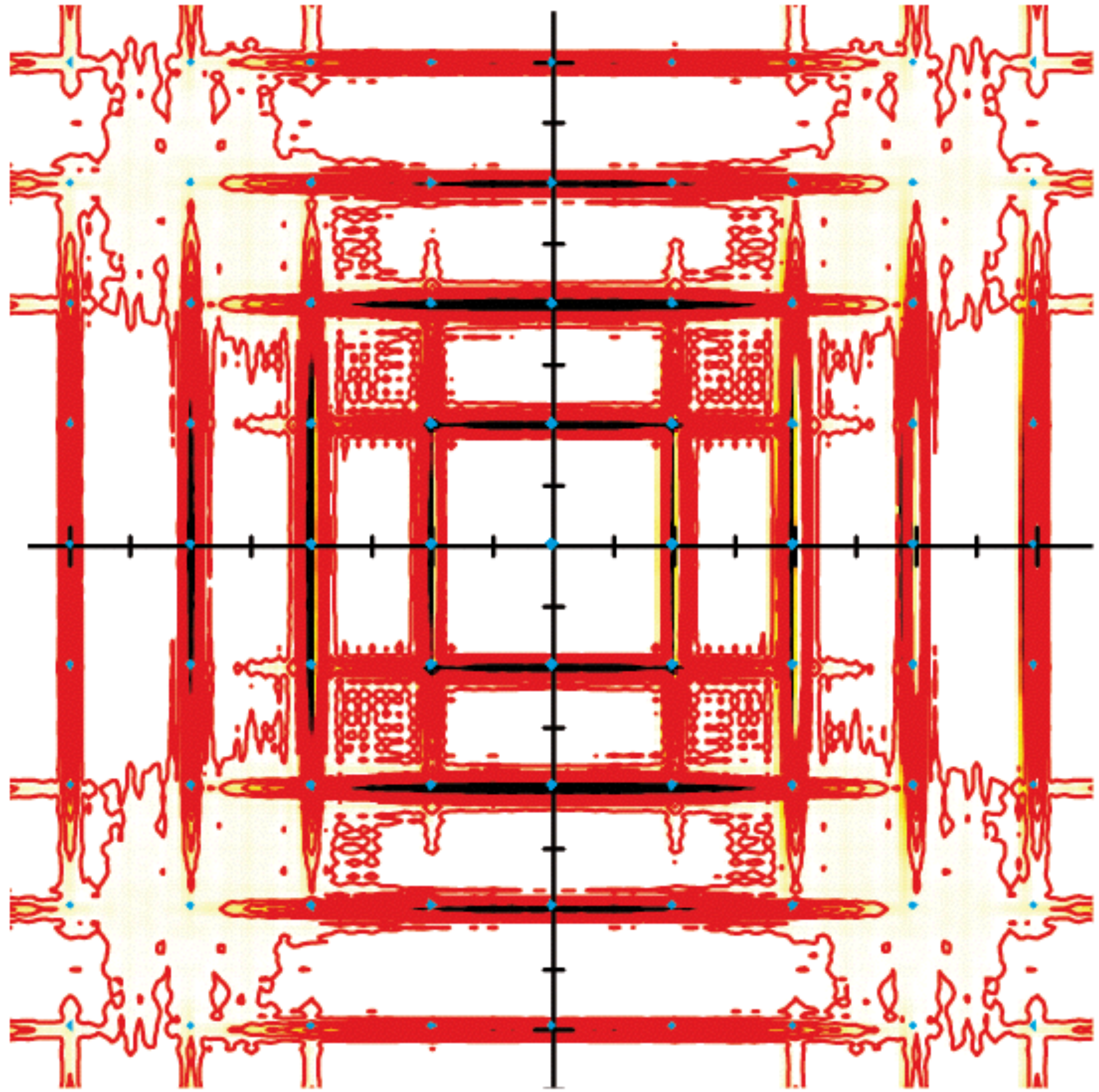
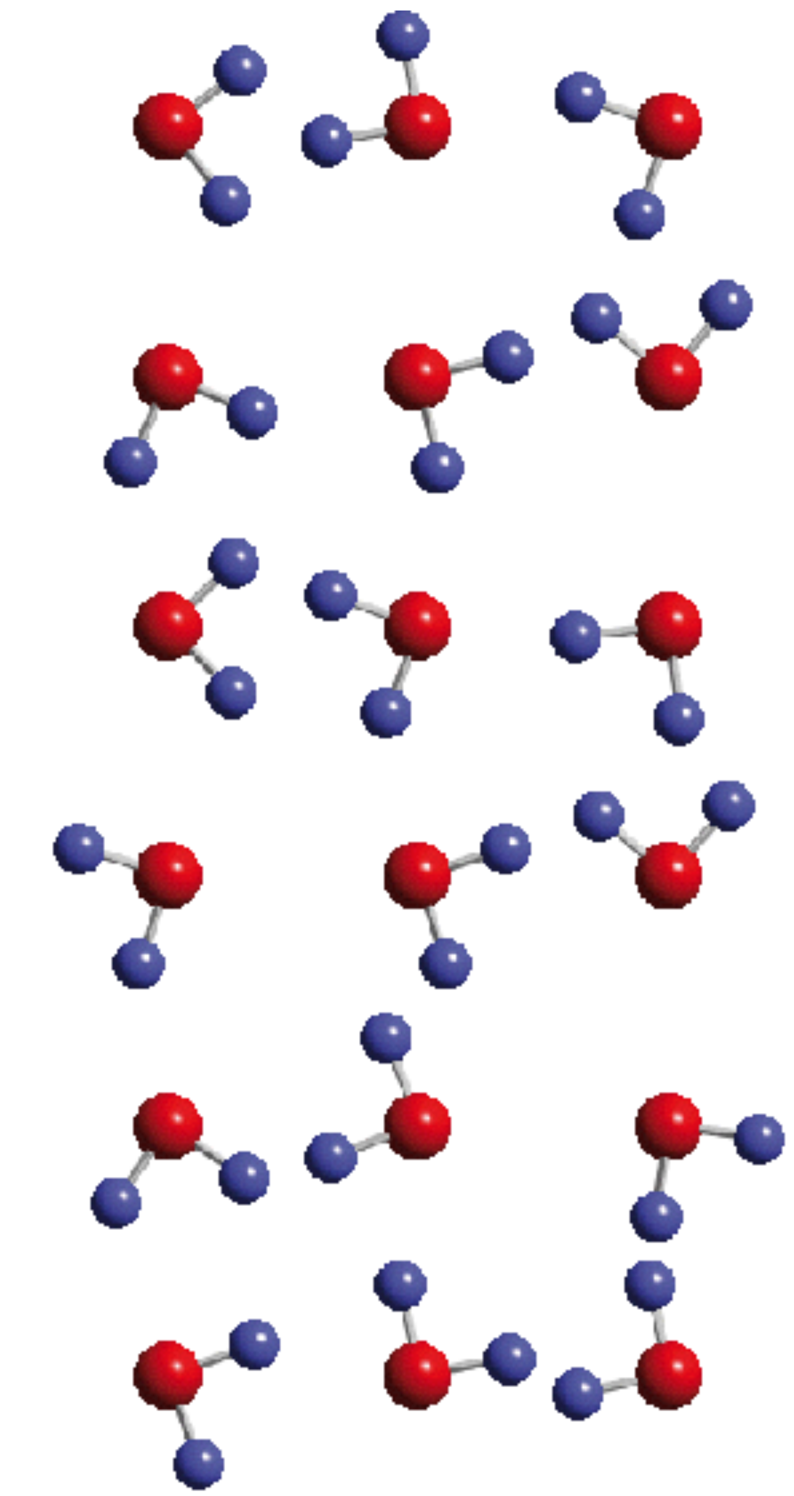
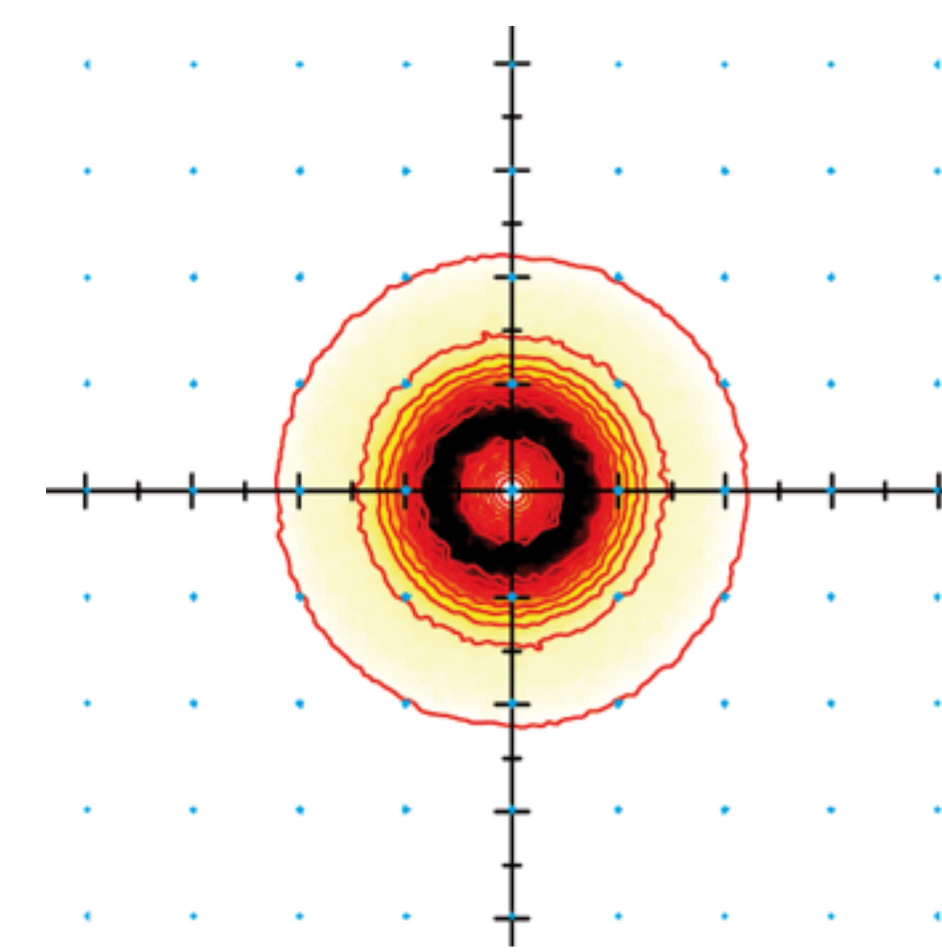
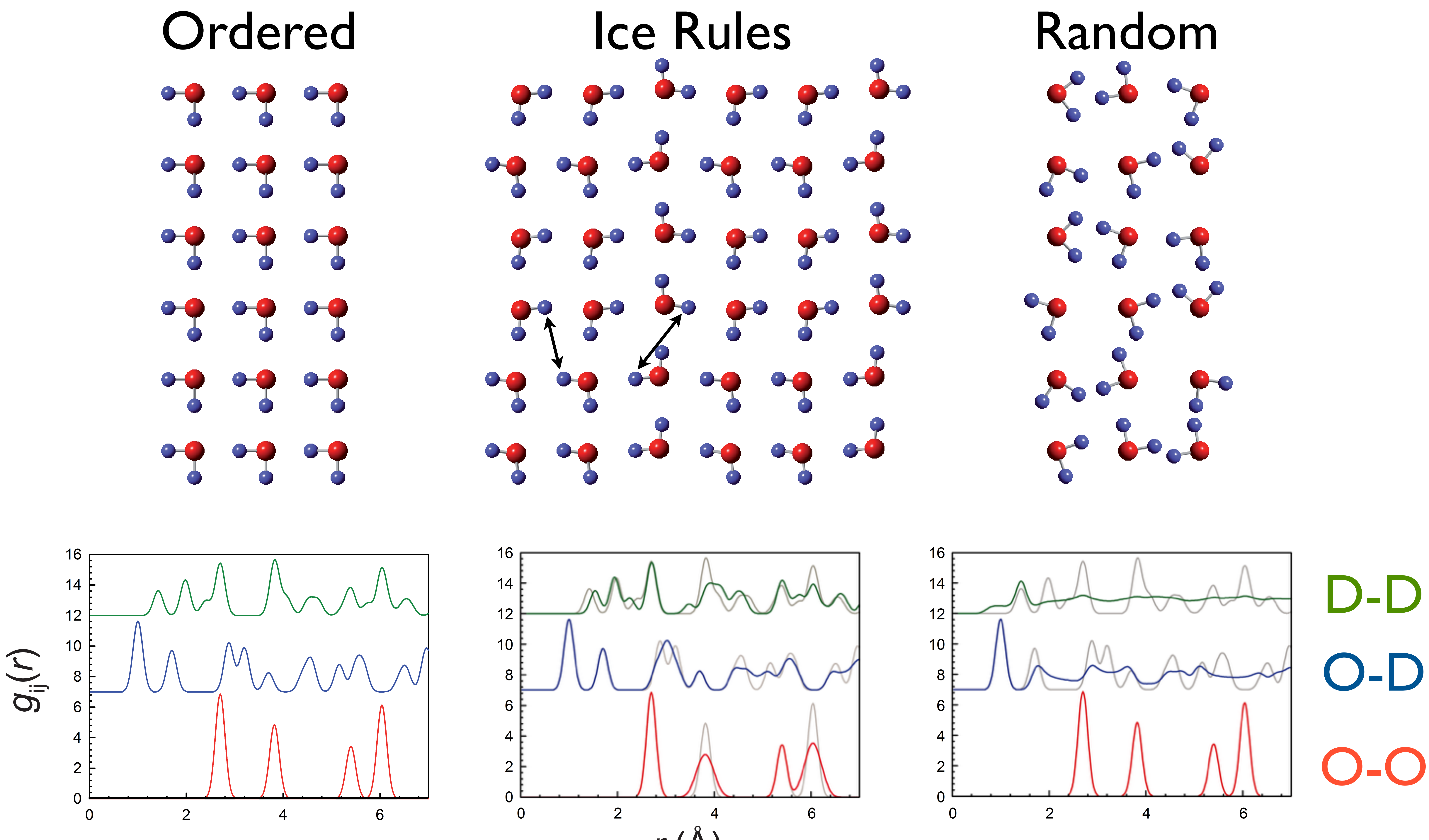






Square Ice and the Pair Distribution Function (PDF)



D A Keen and A L Goodwin, *Nature* **521** (2015) 303

Total Scattering Formalism

$$F(Q) = \sum_{i,j=1}^{n} c_i c_j \bar{b}_i \bar{b}_j [A_{ij}(Q) - 1]$$

Reciprocal Space

$$A_{ij}(Q) - 1 = \rho_0 \int_0^\infty 4\pi r^2 [g_{ij}(r) - 1] \frac{\sin Qr}{Qr} \, \mathrm{d}r$$

Fourier ↕ Transform

$$g_{ij}(r) - 1 = \frac{1}{(2\pi)^3 \rho_0} \int_0^\infty 4\pi Q^2 [A_{ij}(Q) - 1] \frac{\sin Qr}{Qr} \, \mathrm{d}Q$$

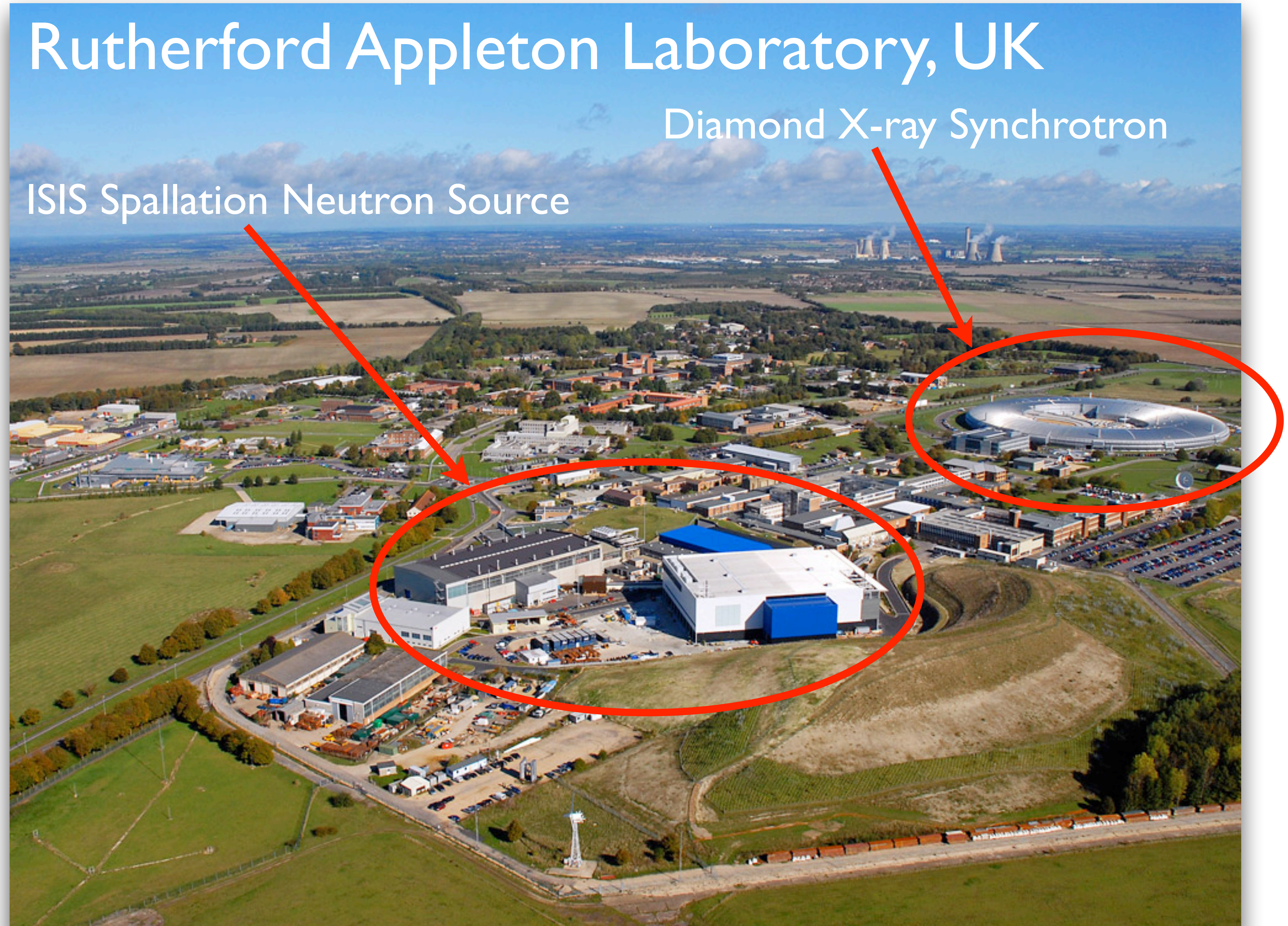
Real Space

$$G(r) = \sum_{i,j=1}^{n} c_i c_j \bar{b}_i \bar{b}_j [g_{ij}(r) - 1],$$

$$g_{ij}(r) = \frac{n_{ij}(r)}{4\pi r^2 \, \mathrm{d}r \, \rho_j}$$

Keen *J Appl Cryst* **34** 172 (2001)

Central Facilities for Total Scattering



Why Use Central Facilities?

