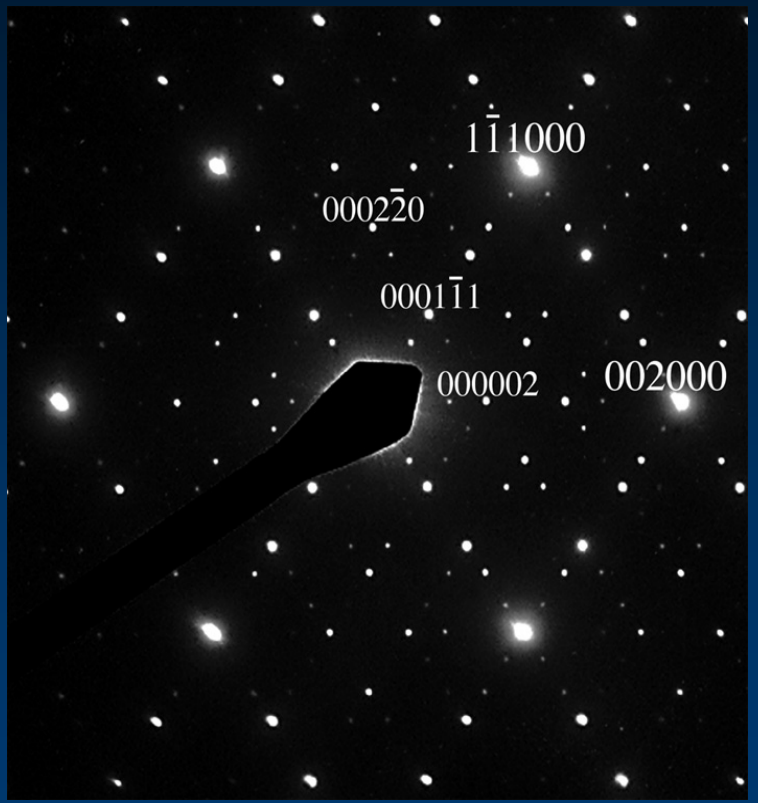
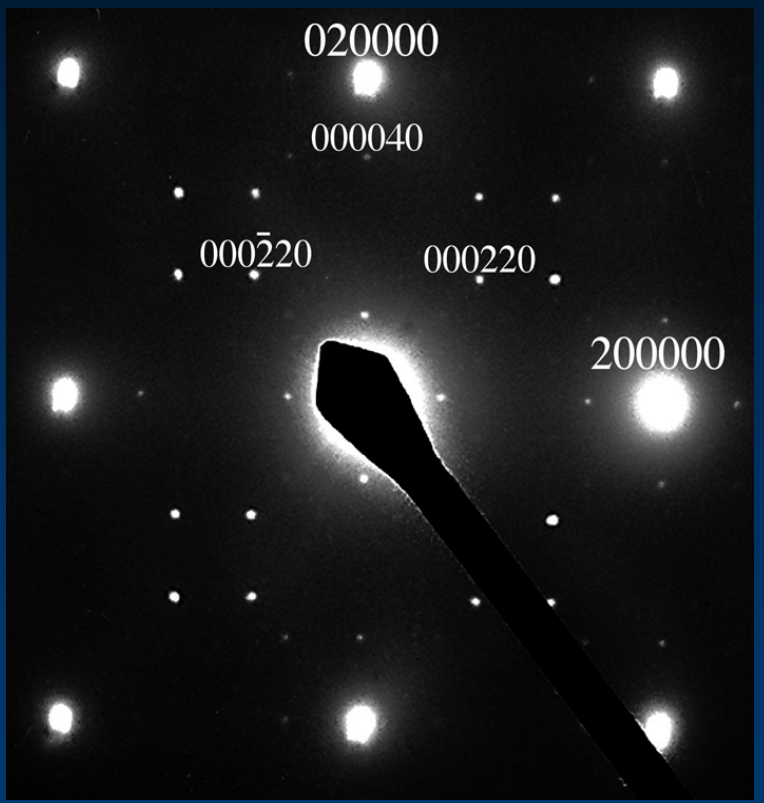
Courtesy of Ray Withers

Electron Diffraction and the Structural Characterization of Modulated and Aperiodic Structures

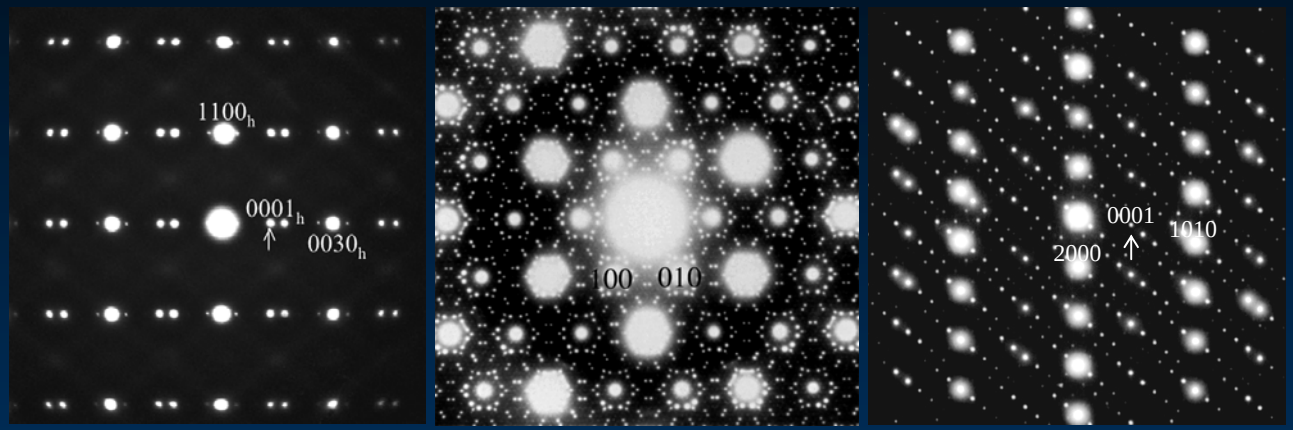
What do we mean by a ‘modulated’ structure?

