Opportunities for Pair Distribution Function Measurements at XFELs

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The X-ray Pair Distribution Function

- The PDF is a weighted sum of all atom pairs within a material

$$G^X(r) = \sum_{i,j=1}^{n} c_i c_j \frac{K_i K_j}{\left(\sum_{i=1}^{n} c_i K_i\right)^2} [g_{ij}(r) - 1]$$

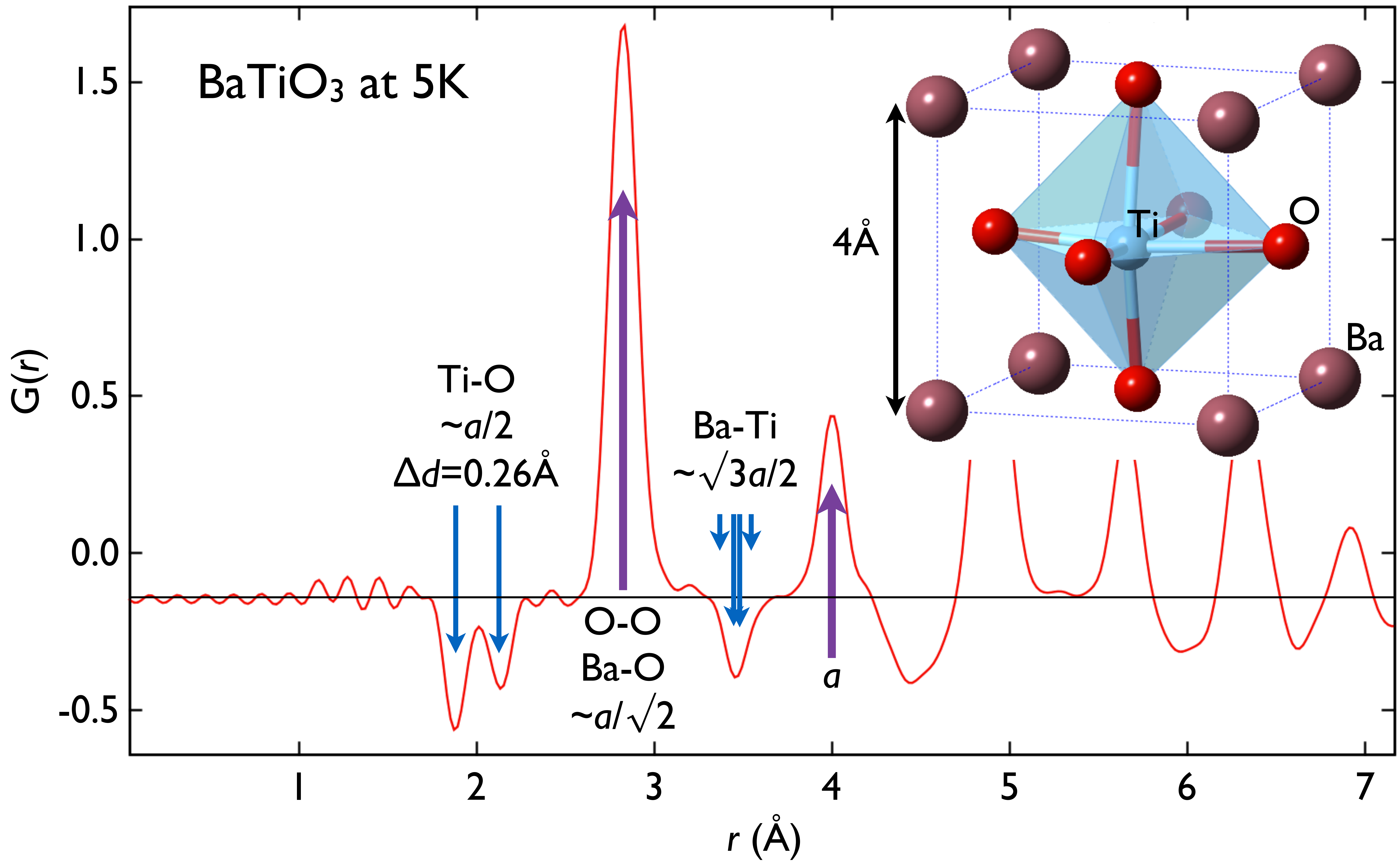
$$g_{ij}(r) = \frac{n_{ij}(r)}{4\pi r^2 \, \mathrm{d}r \, \rho_j}$$