- Neutrons and x-rays ‘see’ things differently

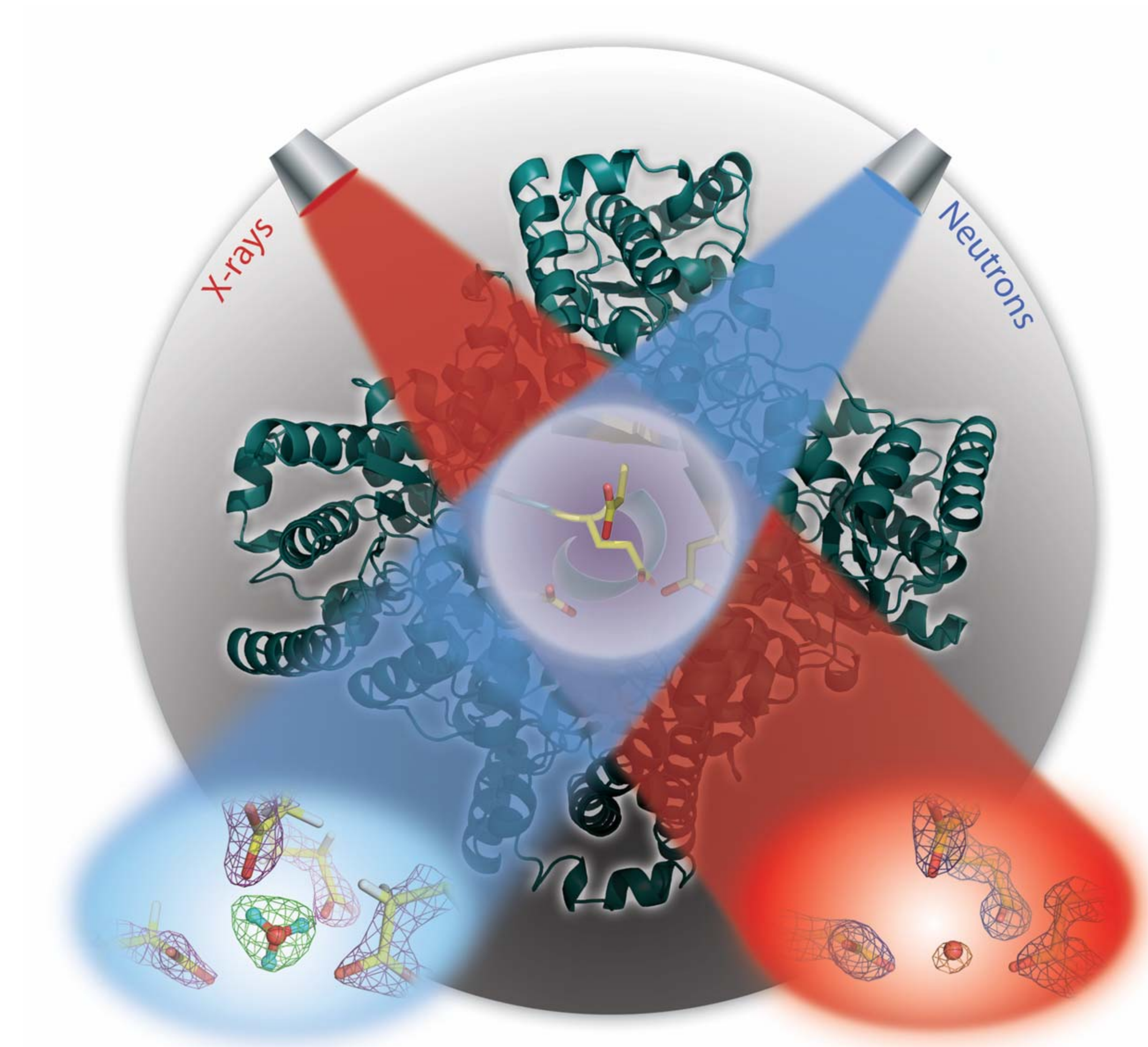
$$F(Q) = \sum_{i,j=1}^{n} c_i c_j \bar{b}_i \bar{b}_j [A_{ij}(Q) - 1]$$

- Data may be measured faster, to higher resolution and with greater precision

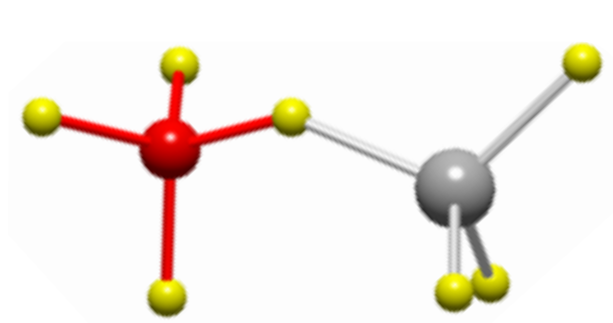
$$g_{ij}(r) - 1 = \frac{1}{(2\pi)^3 \rho_0} \int_0^\infty 4\pi Q^2 [A_{ij}(Q) - 1] \frac{\sin Qr}{Qr} \, dQ$$

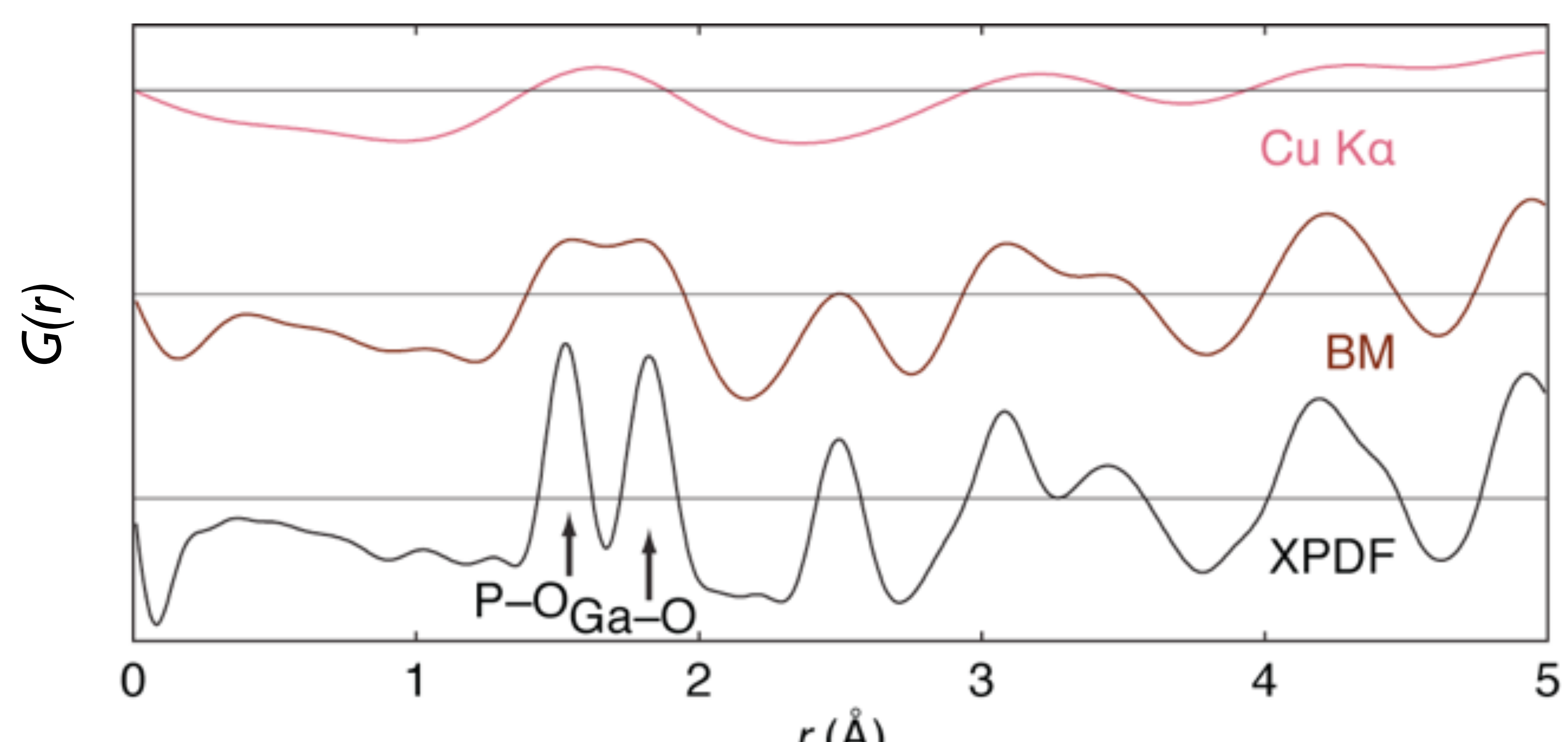
- Neutron PDF is still the ‘gold standard’!

- The resources are there...with more being built

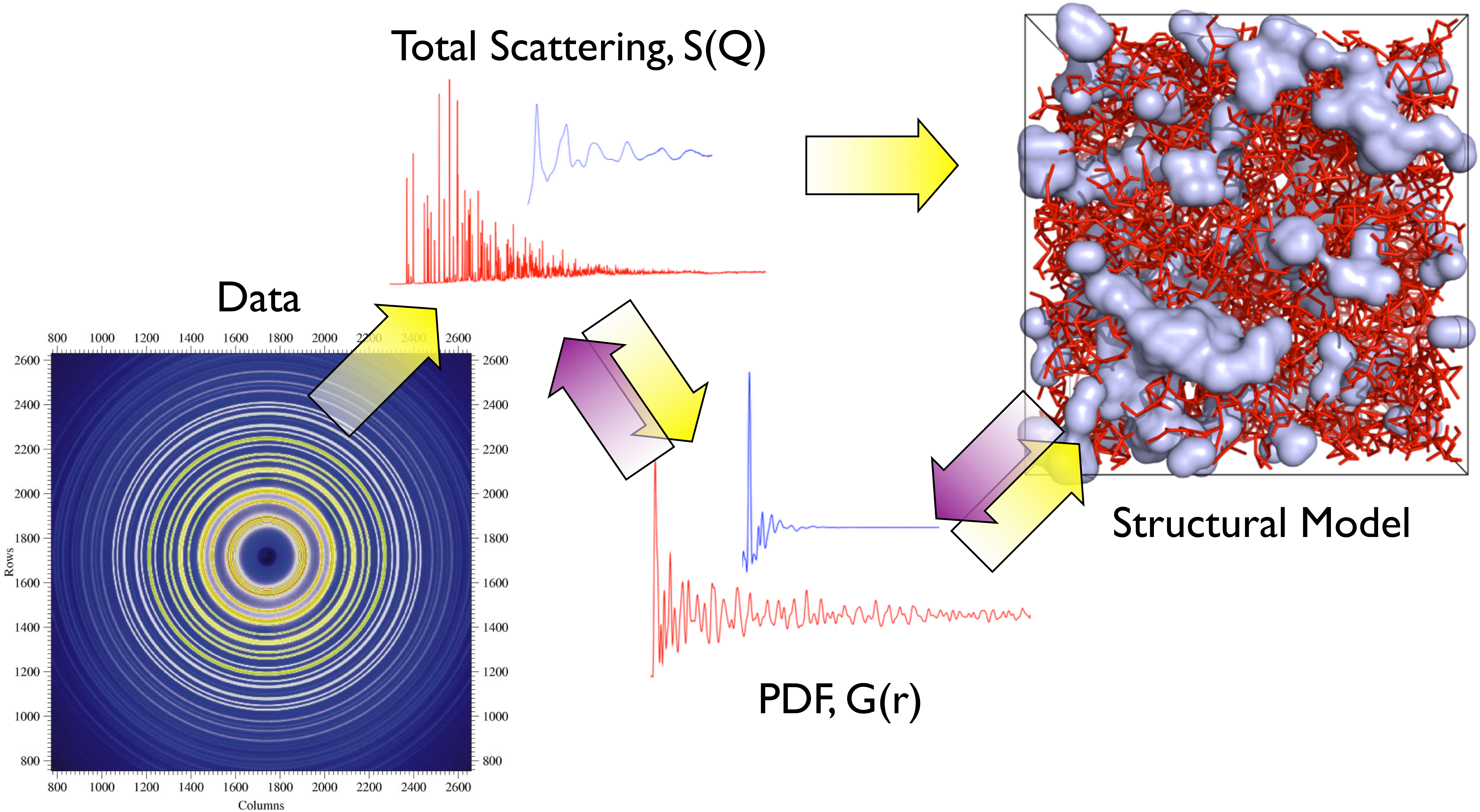


$GaPO_4$





Analysis of Total Scattering Data



RMC method

- Create a starting atomistic (supercell) model
- Calculate an agreement function

$$\chi^2_{\mathrm{RMC}} = \chi^2_{\mathrm{F(Q)}} + \chi^2_{\mathrm{G(r)}} + \chi^2_{\mathrm{Bragg\ Profile}} + \chi^2_{\mathrm{f}}$$

- Move an atom randomly and recalculate χ^2_{RMC}
- Accept a move based on the change in χ^2_{RMC}
- Repeat until convergence
- Critically analyse the resulting atomistic model

Perovskite structure

Crystal Structure of Barium Titanate

It is well known that barium titanate belongs to the group of compounds having structures of the perovskite type[1]. The ideal perovskite structure (*G*5 in the "Strukturbericht") has a simple cubic lattice, with one formula-weight per cell, the atomic parameters being as follows: 2-valent cation, (0,0,0); 4-valent cation, $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$; oxygens, $(0,\frac{1}{2},\frac{1}{2})$, $(\frac{1}{2},0,\frac{1}{2})$, $(\frac{1}{2},\frac{1}{2},0)$. It was early recognized[2] that for many of these compounds, including perovskite ($CaTiO_3$) itself as well as barium titanate, the structure was not truly cubic, but was actually a slightly deformed modification of it. Perovskite itself is generally believed monoclinic; the structure has recently been determined in detail by Naray-Szabo[3], who finds a monoclinic unit cell with all its edges doubled relative to the unit cell of the ideal structure. No detailed work on barium titanate has hitherto been published, and it was thought of interest to investigate it. Powder photographs of the synthetic material taken in a 19 cm.-diameter camera with copper $K\alpha$ radiation provided the data for determining the structure.

The structure is tetragonal, the dimensions of the unit cell at 20° C., for a typical sample of material, being as follows: $a = 3{\cdot}9860 \pm 0{\cdot}0005$ kX., $c = 4{\cdot}0263 \pm 0{\cdot}0005$ kX., $c/a = 1{\cdot}0101 \pm 0{\cdot}0002$. This cell contains one formula-weight, $BaTiO_3$. The atomic parameters are the same as in the ideal cubic structure. The relationship between the tetragonal and cubic structure is close; the tetragonal unit cell may be simply derived from the cubic by stretching it homogeneously by about 1 per cent along one tetrad axis, which becomes the *c* axis.

This close relationship suggests that a transition to the cubic structure may occur at higher temperatures. This was verified from photographs taken with a high-temperature camera. At 200° C., barium titanate has the ideal cubic structure, with $a_0 = 4{\cdot}0040 \pm 0{\cdot}0005$ kX.

Further work is in progress.

I wish to express my gratitude to Sir Lawrence Bragg for allowing me the use of the high-temperature camera in his laboratory. I wish also to thank Mr. J. A. M. van Moll (head of the Material Research Laboratory) and the directors of Philips Lamps, Ltd., for permission to publish this work.

HELEN D. MEGAW.

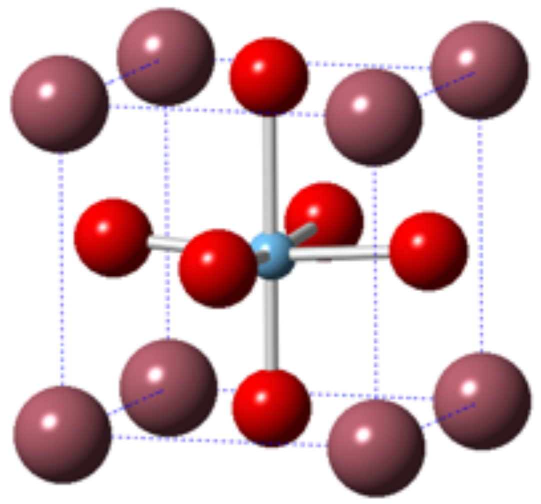
Material Research Laboratory,
(Philips Lamps, Ltd.),
New Road, Mitcham Junction,
Surrey.

Feb. 24.

[1] Goldschmidt, V. M., "Geochem. Verteilungsgesetze d. Elem.", 8, 153 (1927).
[2] *ibid.*, and also 7, 37 (1926).
[3] Naray-Szabo, I., *Naturwiss.*, 31, 202 (1943).