The standard answer is a material whose reciprocal space exhibits sharp Bragg reflections in more than 3-d

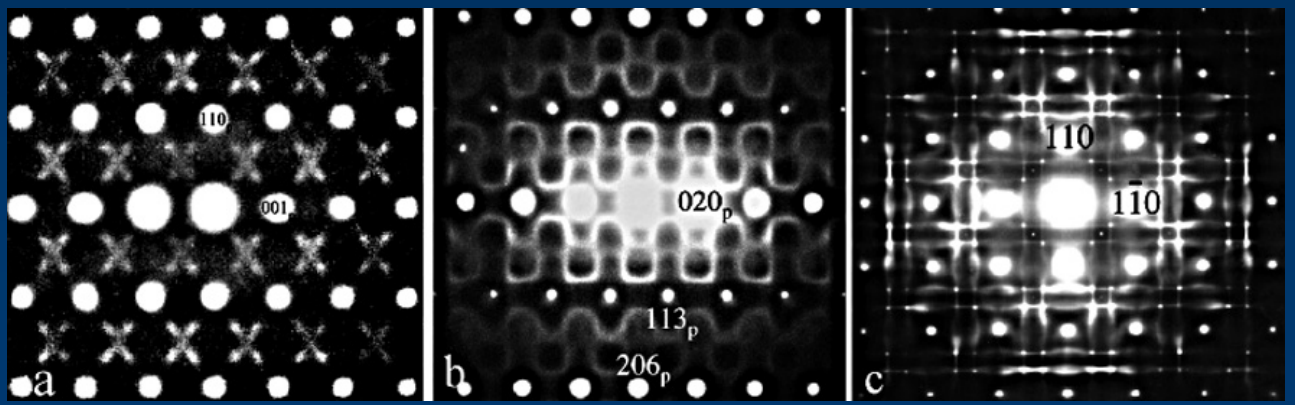




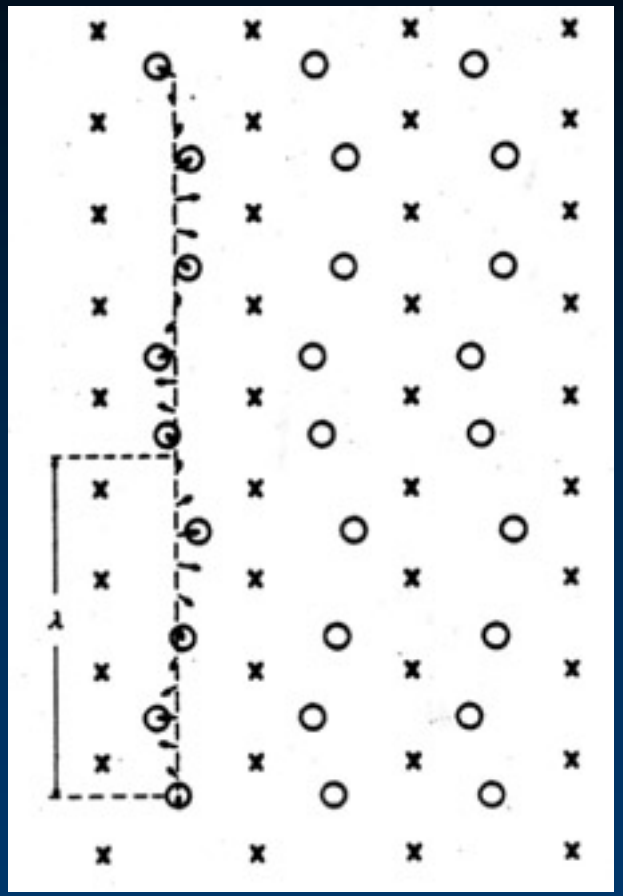
Why is the TEM a good place to investigate modulated structures?



very sensitive to weak subtle features of reciprocal space, whether the modulations are long or ‘short’ range ordered!



In ‘real’ space?