- Obtained by Fourier transform of the total scattering structure factor

$$G^X(r) = \frac{1}{(2\pi)^3 \rho_0} \int_0^\infty 4\pi Q^2 F^X(Q) \frac{\sin Qr}{Qr} \, \mathrm{d}Q$$

- You can measure it–and calculate it–for any material in any state
- It is especially effective when local structure breaks away from the periodic structural description

An example: The (neutron) PDF from $BaTiO_3$

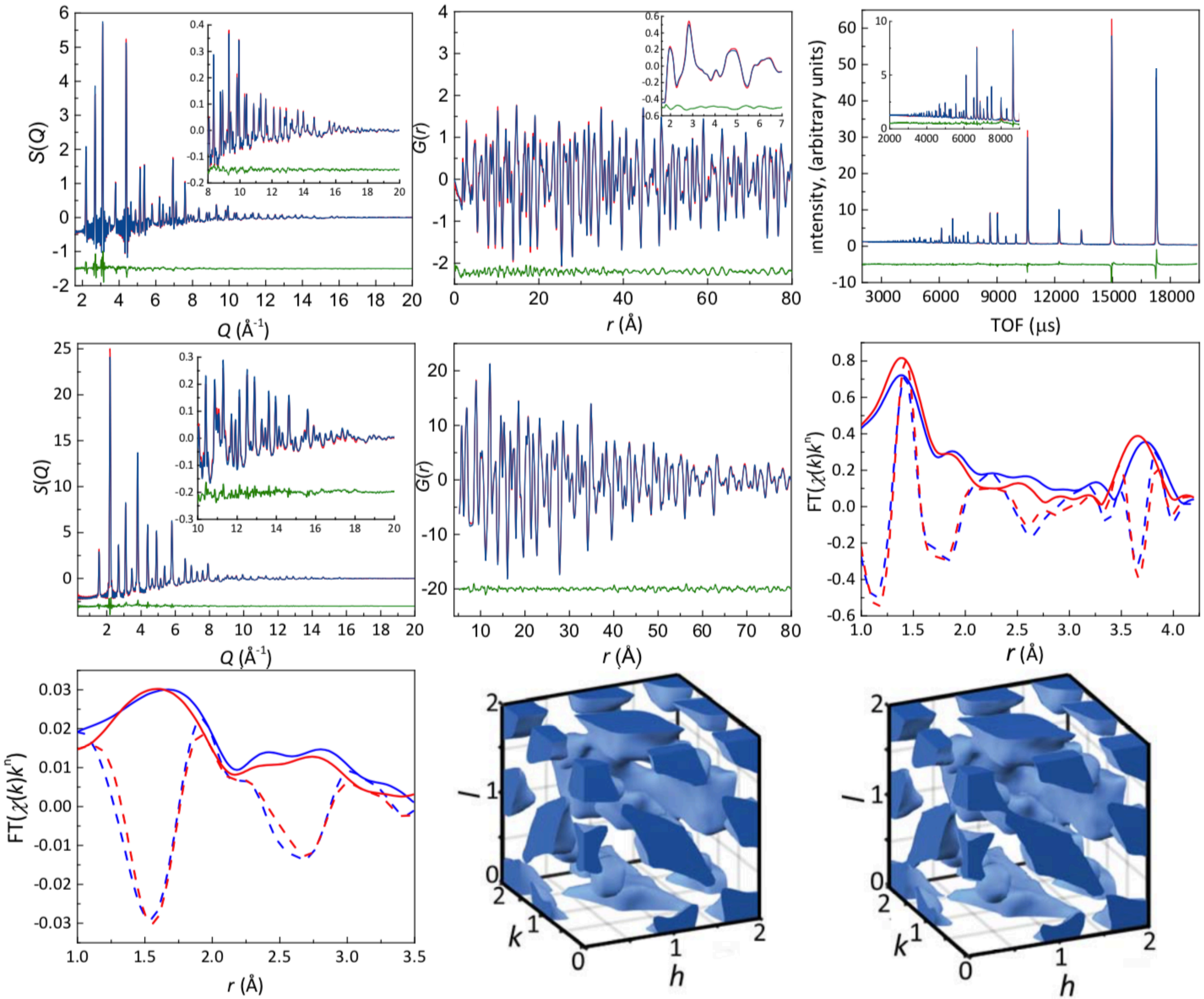


Fitting PDF etc. in analysis of polar nanoregions in PMN

Neutron
S(*Q*), PDF
and Bragg profile