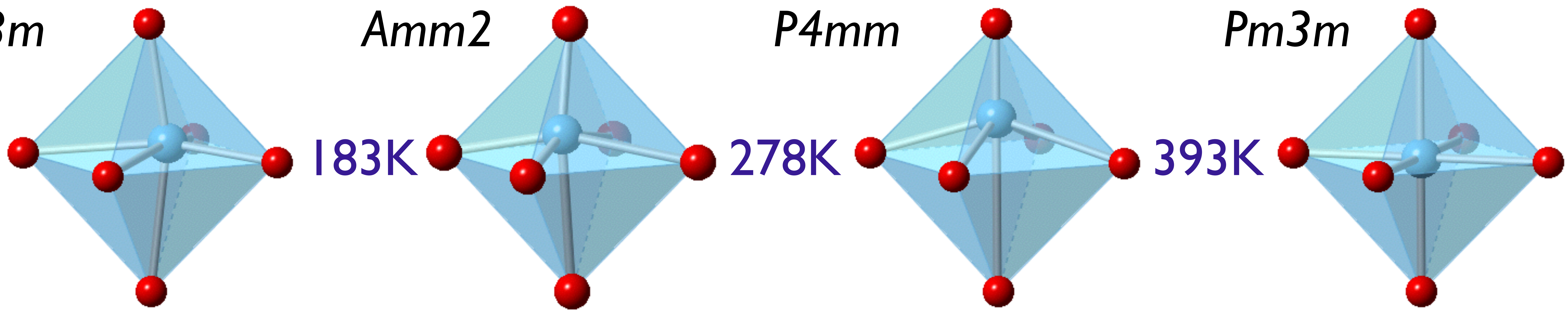
Megaw *Nature* **155** (1945) 484

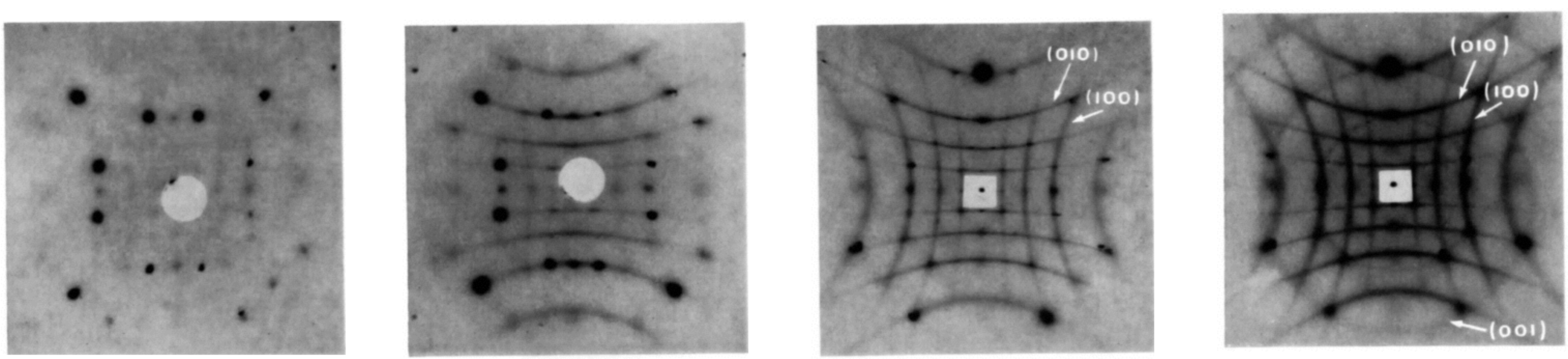
$BaTiO_3$ structure and temperature



Increasing Temperature →

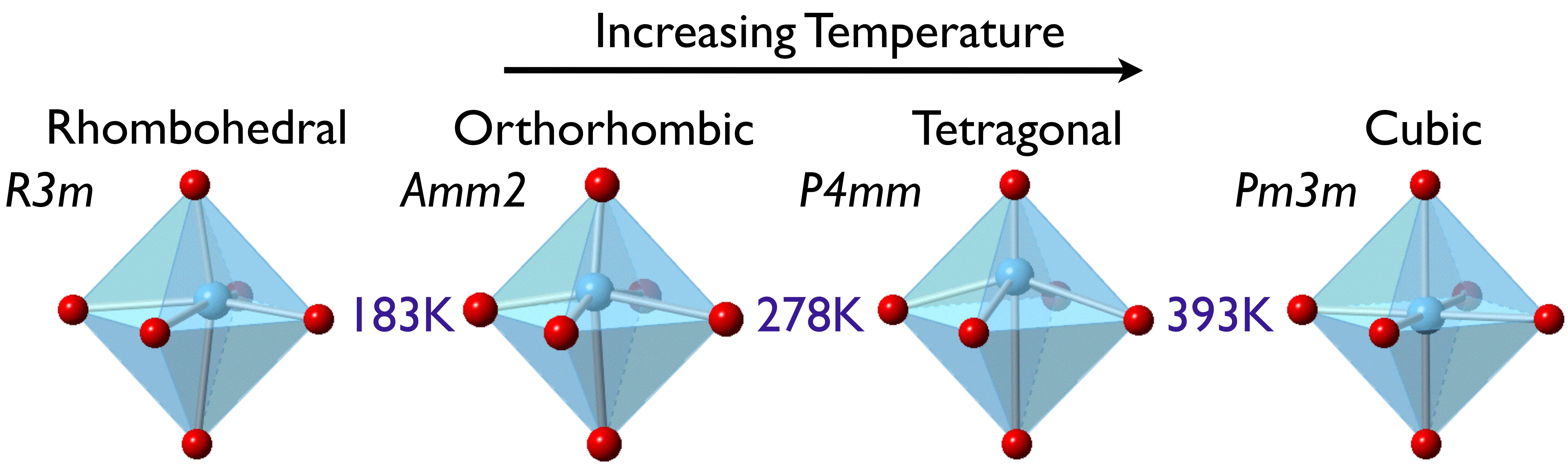
Rhombohedral	Orthorhombic	Tetragonal	Cubic
R3m	*Amm2*	*P4mm*	*Pm3m*





Comes et al *Acta Cryst A* **26** (1970) 244

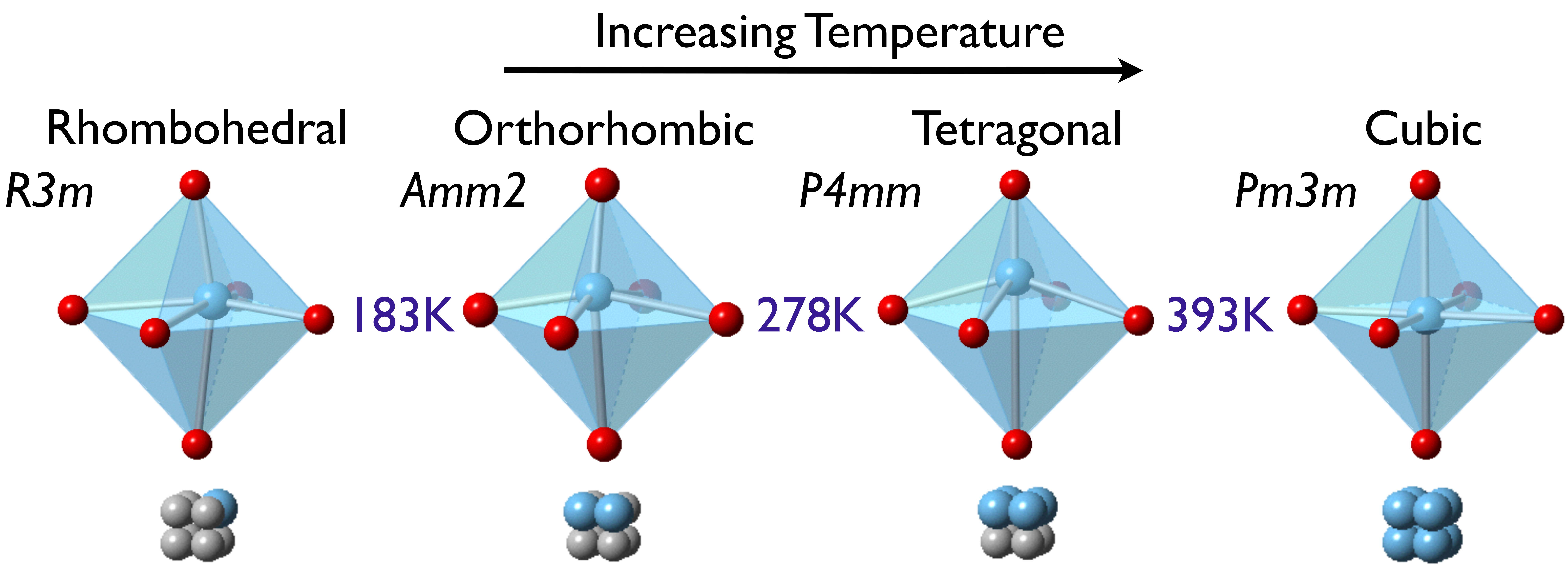
$BaTiO_3$ structure and temperature



La position d'équilibre de l'atome Nb (*ou* Ti) *n'est pas le centre de la maille, mais elle est légérement déplacée le long d'une des diagonales du cube.* Il y a donc 8 sites équivalents possibles.

Comes et al *Acta Cryst A* **26** (1970) 244

BaTiO$_3$ structure and temperature



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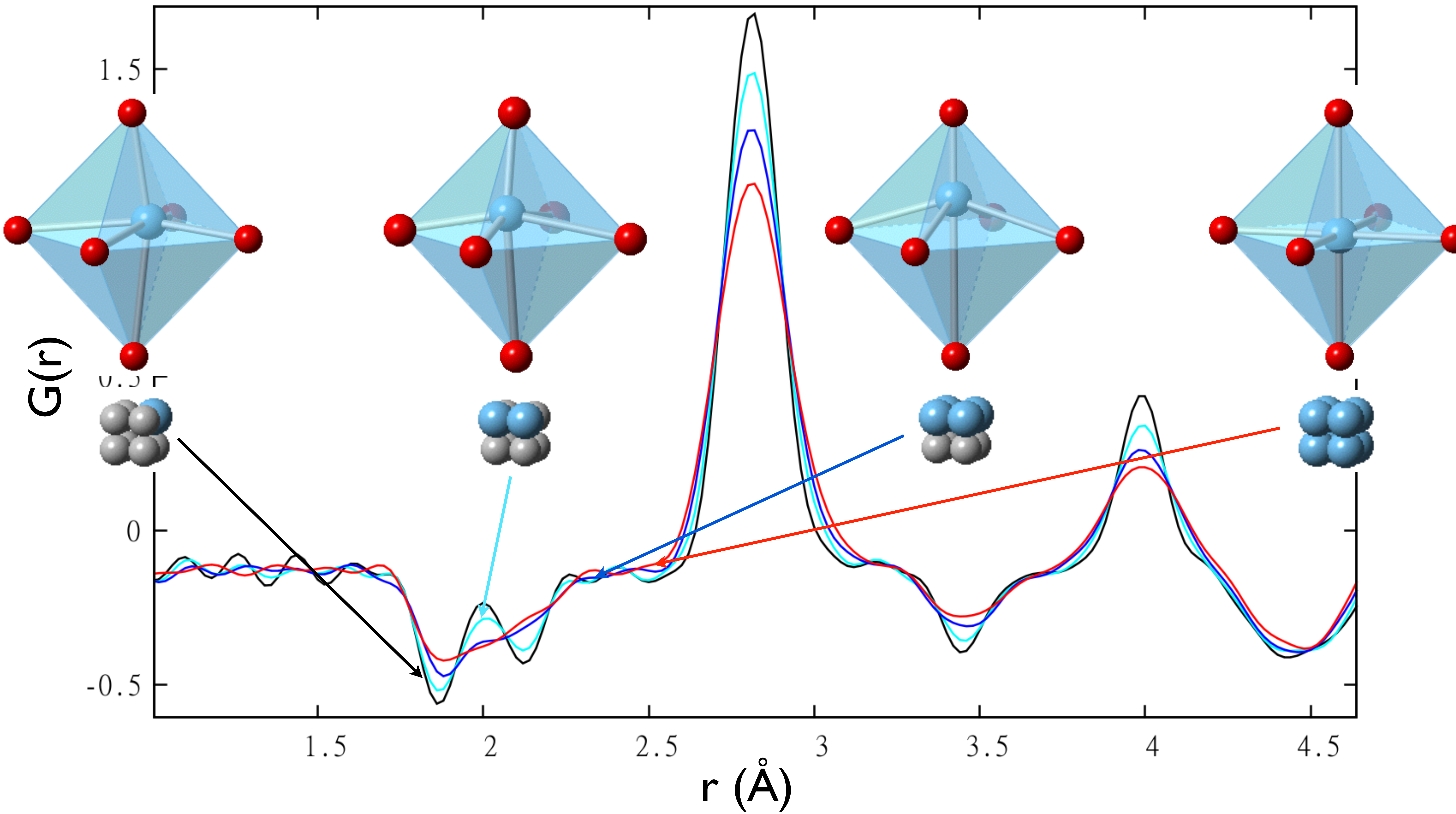
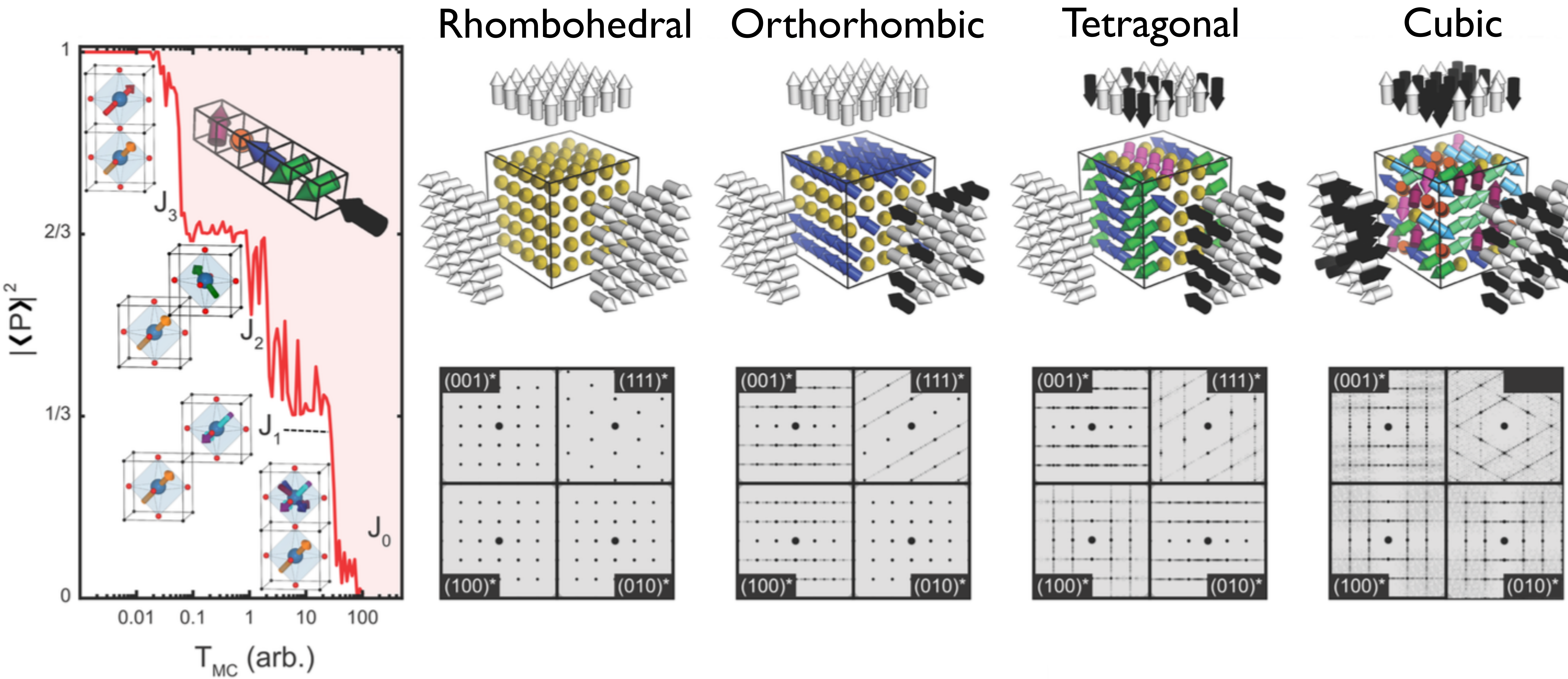
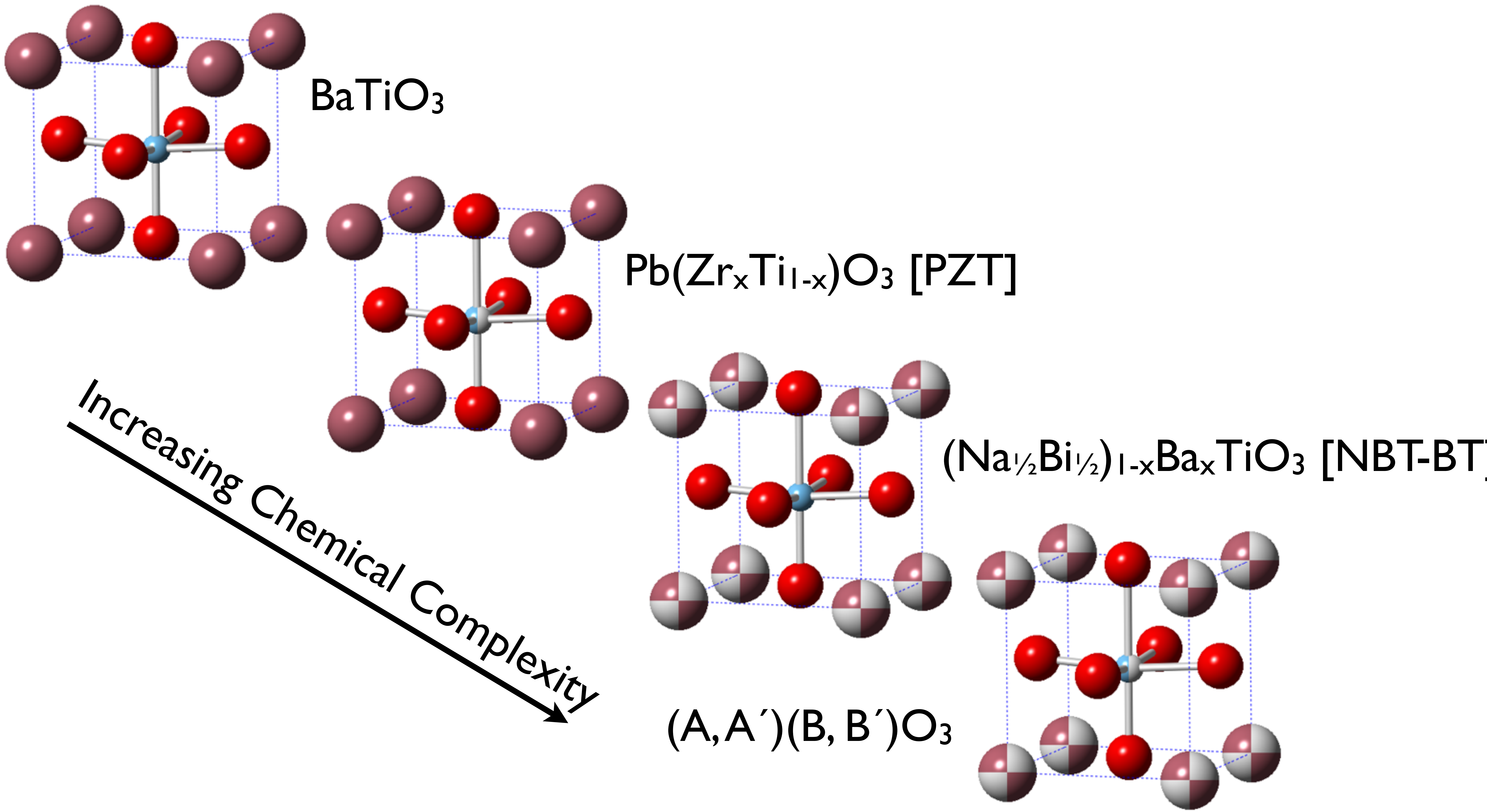