An average structure plus a modulation
e.g. a displacive modulation

$\mathbf{u}_\mu(\mathbf{r}_\mu+\mathbf{t}) = \mathbf{e}_\mu(\mathbf{q}) \exp 2\pi i\mathbf{q}.(\mathbf{r}_\mu+\mathbf{t})$

with $\mathbf{e}_\mu(\mathbf{q}) = \mathbf{e}_\mu(-\mathbf{q})^*$

And/or we could have a compositional modulation
i.e. a periodic variation in the composition or occupancy of a particular site in our average structure

$\delta \boldsymbol{f}_\mu(\mathbf{r}_\mu+\mathbf{t}) = a_\mu(\mathbf{q}) \exp 2\pi i\mathbf{q}.(\mathbf{r}_\mu+\mathbf{t})$

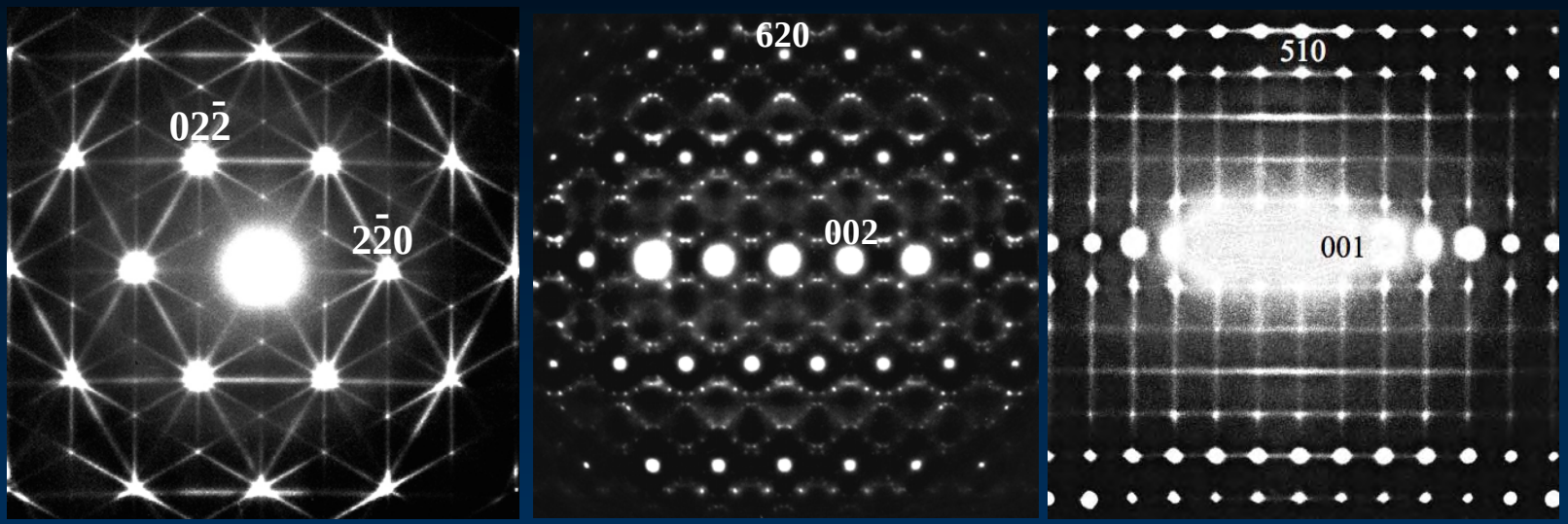
Both will give rise to additional satellite reflections
At $\mathbf{G} \pm m\mathbf{q}$, m an integer, in general

The differences between the average or parent structure and the modulated structure for each atom are given by finite, periodic functions of the dot product of the modulation wave-vector q with the position of this atom in the parent structure *I.e.* with $\mathbf{q}.(\mathbf{r}_\mu+\mathbf{t})$.

These functions are known as Atomic Modulation Functions or AMF’s. Knowledge of these (as well as the average structure) is equivalent to refinement in the case of modulated structures.

Why restrict ourselves to only one modulation wave-vector *I.e.* to sharp Bragg reflections, albeit in (3+n)-d?

Are materials like these also not 'modulated' in a very real sense!?

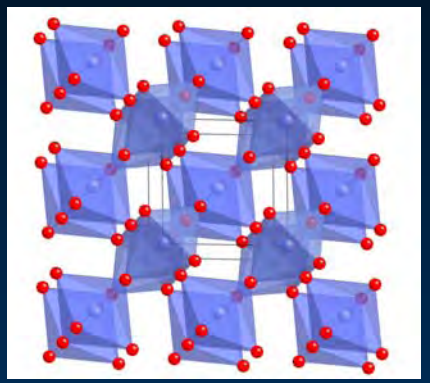


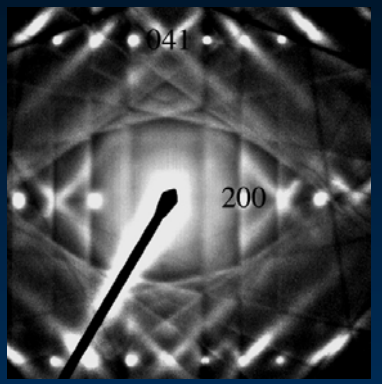
… There is a virtual continuum from conventional 3-d structures through (3+n)-d incommensurately modulated structures to materials that exhibit sharp, highly structured diffuse intensity distributions to virtually completely disordered (random) structures ..?

.. We learn much more about the balance of competing interactions/free energy terms giving rise to complex "crystalline" structure in the broadest sense from taking into account all scattering and not just the average structure Bragg reflections .. !?

Example

FeOF - a ‘simple’ case study of order in ‘disorder’
Spectroscopically fully ordered but 3-d crystallographically disordered!