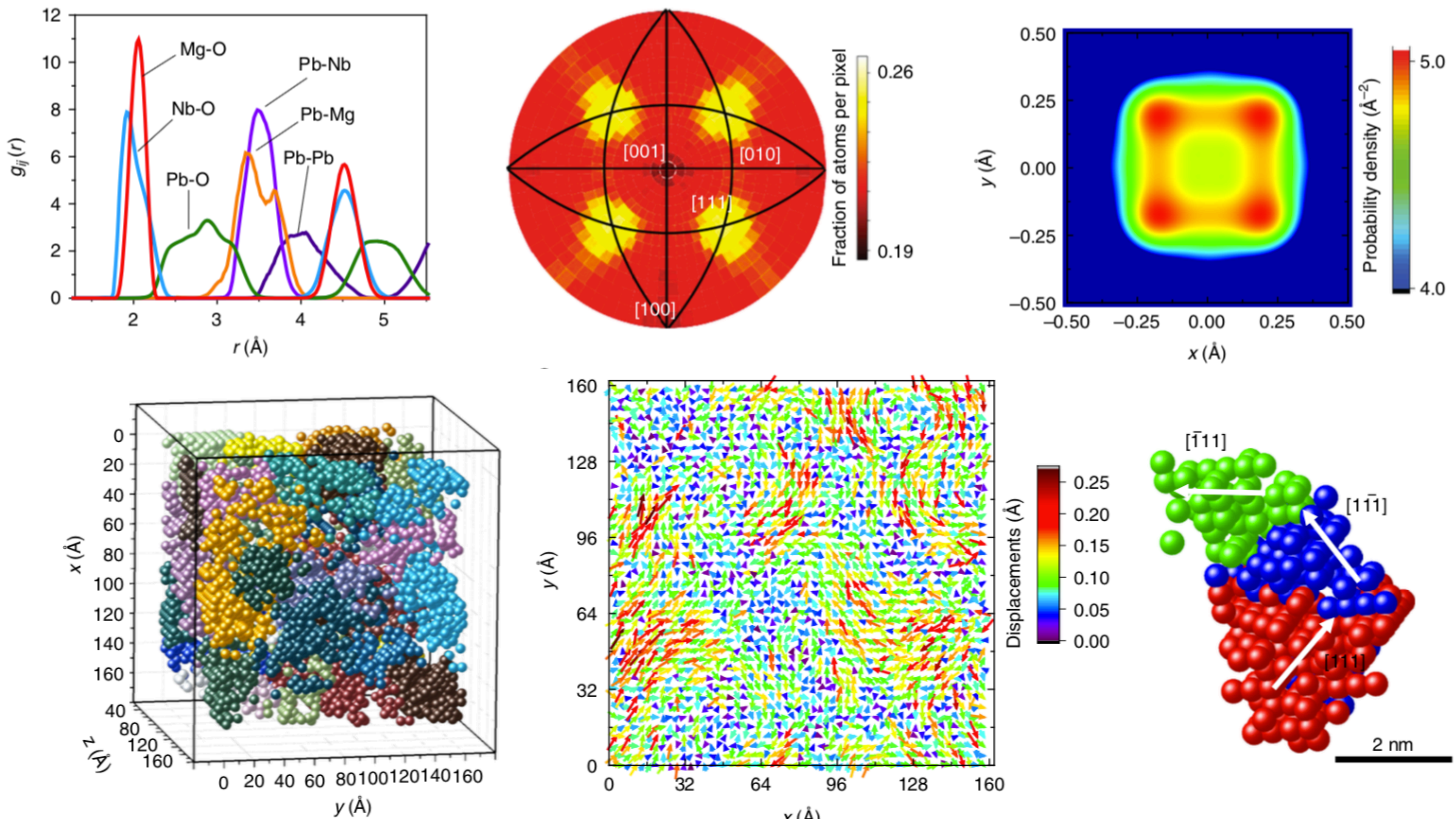
X-ray
S(*Q*), PDF
and Nb EXAFS

Pb EXAFS;
X-ray diffuse
scattering



M Eremenko *et al* *Nature Comm* **10** (2019) 2728

Polar nanoregions in $PbMg_{1/3}Nb_{2/3}O_3$ (PMN)



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Other examples?

- Amorphous materials
- Nanoparticles
- Battery materials (ionic conductors)
- Phase transitions
- (Multi-)ferroics
- Negative thermal expansion
- Gas absorption

PDF measurements on an XFEL?

- Optimising the Fourier transform of the total scattering structure factor