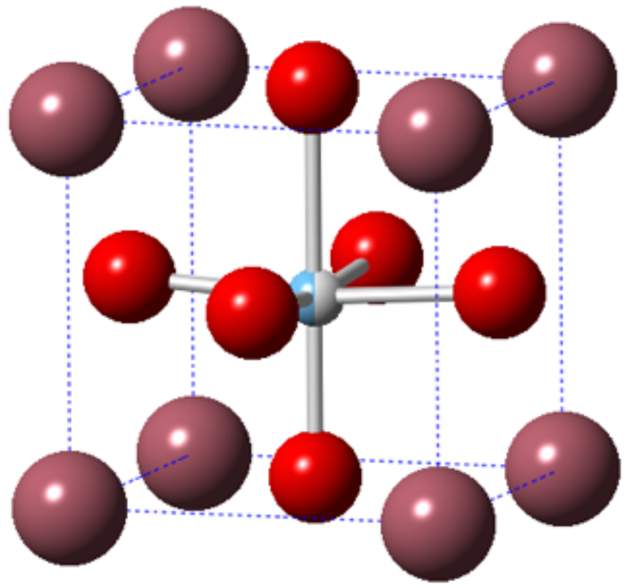
Phase Transitions in $BaTiO_3$ from Local Correlations



M Senn et al, *Phys Rev Lett* **116** (2016) 207602

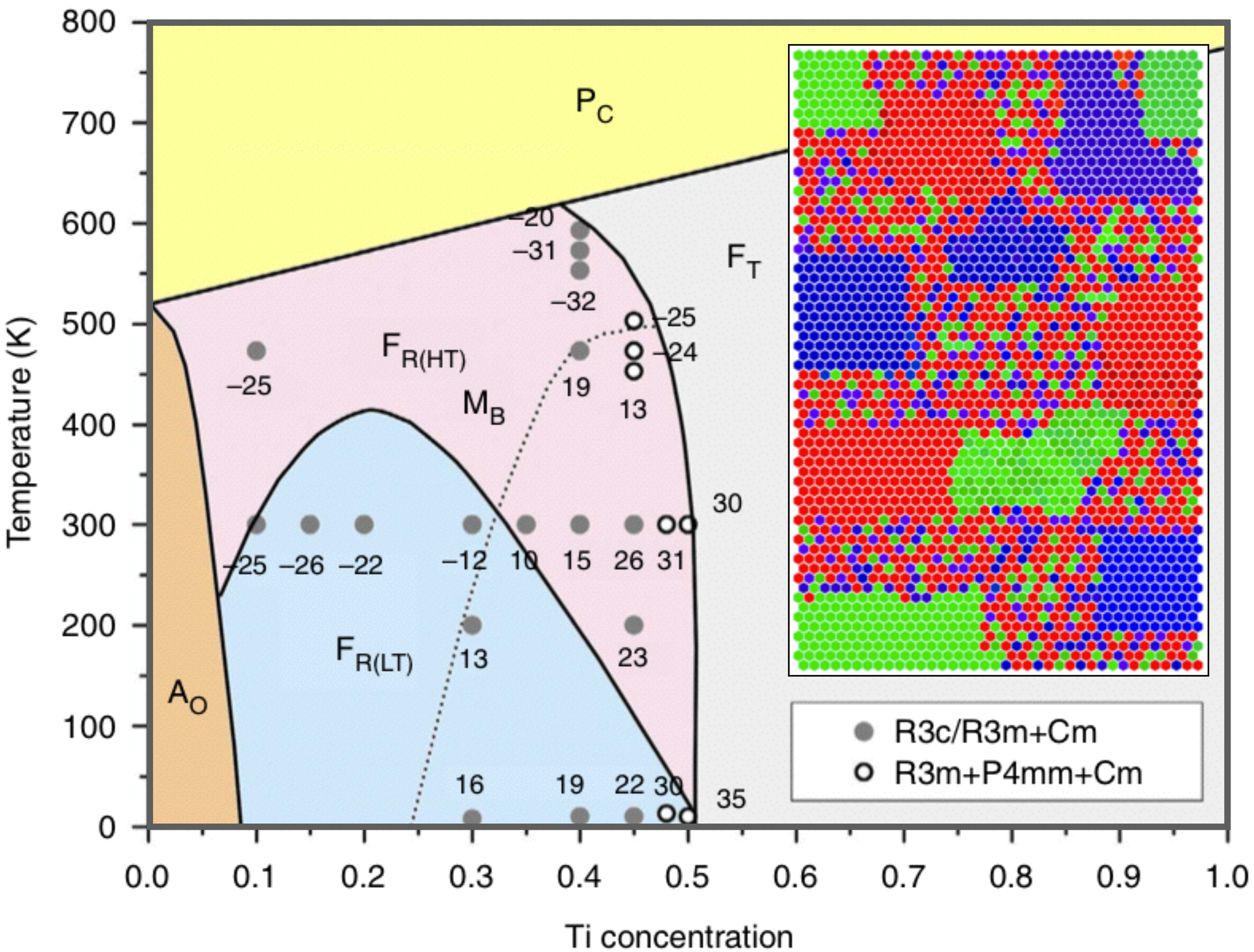
Perovskite Ferroelectrics

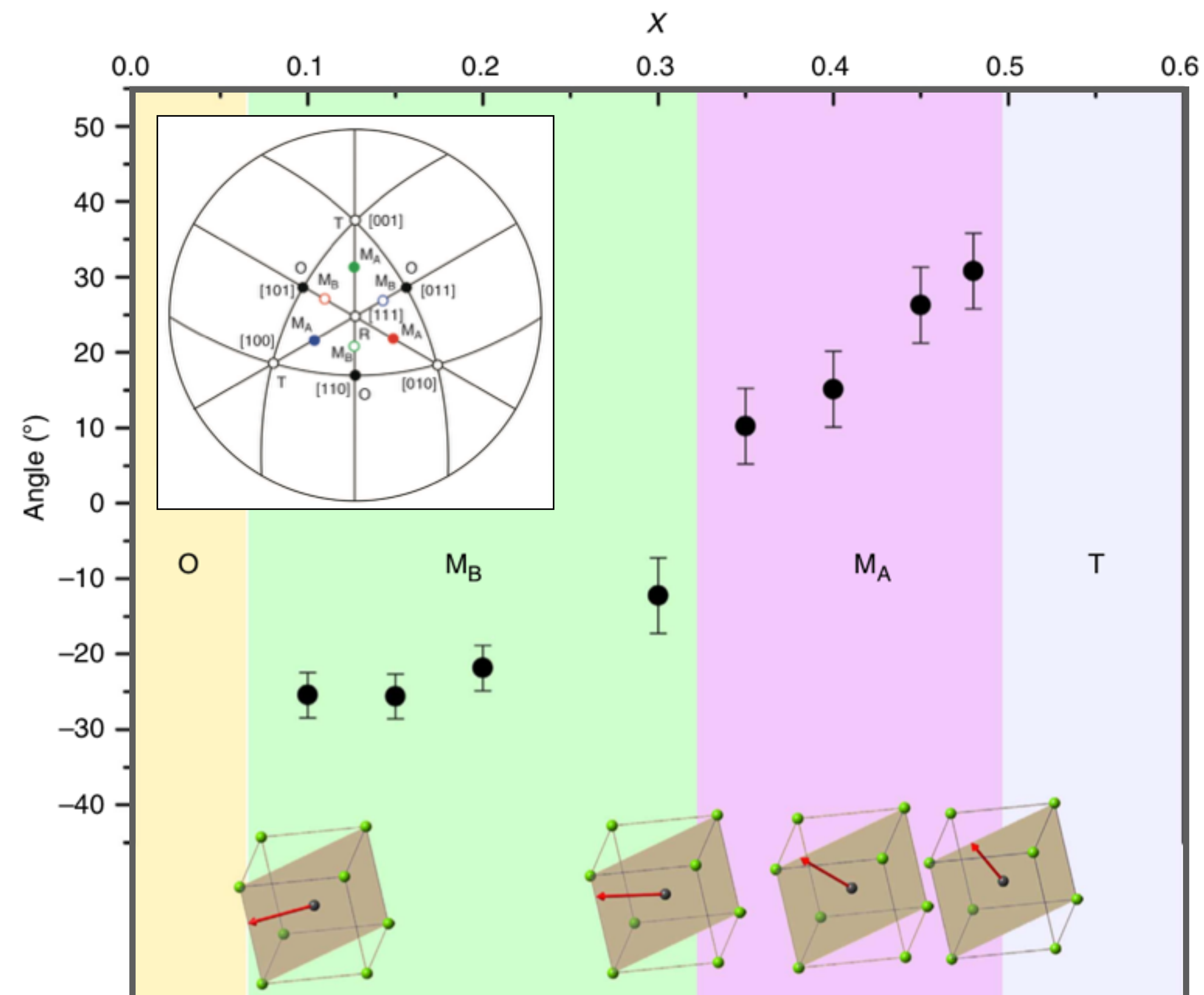




The missing phase boundary in PZT

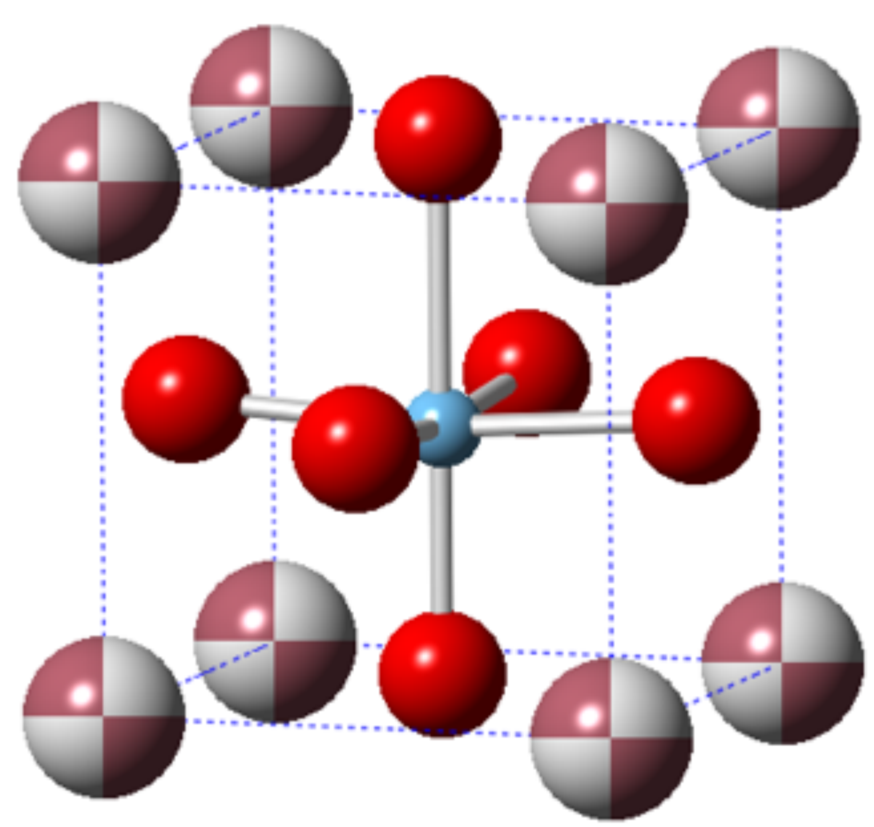
$Pb(Zr_xTi_{1-x})O_3$ [PZT]



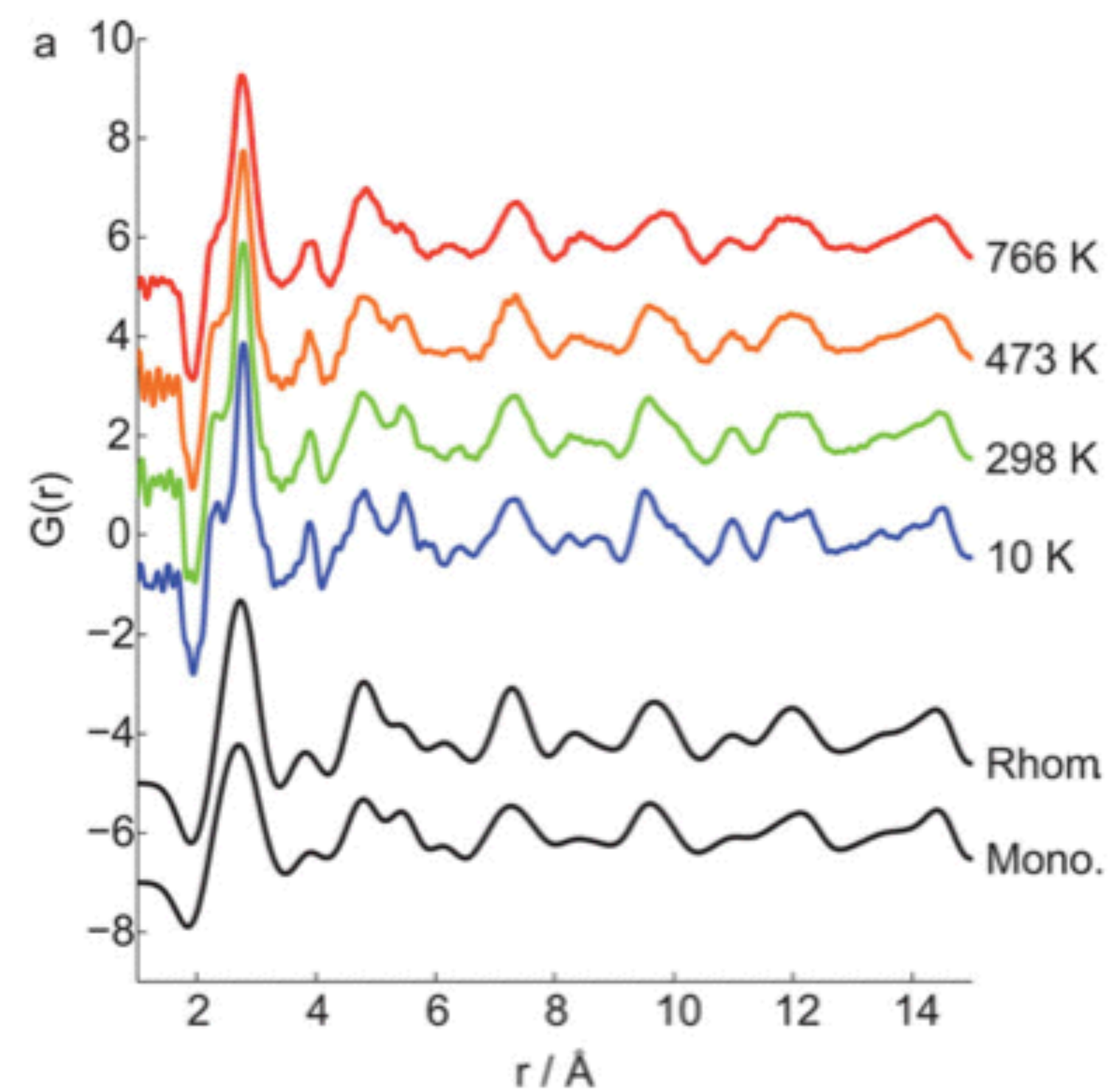


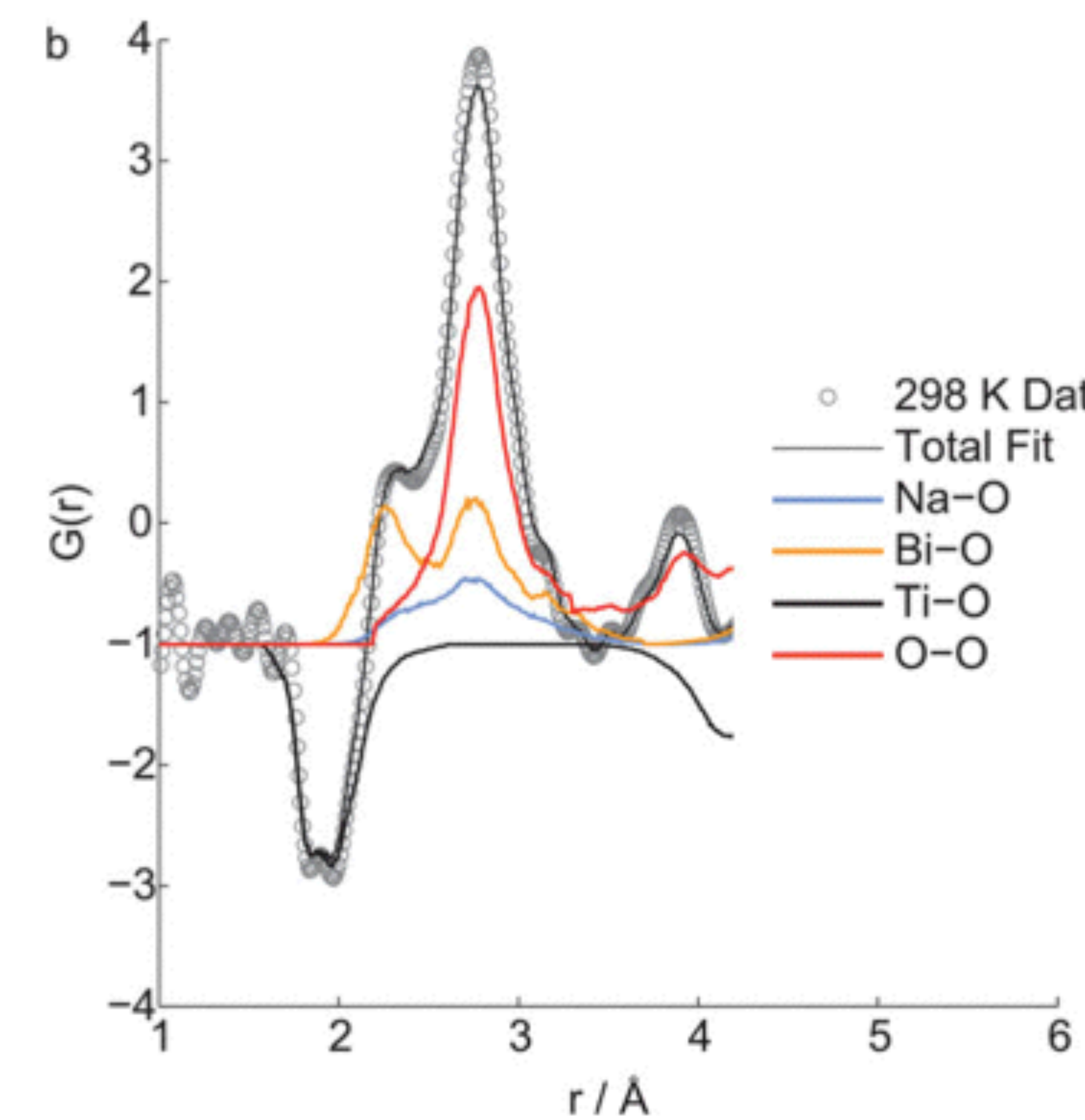
N Zhang et al *Nature Comm.* **5** (2014) 5231