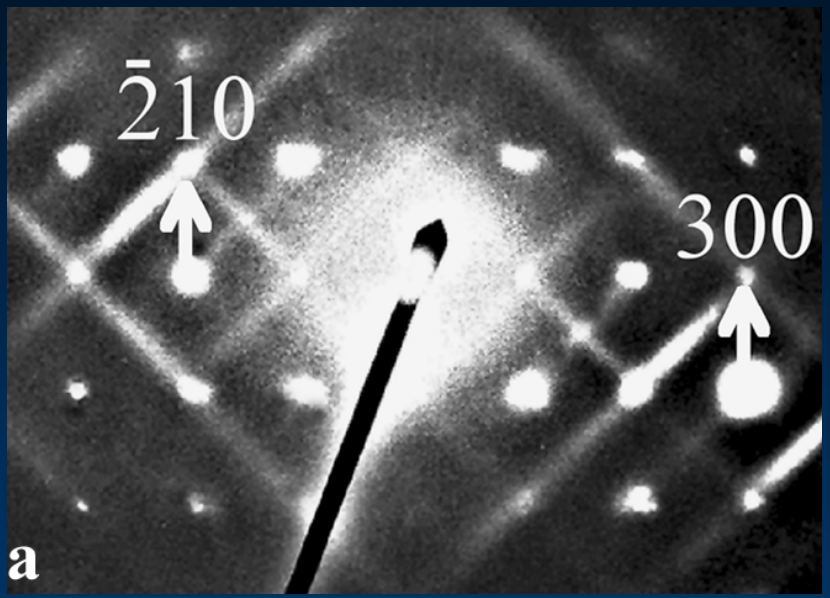


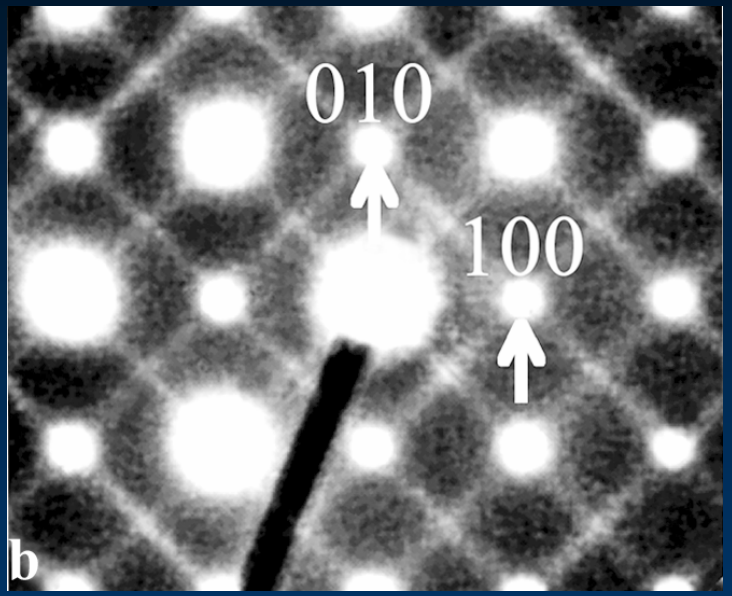
Structure factors and characteristic diffraction signatures (extinction conditions, polarization ..) applied to FeOF and $CaCu_3Ti_4O_{12}$

The various types of modulated structure and the advantages of electron diffraction when seeking to structurally characterize them.

Warning! Watch out for multiple scattering

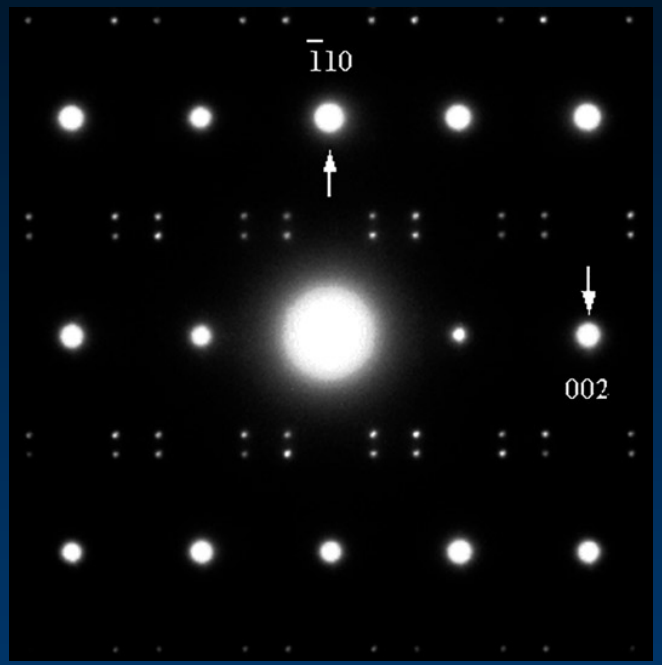
if you're an electron microscopist and looking for characteristic extinction conditions in diffuse distributions