$$G^X(r) = \frac{1}{(2\pi)^3 \rho_0} \int_0^\infty 4\pi Q^2 F^X(Q) \frac{\sin Qr}{Qr} \, \mathrm{d}Q$$

- Where the total scattering structure factor is obtained from the normalised X-ray scattering

$$F^X(Q) = \left[\frac{1}{N} \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} - \sum_{i=1}^{n} c_i f_i(Q)^2 \right] \Big/ \left[\sum_{i=1}^{n} c_i f_i(Q) \right]^2$$

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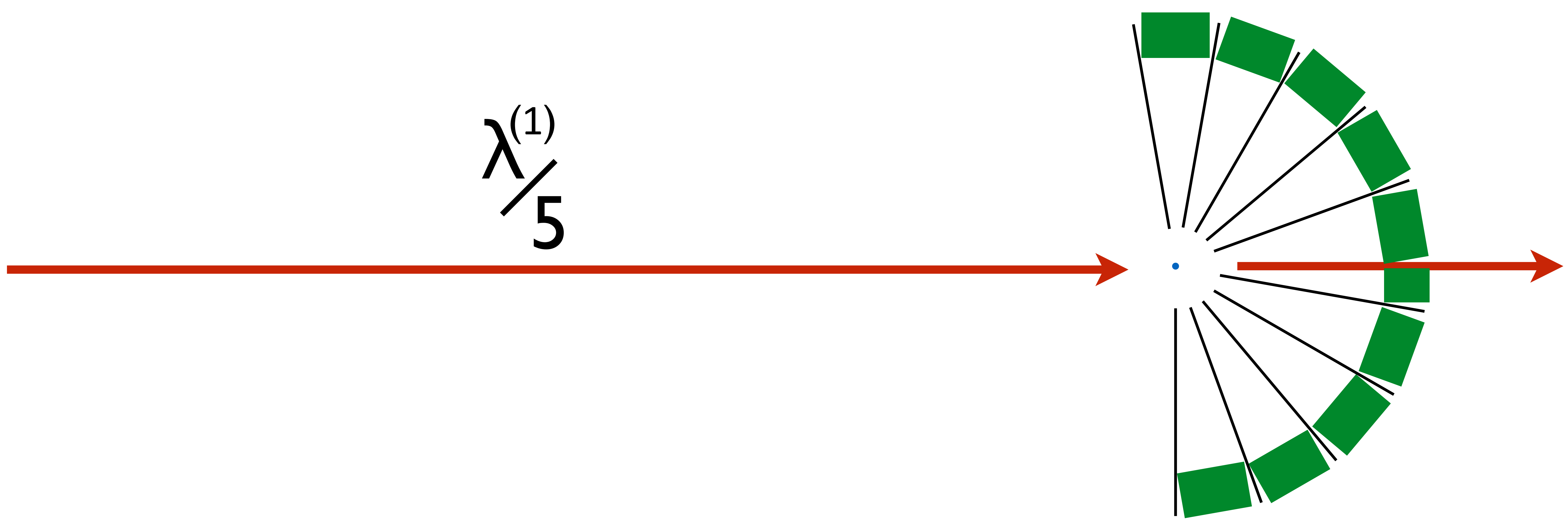
Requirements for an XFEL PDF instrument…