Lead-free piezoelectric $Na_{0.5}Bi_{0.5}TiO_3$ [NBT]



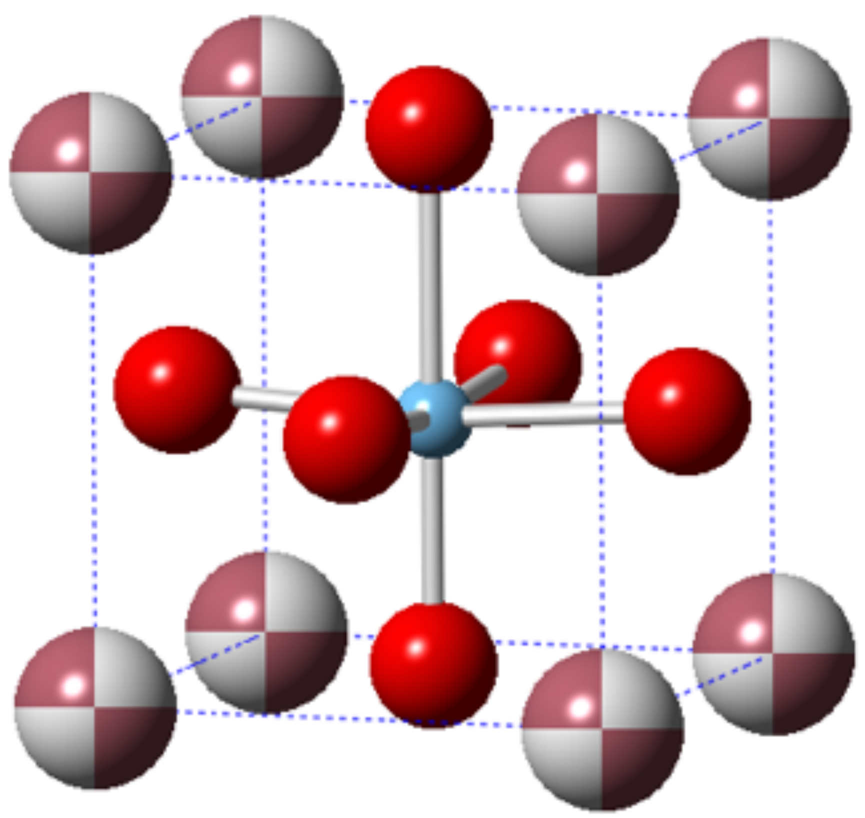
$(Na_{1/2}Bi_{1/2})TiO_3$
[NBT]





D S Keeble et al *Adv. Funct. Mater.* **23** (2013) 185

Rotation of polarisation vector in $Na_{0.5}Bi_{0.5}TiO_3$



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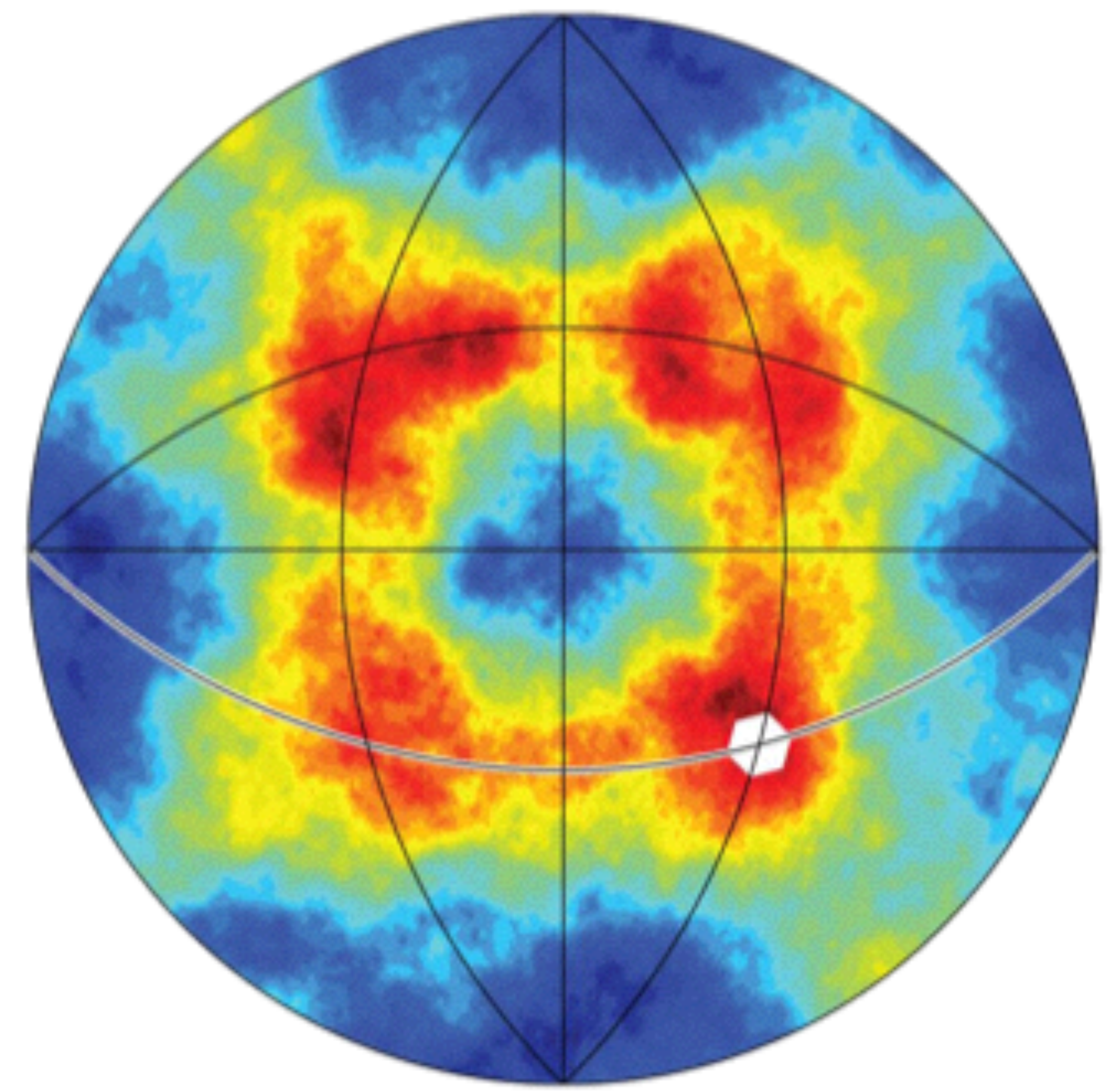
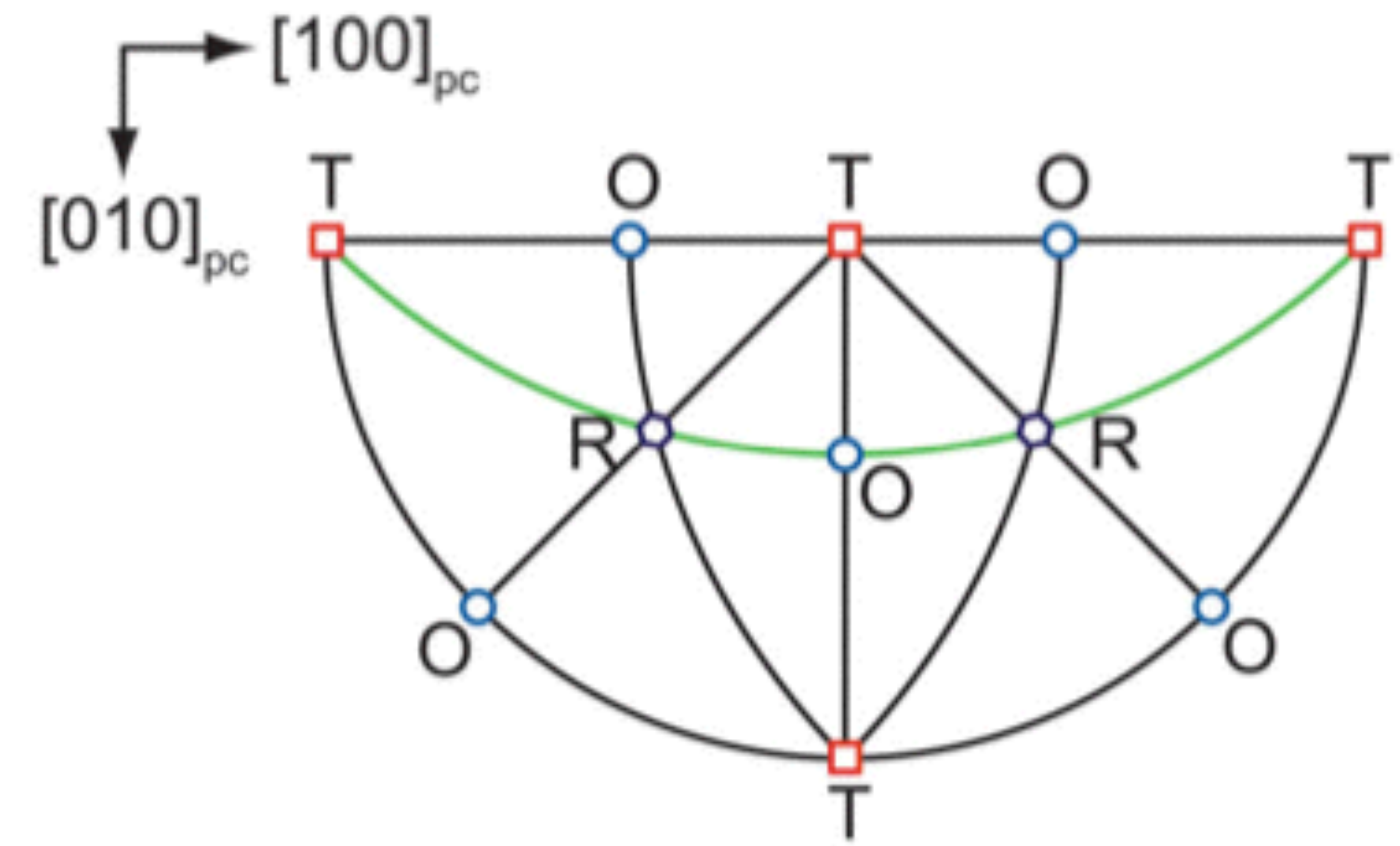


Ti displacements
766K



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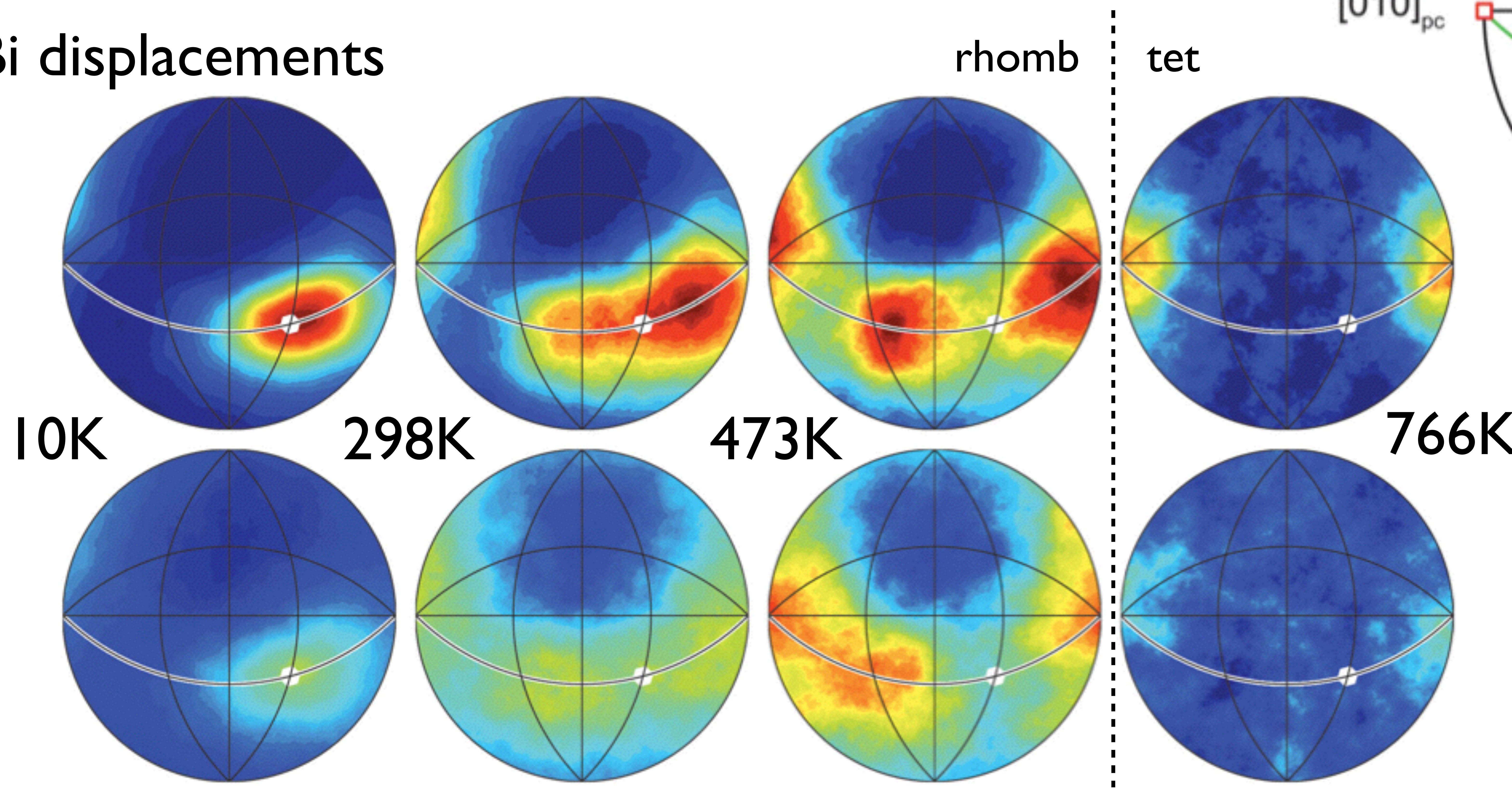
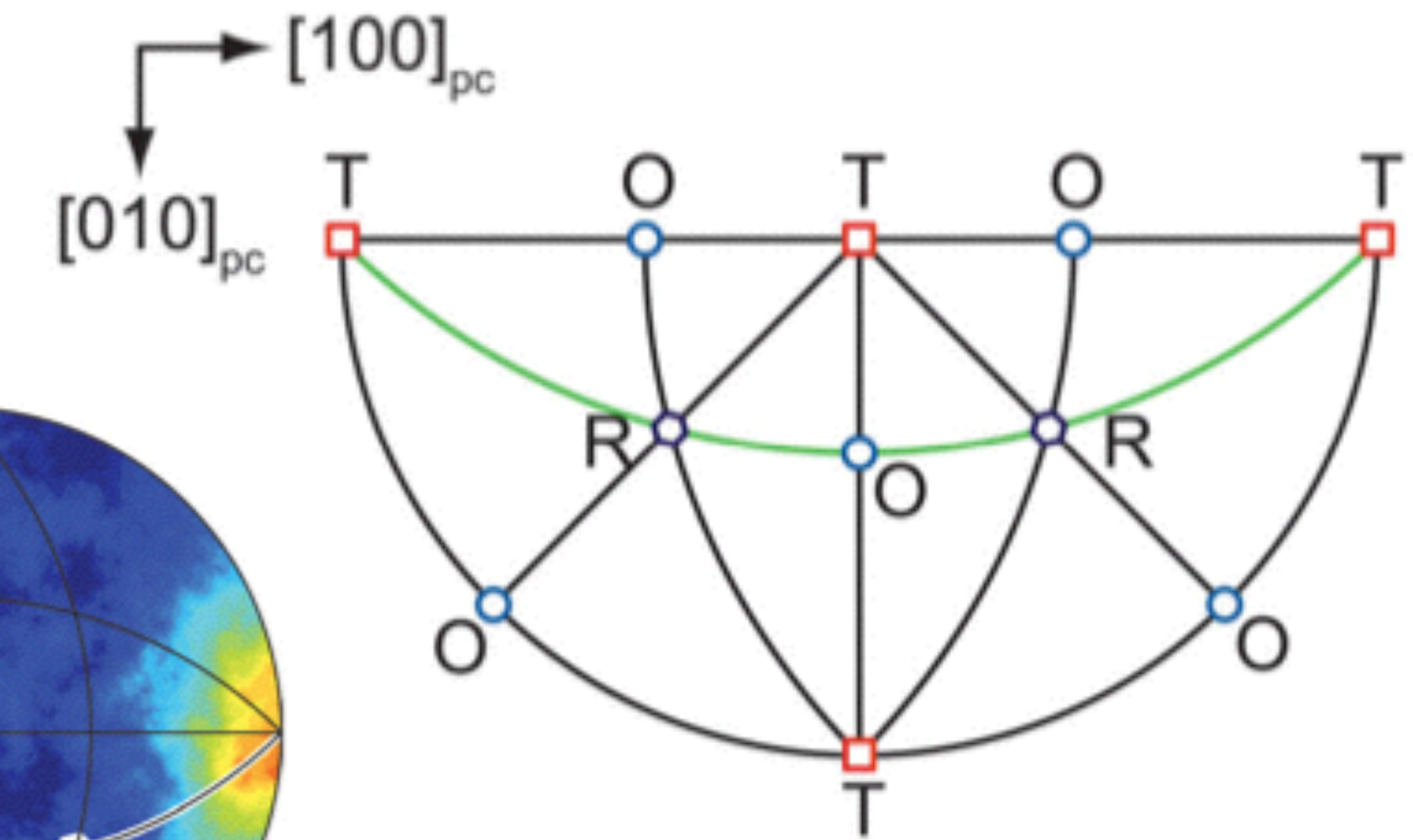
Rotation of polarisation vector in $Na_{0.5}Bi_{0.5}TiO_3$