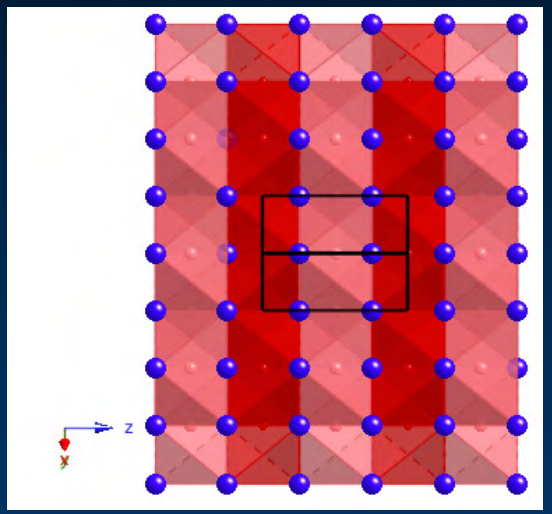


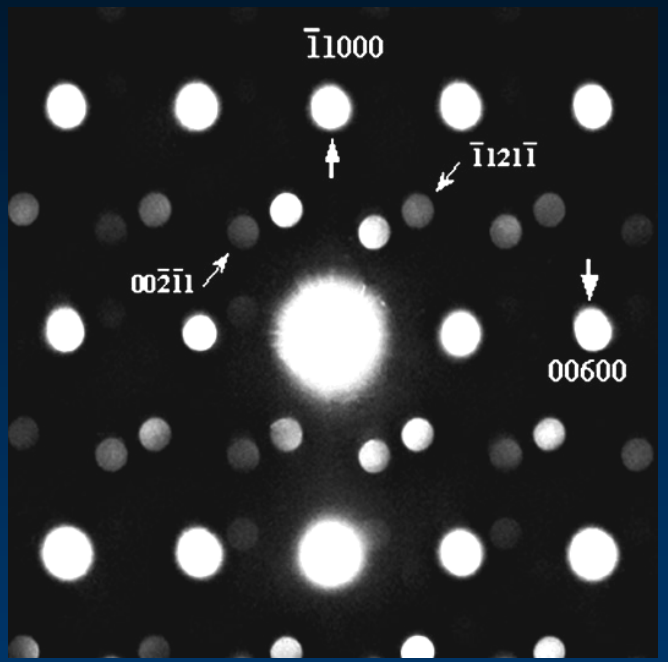


sometimes it pays to be off-axis!

If microstructure is too fine scale for conventional electron diffraction, can use micro-diffraction *e.g* $Co_{2-x}Se_2$, 0.06 < x < 0.25, a (3+2)-d incommensurately modulated structure of *P*-3*m*1, $Cd(OH)_2$, average structure type.





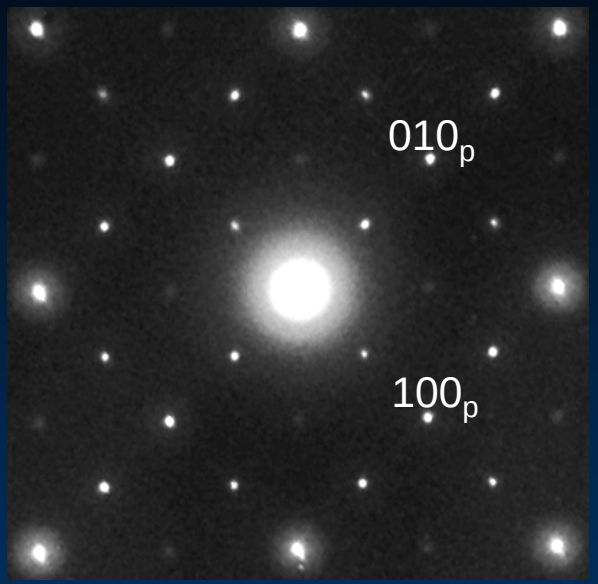


Looks like there is a mirror plane perpendicular to **c*** in the spot pattern

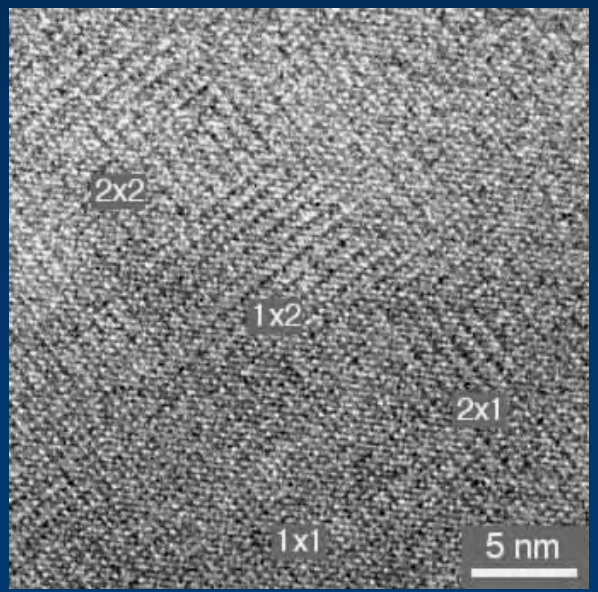
but ..

.. not in the equivalent micro-diffraction pattern. The original EDP is twinned!