- Hard X-rays - use of higher (3^{rd} or even 5^{th}) harmonics.
- Wide detector coverage
- Stability

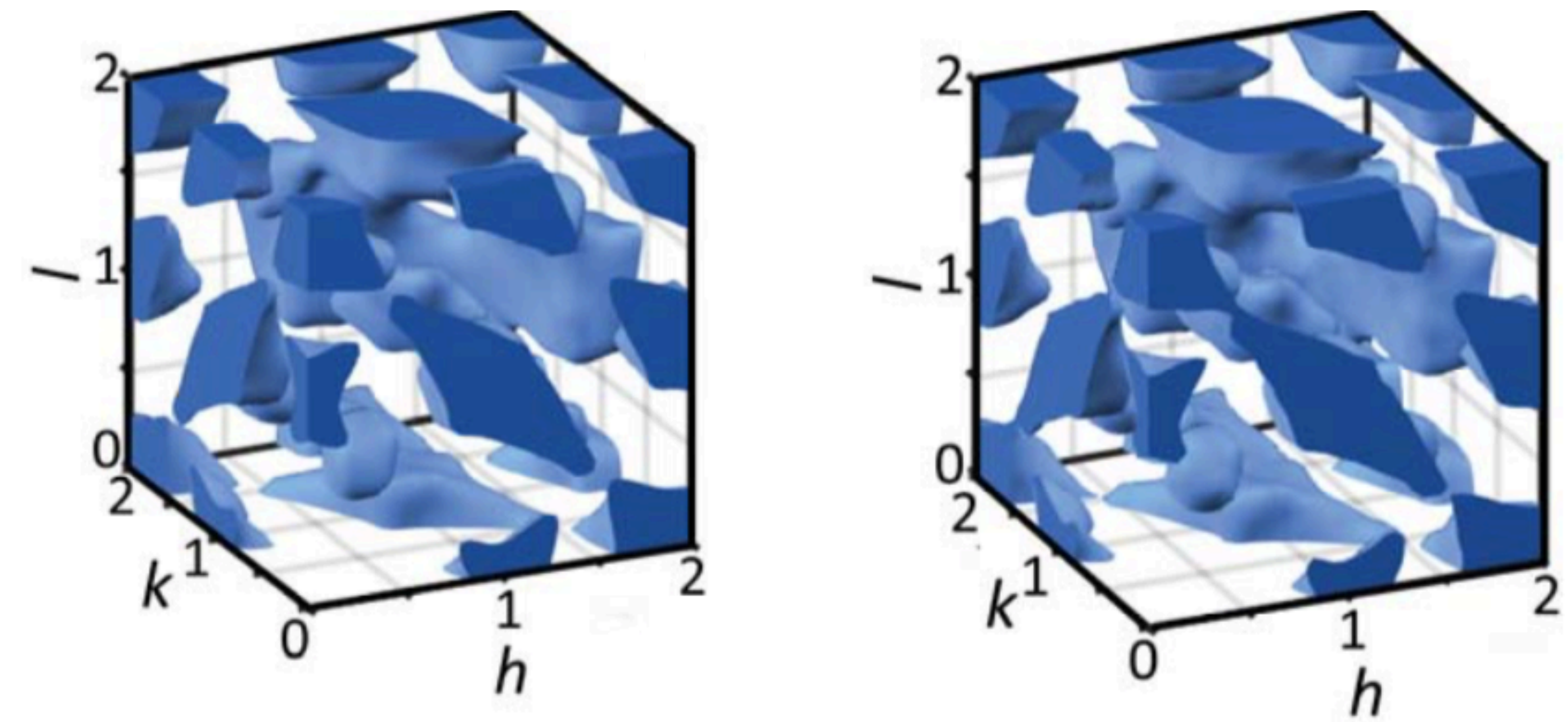


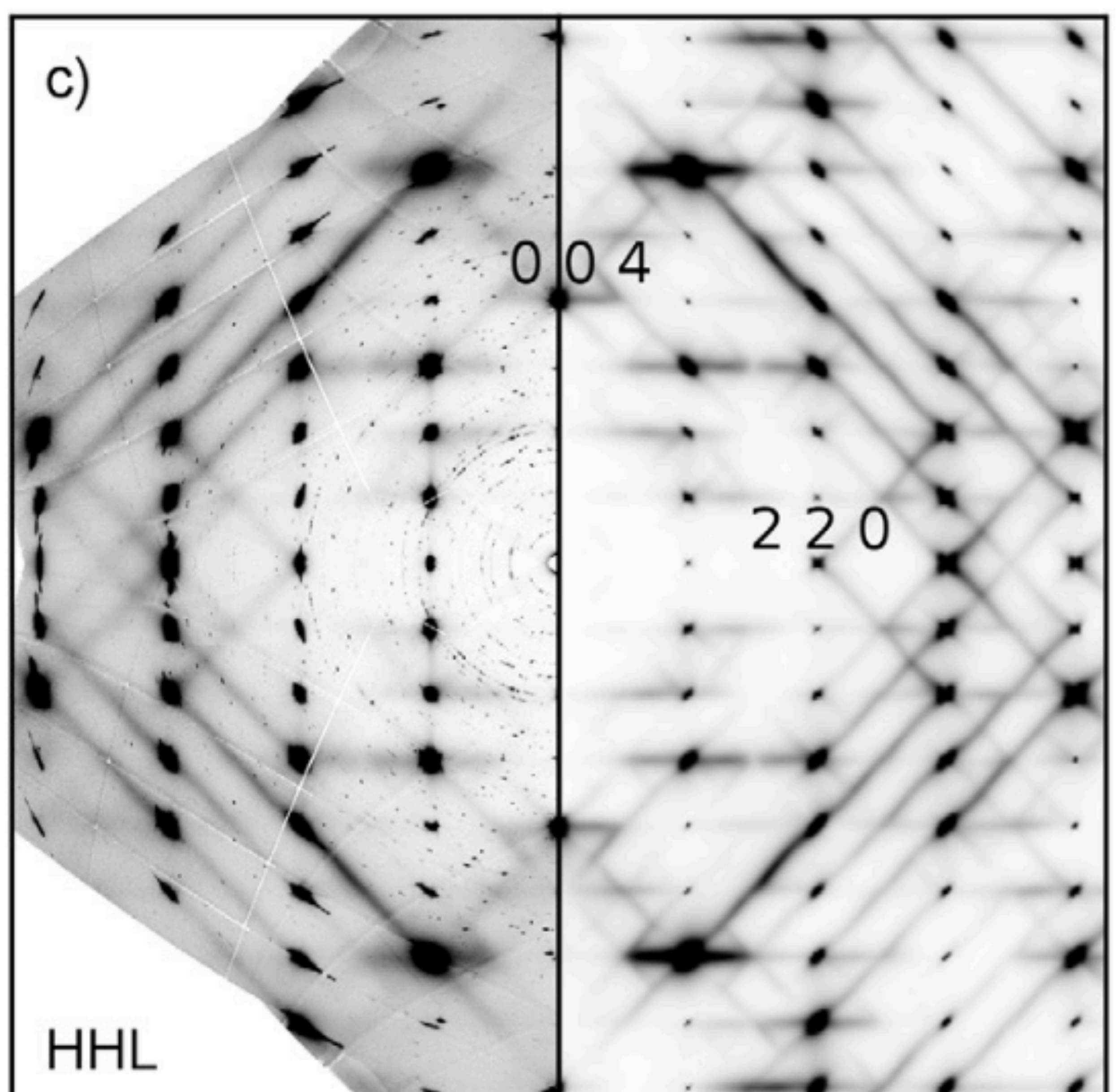
What PDF experiments might we envisage?