Bi displacements





Na displacements

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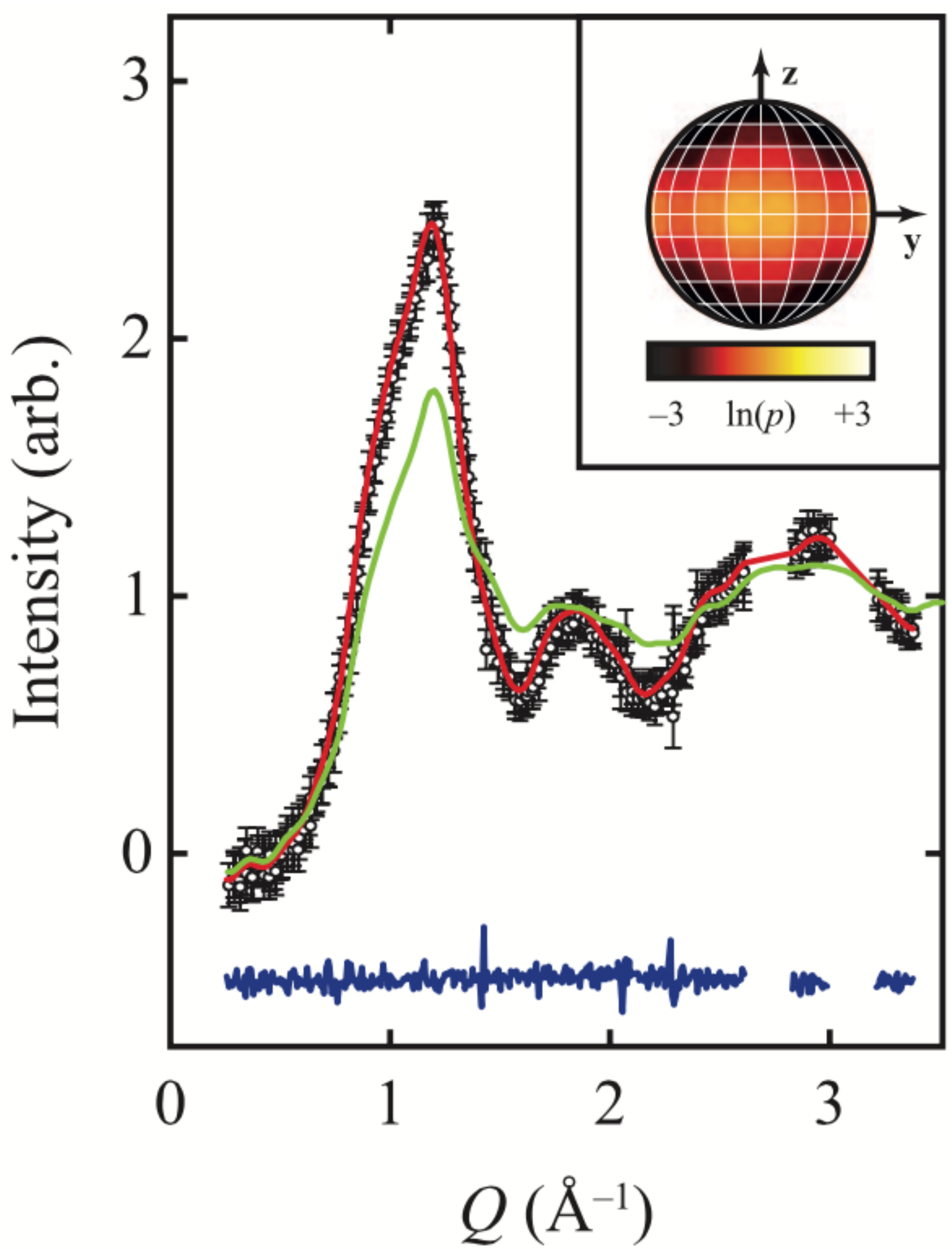
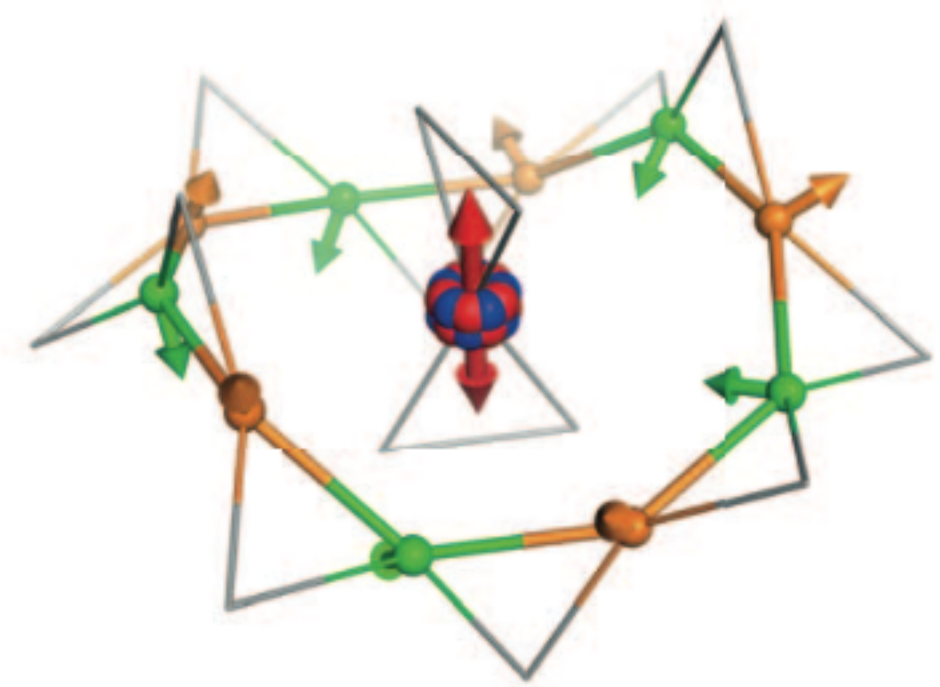
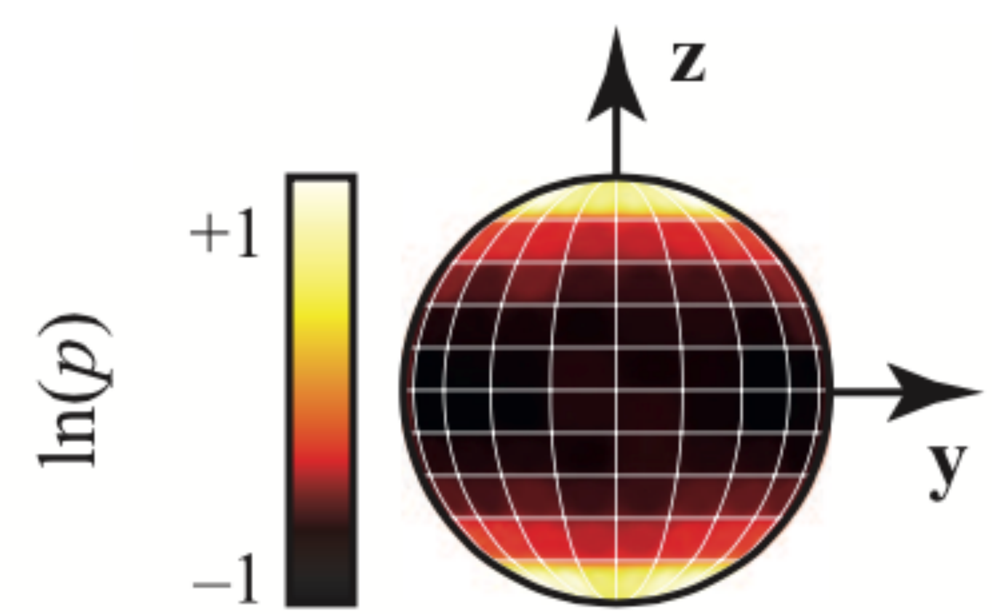
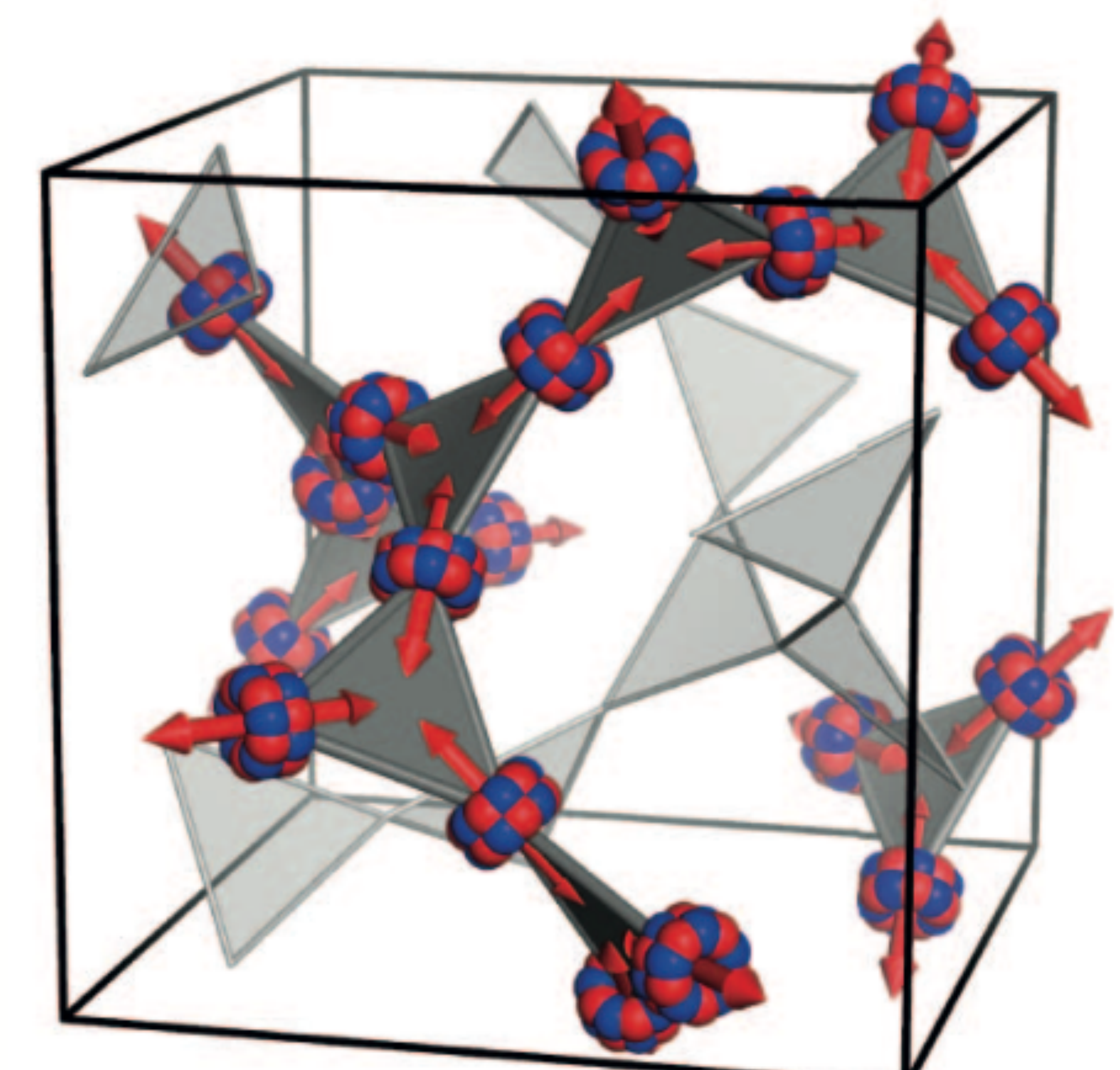
Hidden order in spin-liquid $Gd_3Ga_5O_{12}$

$$S_{\mathrm{mag}}(Q) = \frac{2}{3} c_{\mathrm{M}} \left[\frac{e^2 \gamma}{2 m_e c^2} g J f(Q) \right]^2 + 4 \pi \rho c_{\mathrm{M}} \left[\frac{e^2 \gamma}{2 m_e c^2} f(Q) \right]^2 \times \int r^2 \left\{ A(r) \frac{\sin Qr}{Qr} + B(r) \left[\frac{\sin Qr}{(Qr)^3} - \frac{\cos Qr}{(Qr)^2} \right] \right\} dr,$$