If finer scale still .. can use imaging *e.g* $(Ba_{1-x}La_x)_2In_2O_{5+x}$, x = 0.2

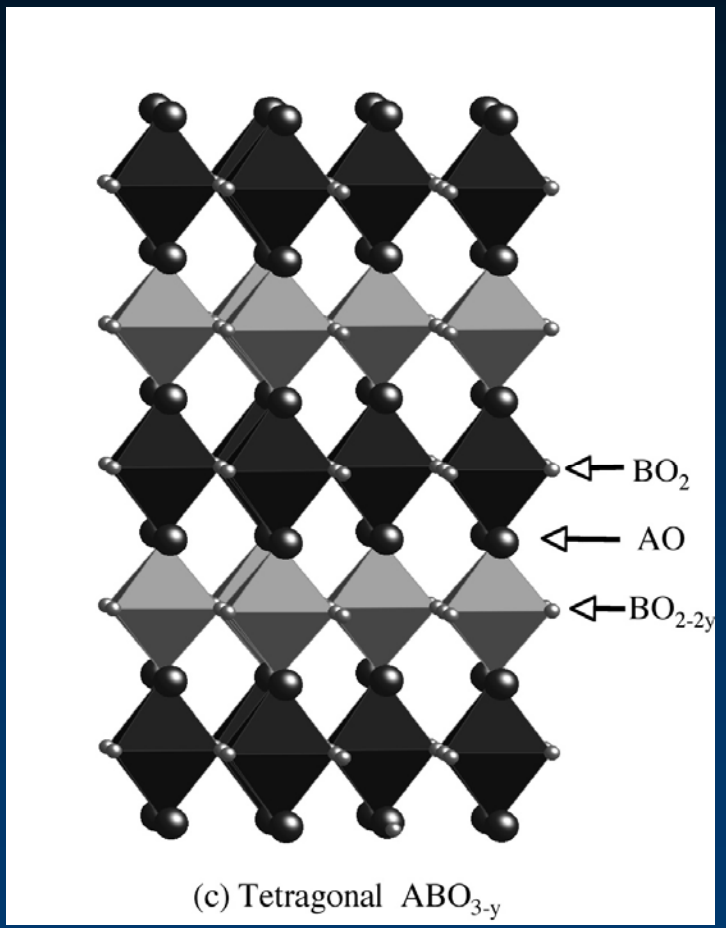


1x1x2
2x2x1
or
2x2x2?

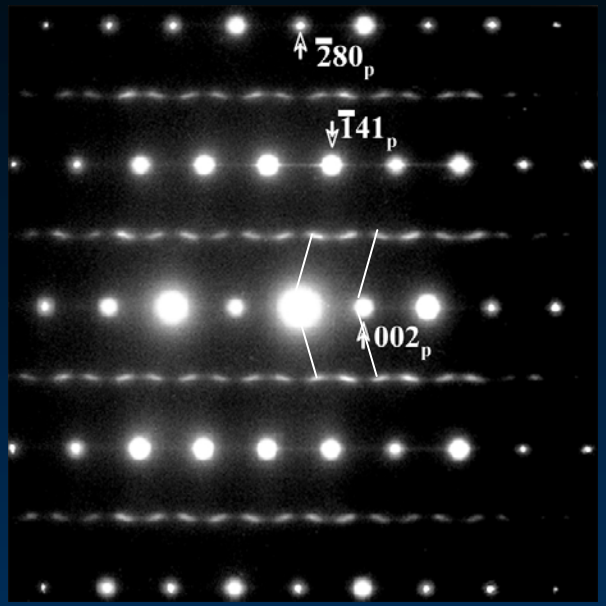


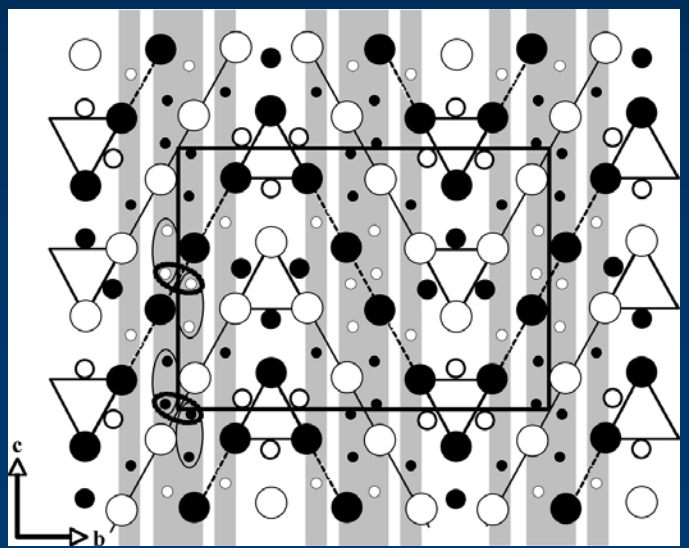
Imaging
strongly suggests
1x1x2?