- Amorphous materials
- Nanoparticles
- Battery materials (ionic conductors)
- Phase transitions
- (Multi-)ferroics
- Negative thermal expansion
- Gas absorption

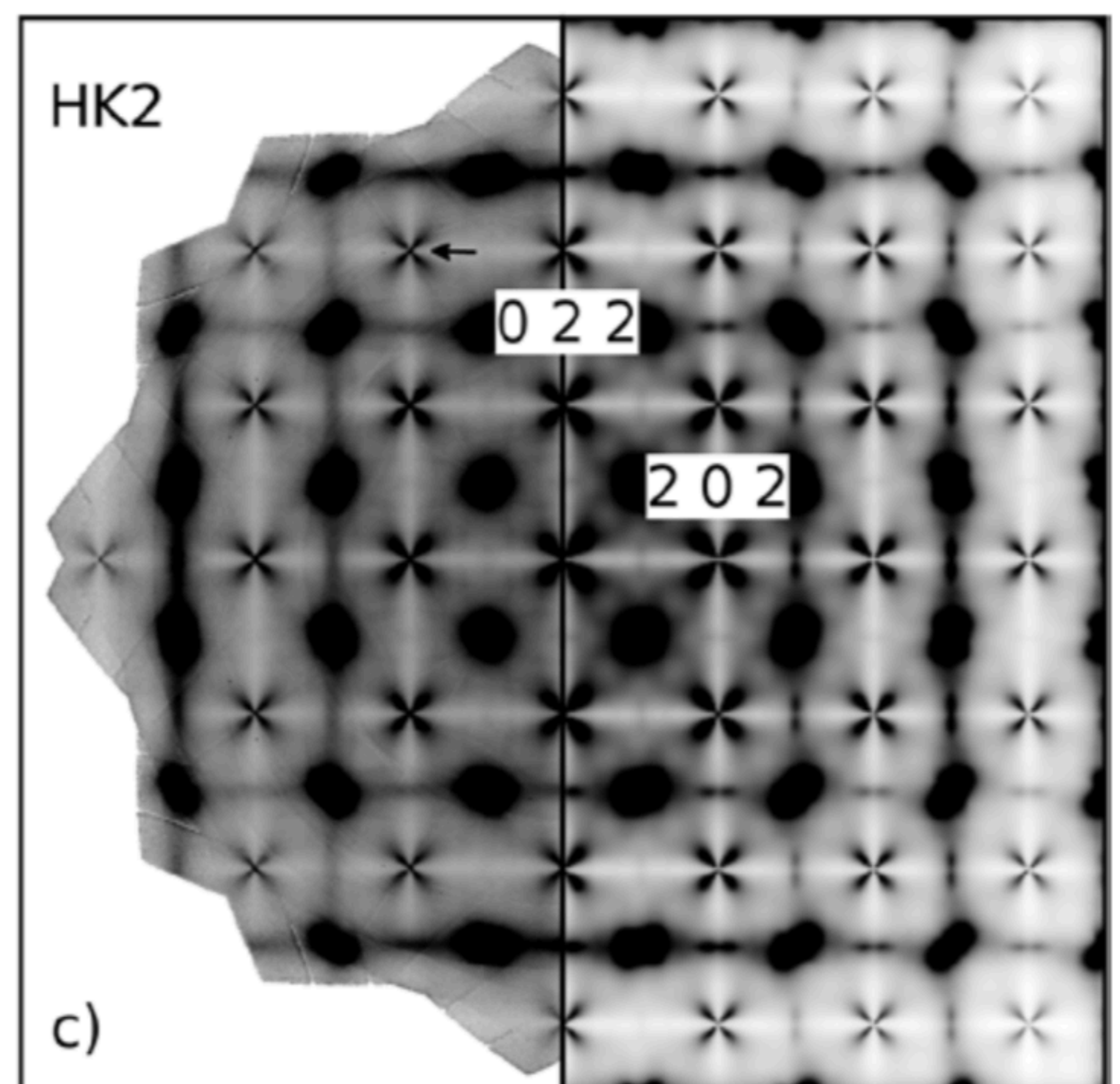
→ Any experiment where the local structure changes 'quickly' in response to external 'stimuli'

P.S. Single crystal diffuse scattering?