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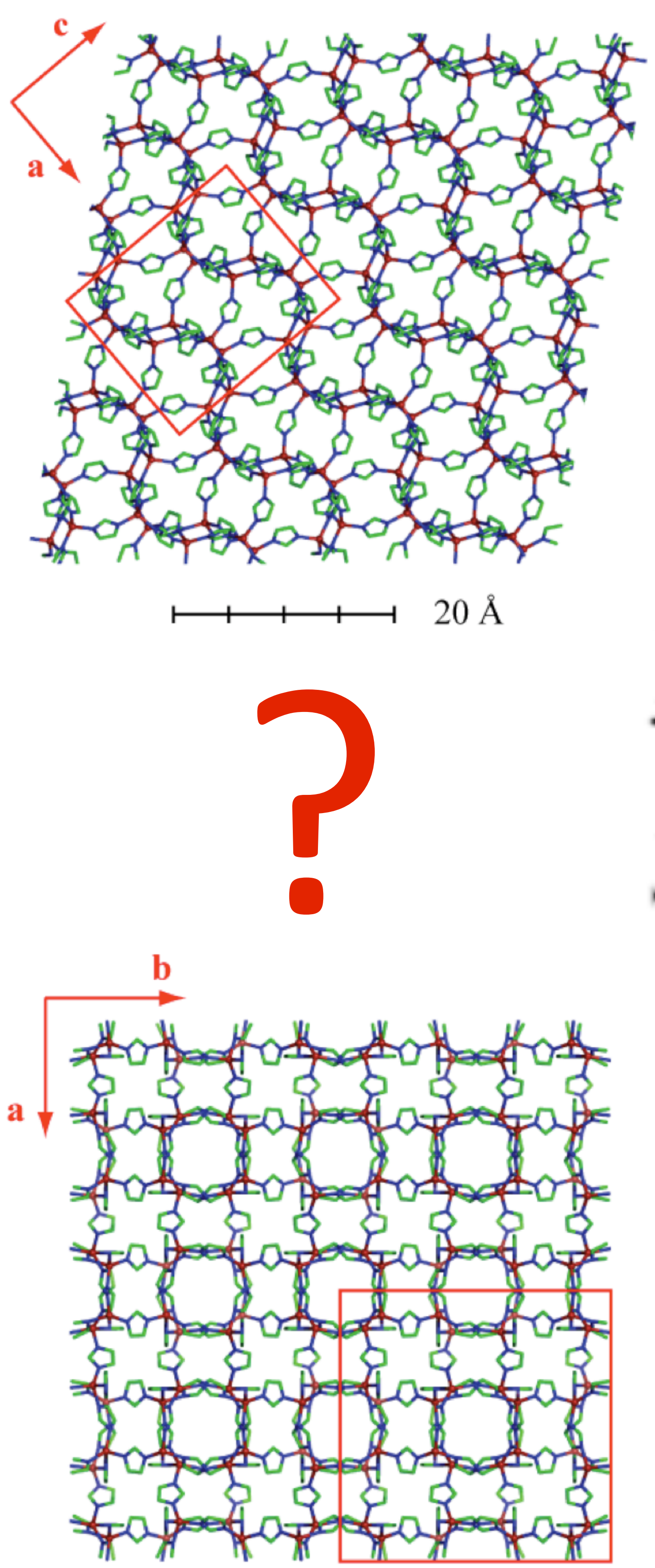
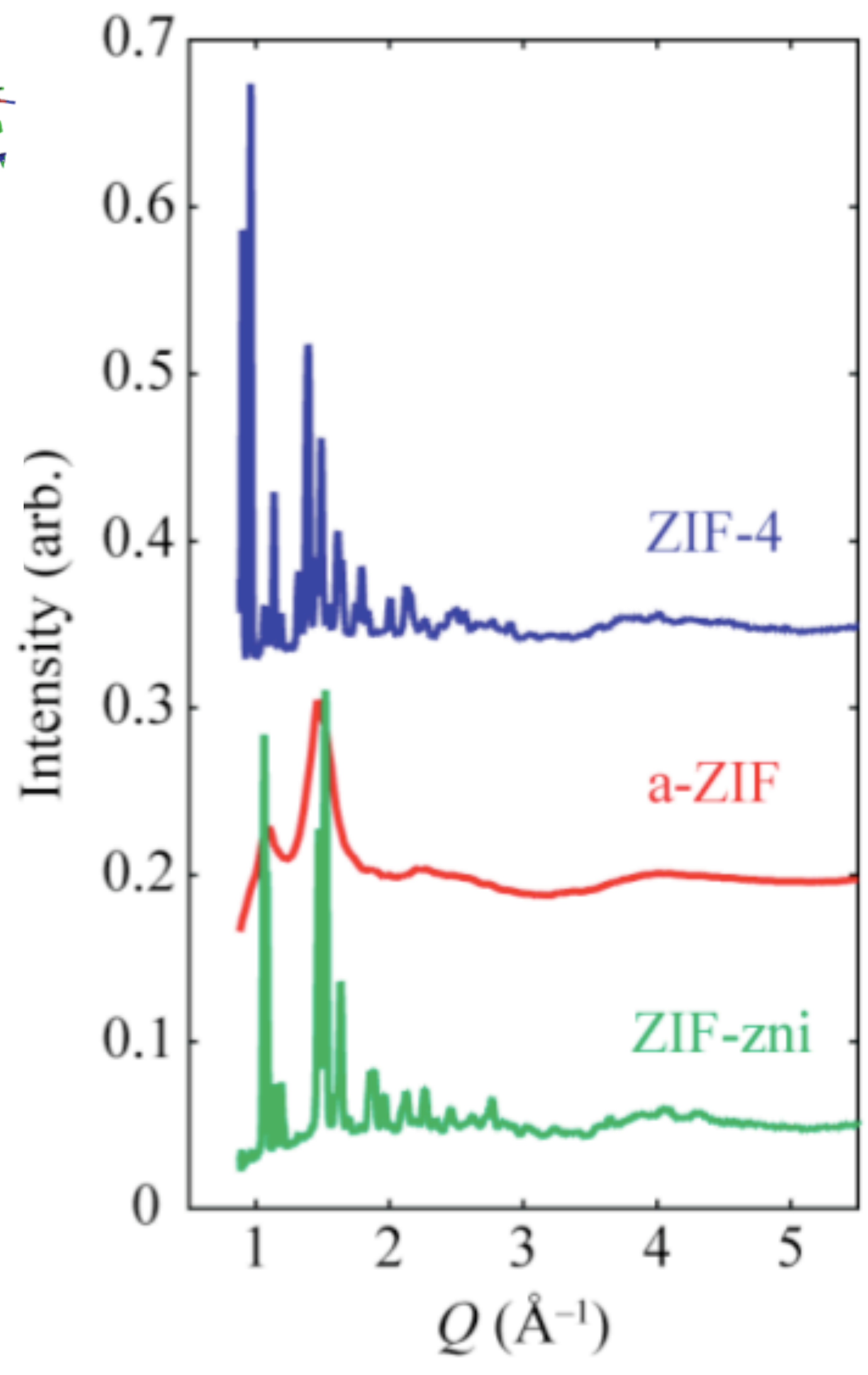
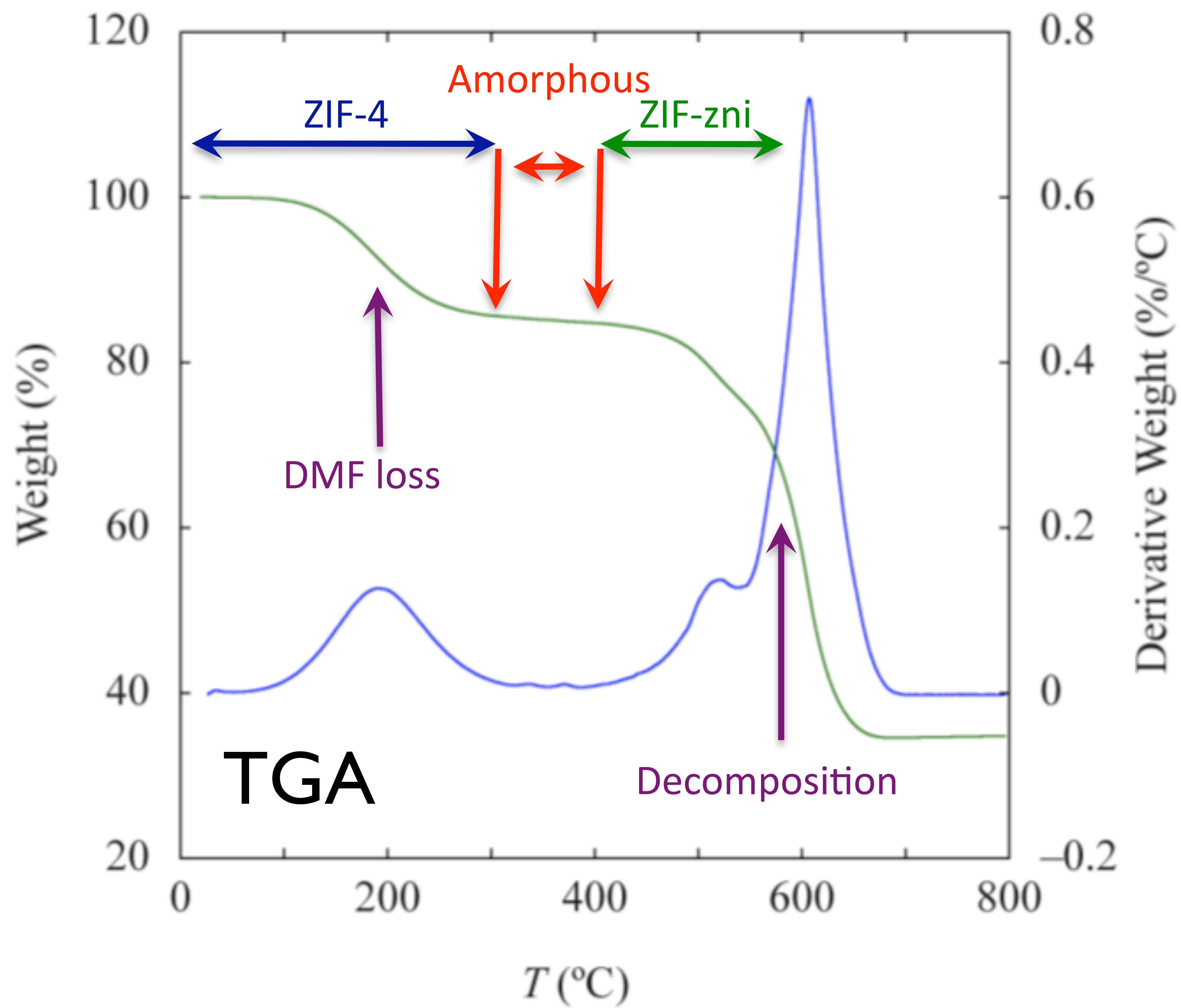
Neutron diffraction from ZIF-4

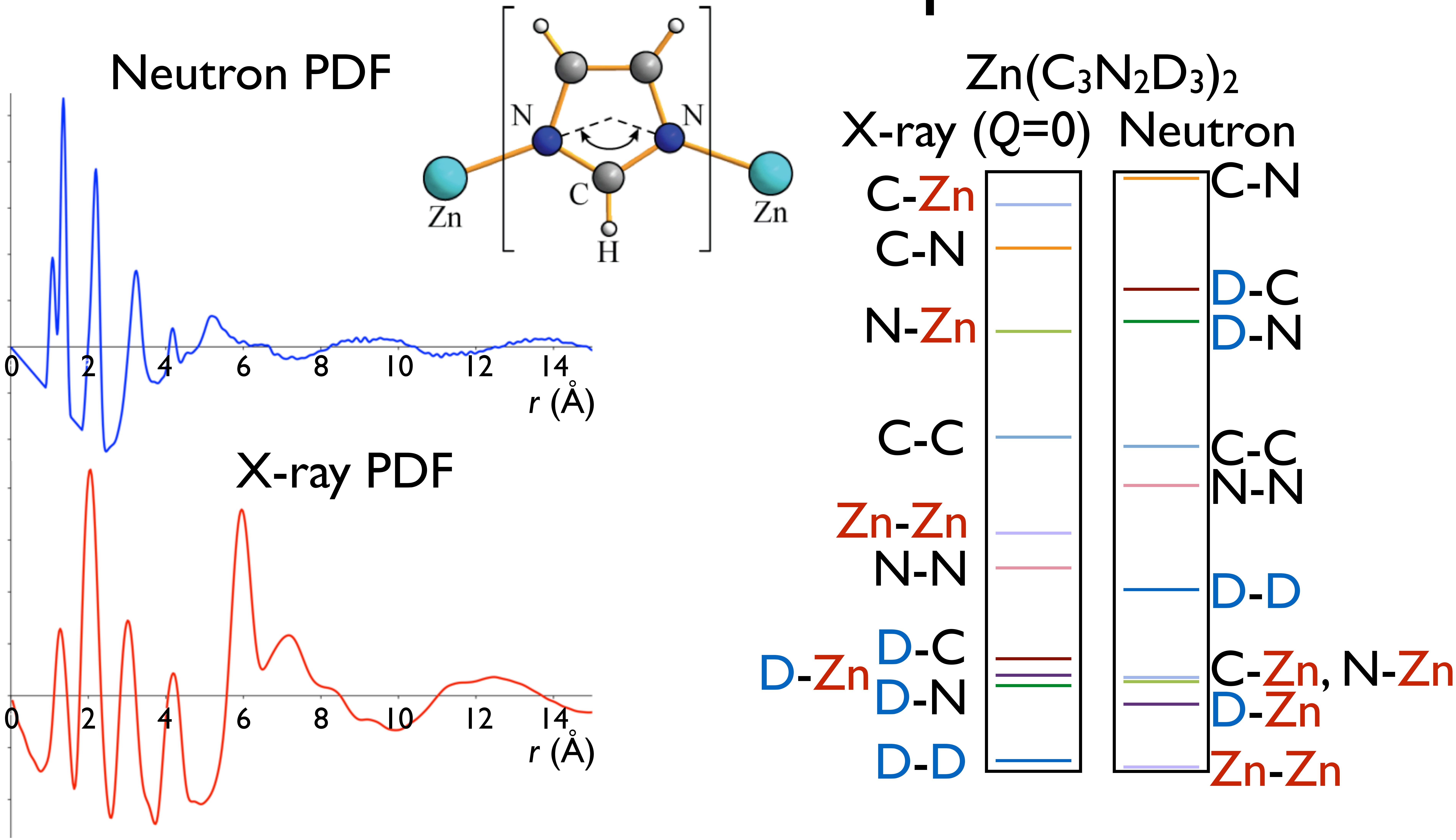




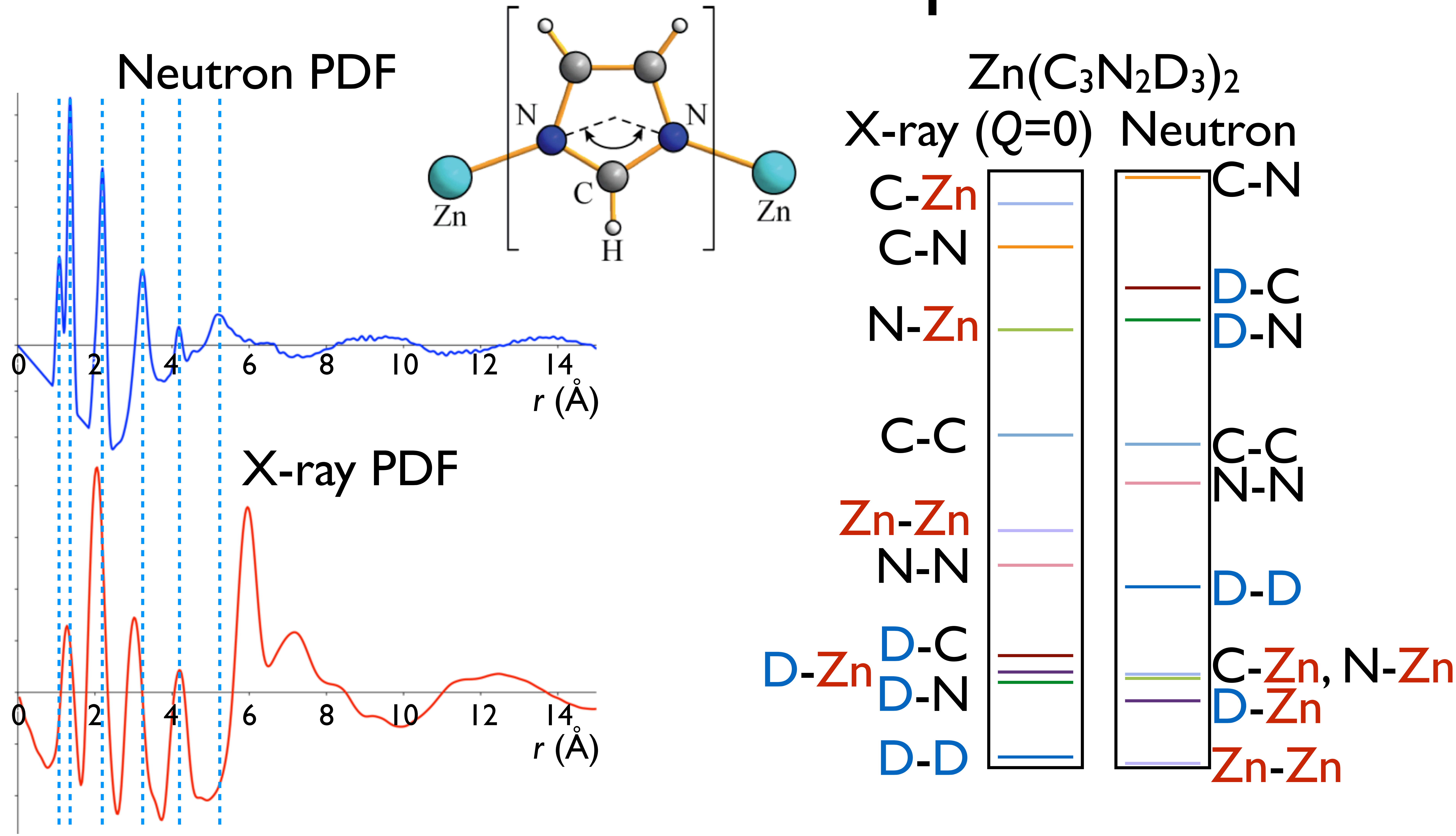


T D Bennett *et al*, *Phys Rev Lett*, **104** 115503 (2010)