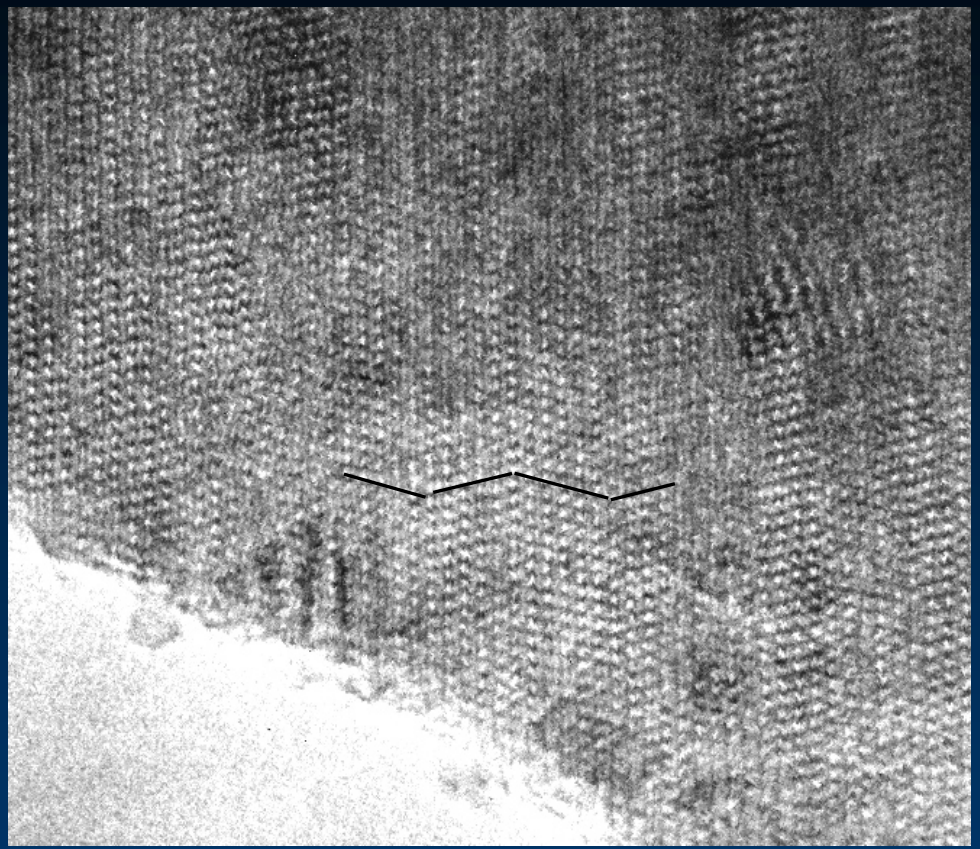
a disordered Brownmillerite



$Ni_6Se_{5-x}Te_x$, x ~ 0.5, *Bmmb* parent structure



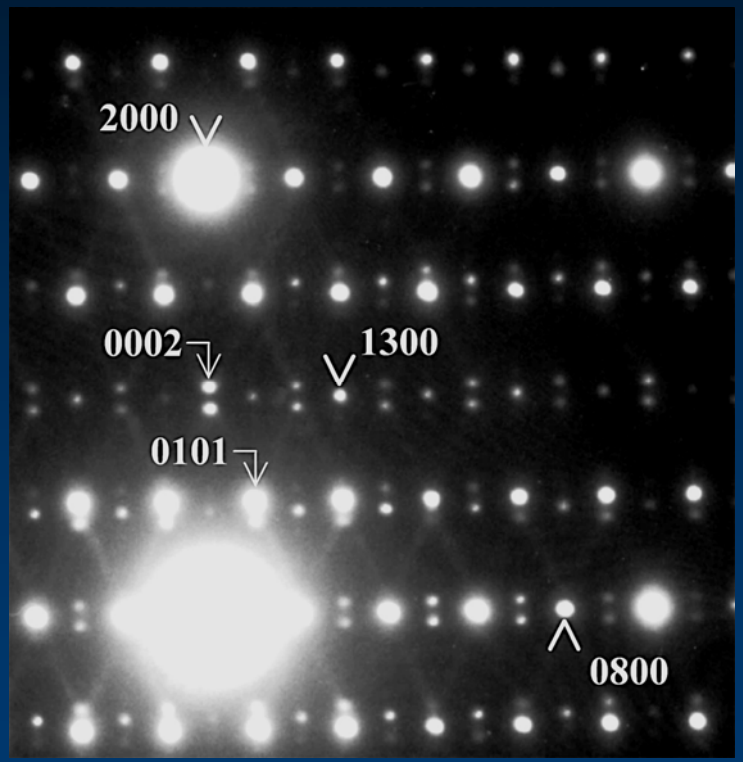


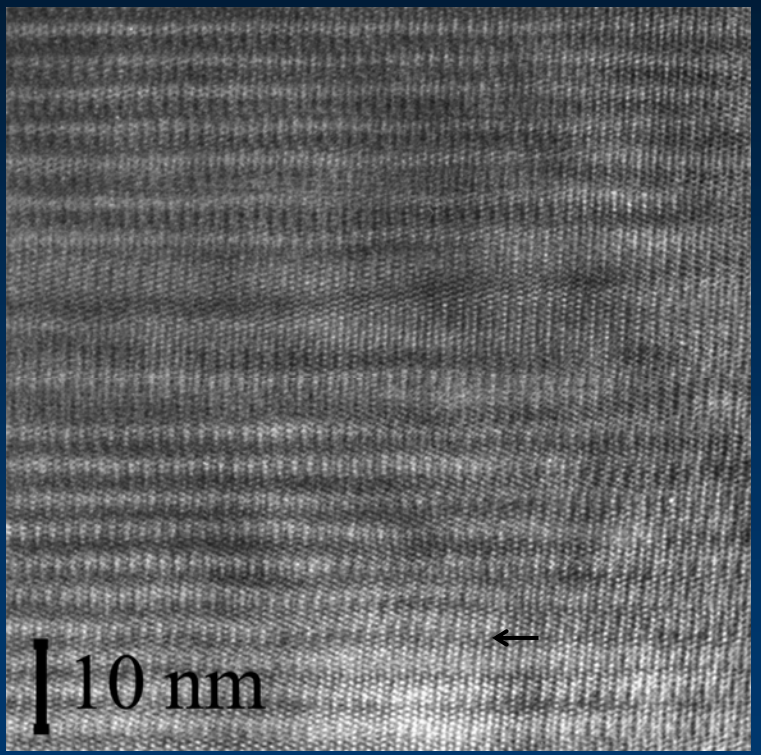


Ordering of partially occupied Ni sites gives rise to a **q** ~ $^1/_2[-101]_p^*$ (or $^1/_2[101]_p^*$) modulation which is twinned perpendicular to **c*** on quite a fine scale

Interface modulated structures