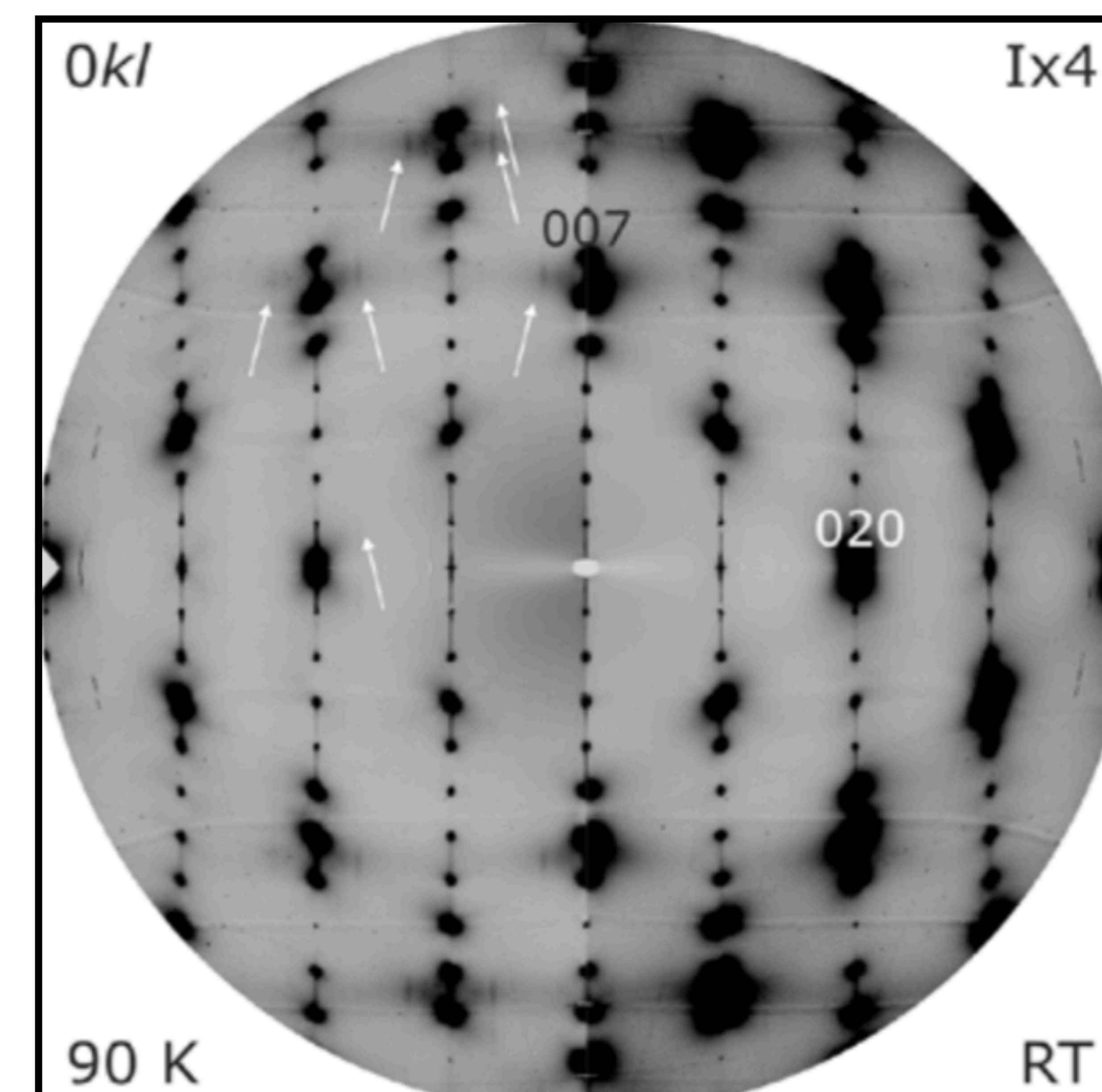




TDS in α-cristobalite



TDS in β-tin



CDW superstructure peaks in $YBa_2Cu_3O_{6.6}$

A Bosak *et al* (2015) *J. Phys. D* **48** 504003