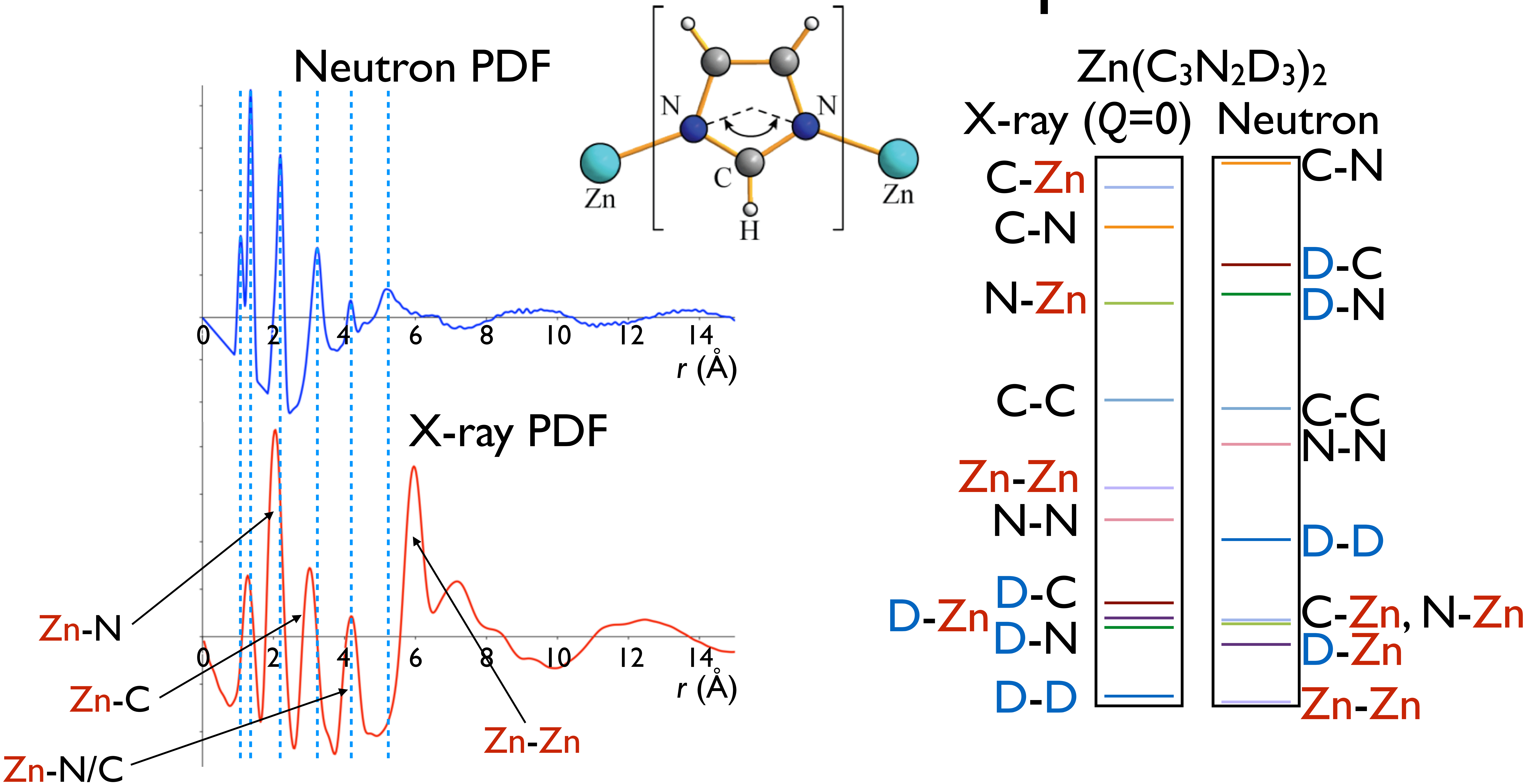
n-PDF and X-PDF from amorphous ZIF-4



n-PDF and X-PDF from amorphous ZIF-4

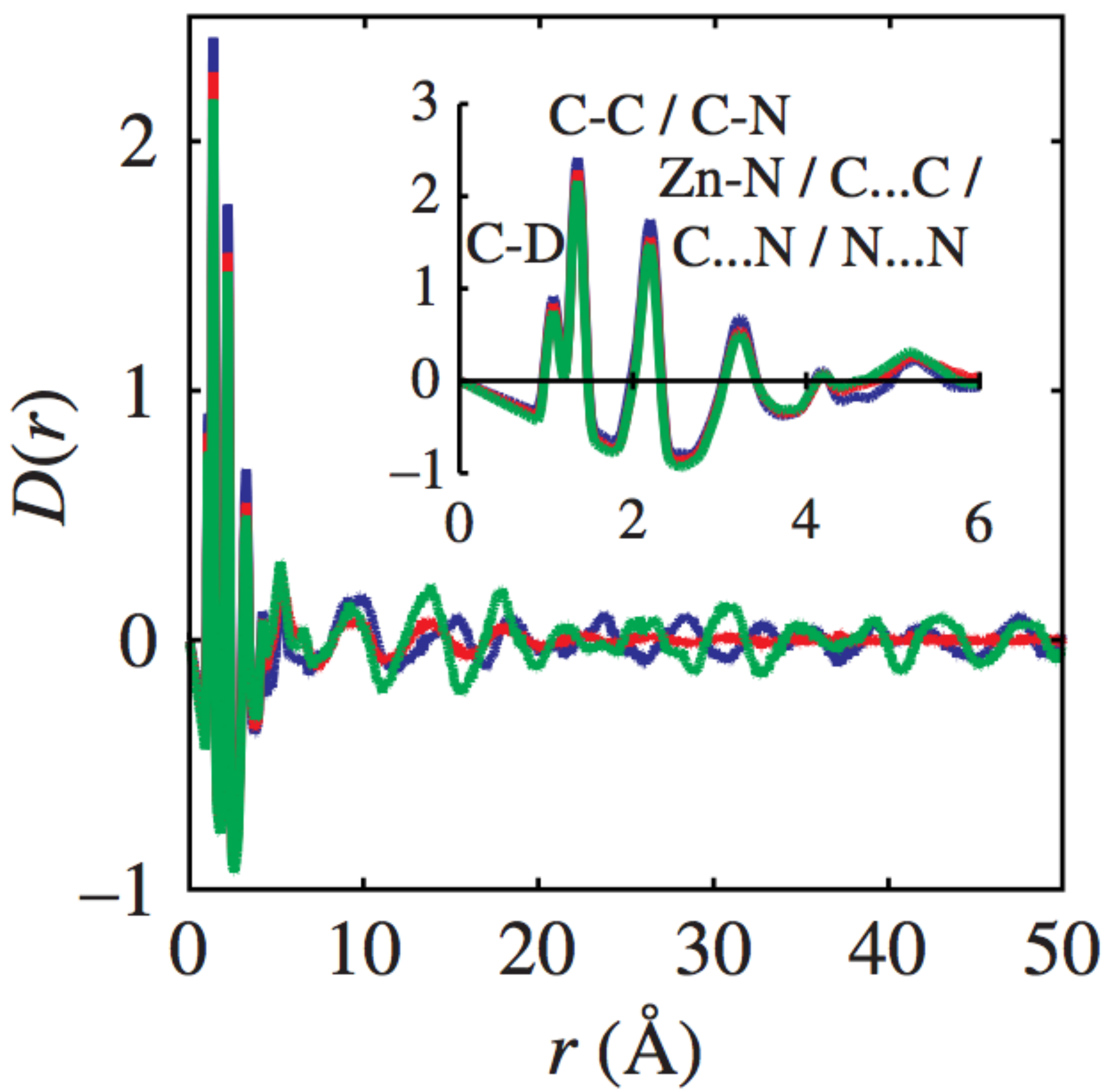


n-PDF and X-PDF from amorphous ZIF-4

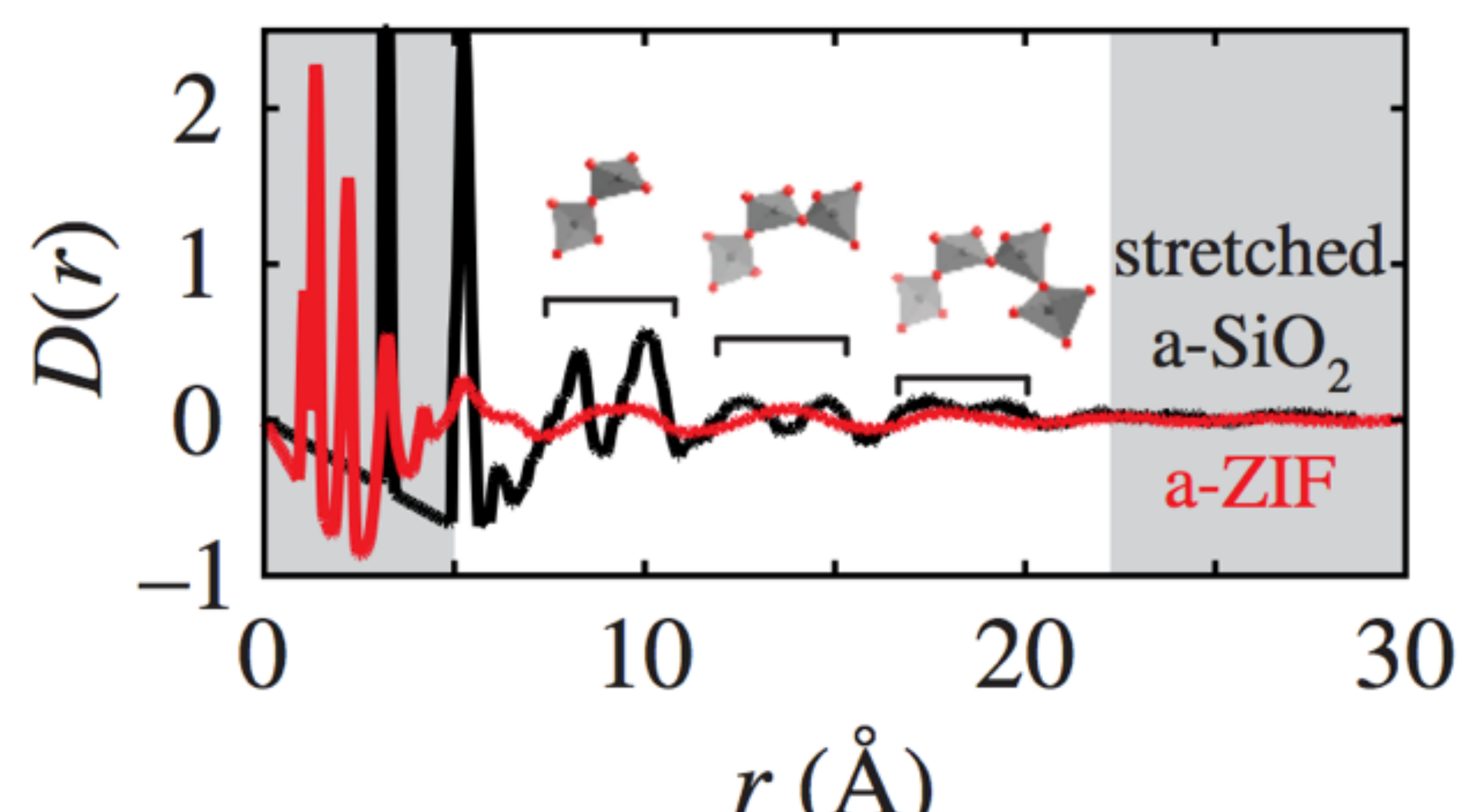


RMC starting models

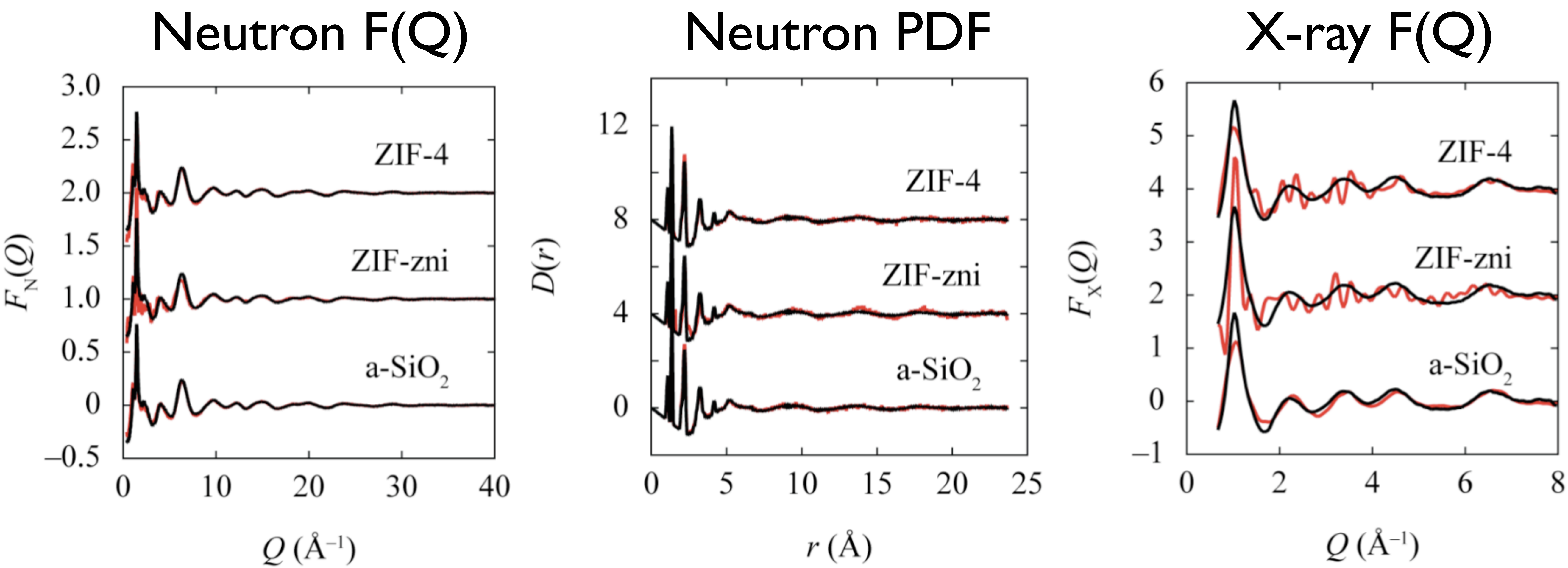
3 models, all with 512 $Zn(Im)_2$ and $\rho = 0.0693$ atoms $Å^{-3}$



- ZIF-4 - ~$2\sqrt{2}\times4\times2\sqrt{2}$ supercell of *Pbca* *(0.0618 atoms $Å^{-3}$)*
- ZIF-zni - 2×2×4 supercell of $I4_1cd$ *(0.0789 atoms $Å^{-3}$)*
- SiO_2-based continuous random network



RMC fits to amorphous-ZIF data



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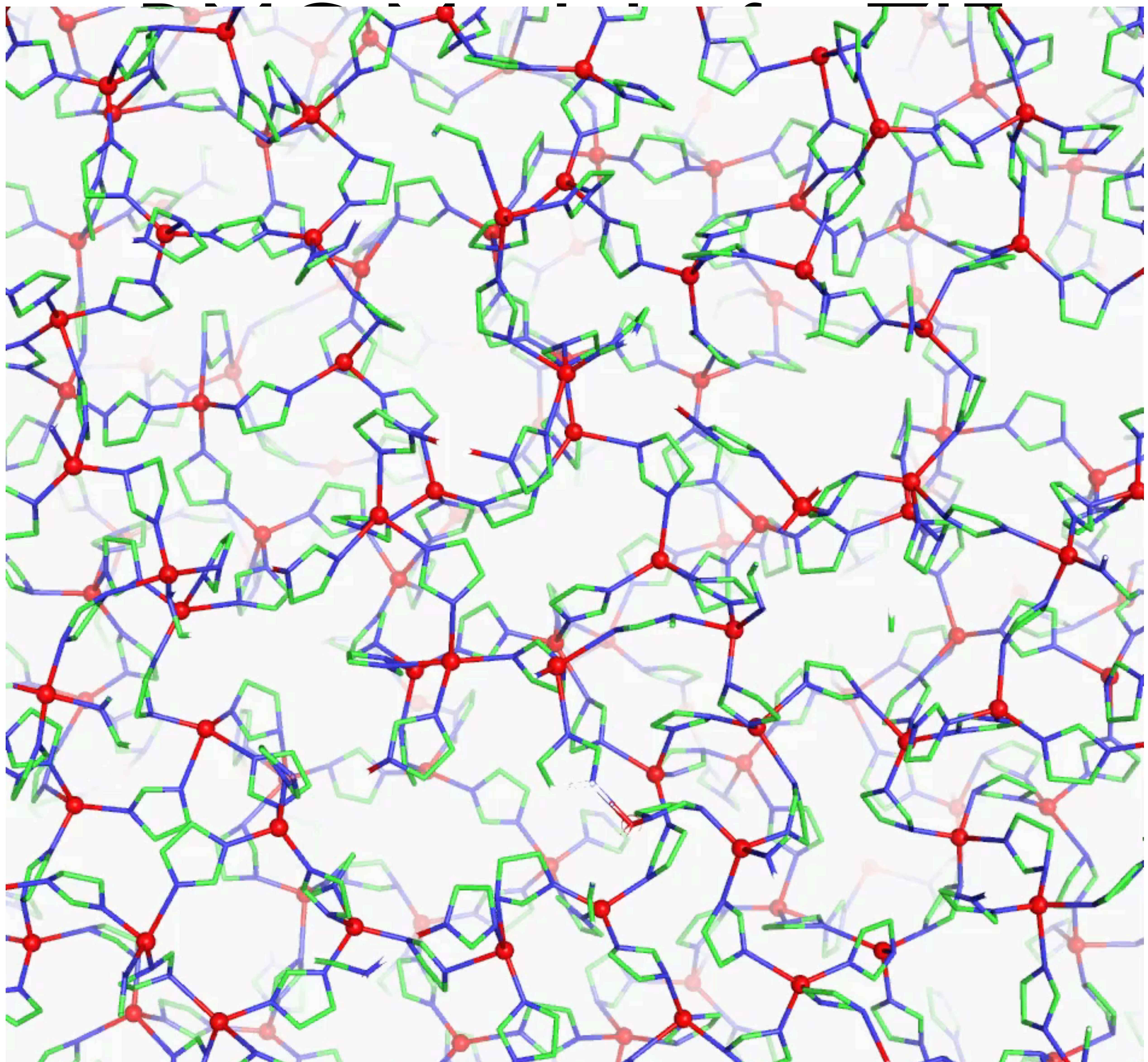


Conclusions

- There is a huge variety of interesting materials out there with correlated disorder (e.g.):

  Ices

  Thermoelectric PbTe

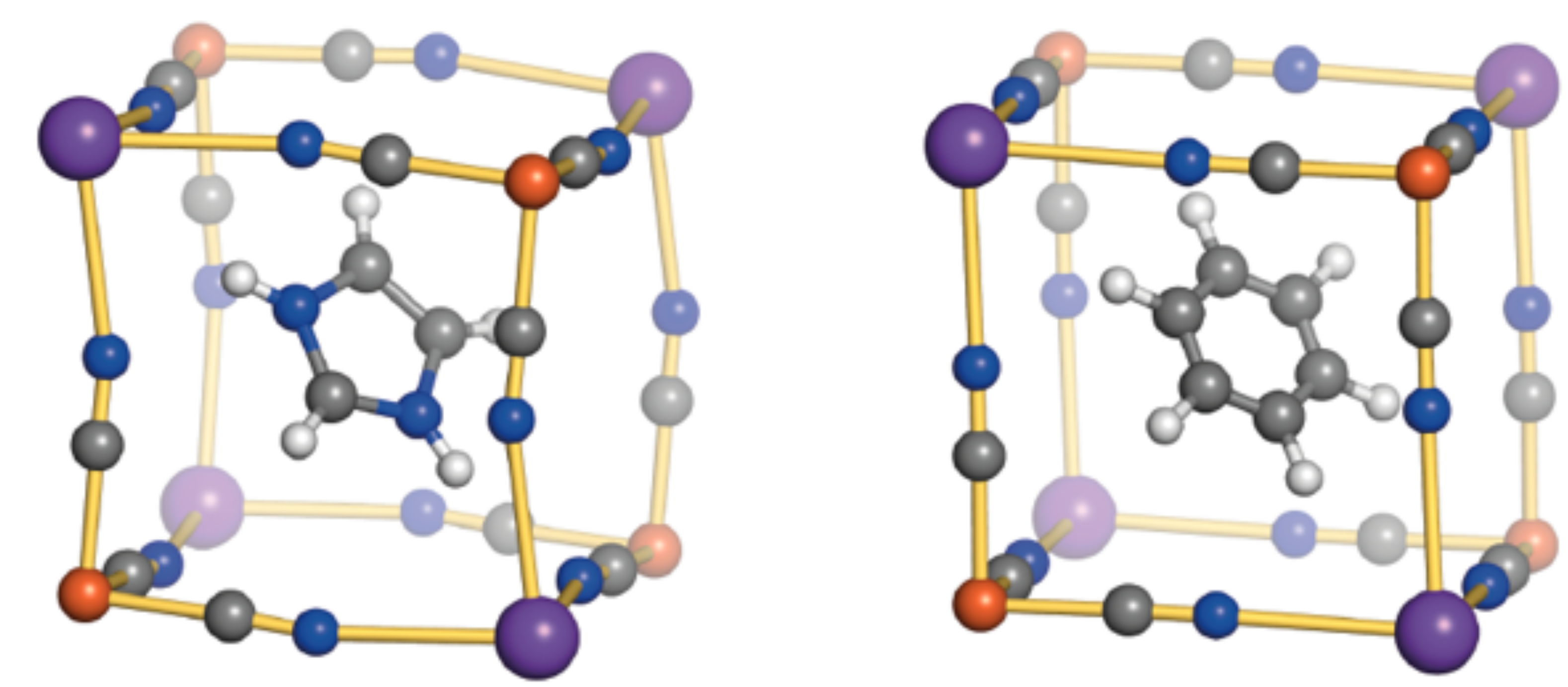
  Perovskite ferroelectrics BTO, PZT, NBT

  Disordered magnets

  C_{60}

  Molecular ferroelectrics

  ...even some proteins!



H_2im^+ in $KFe(CN)_6.H_2im$

- Careful analysis of total scattering (PDF) is an important tool for understanding their complexity and is increasingly key to determining how correlated disorder impacts on function (e.g. CMR, NTE, *amorphization*).

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Acknowledgements

D A Keen & A L Goodwin
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