For complete ordering on the local scale in real space, compositional AMF's must of necessity take an infinitely sharp (crenel type) form in superspace which implies many higher order harmonics or .. disorder .. (phason fluctuations!) *i.e* variability of the spacing between the boundaries in real space.

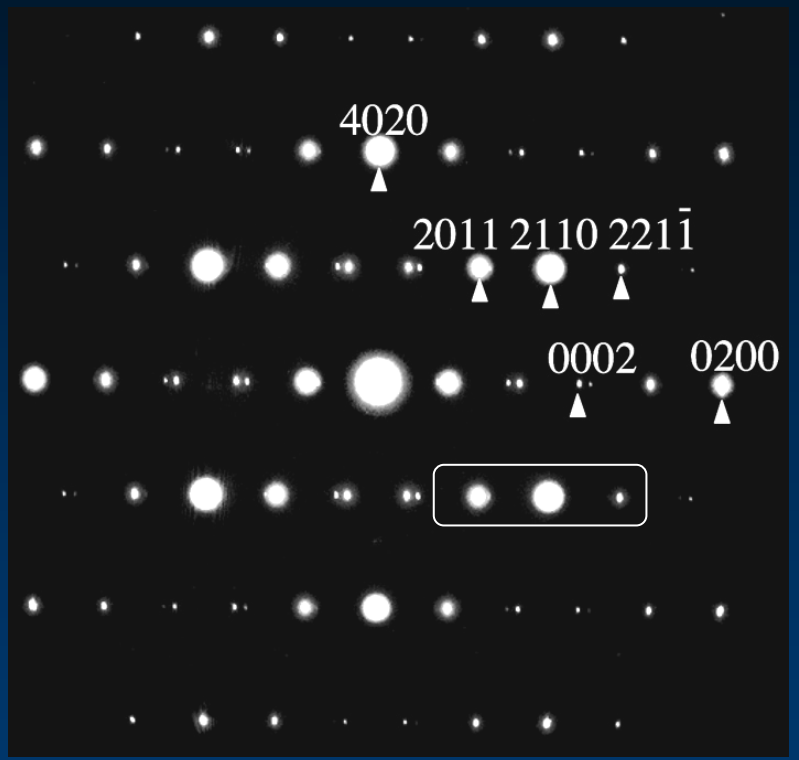


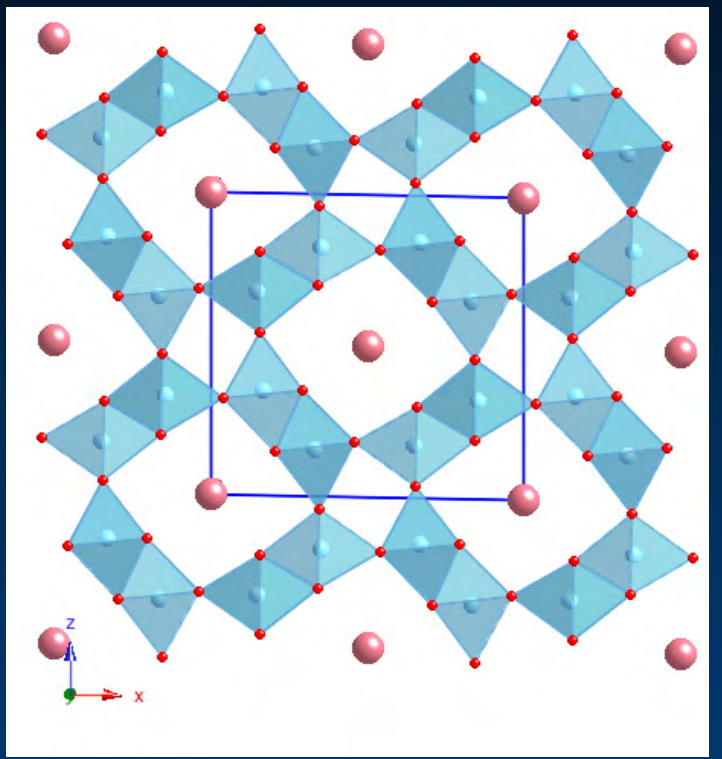


e.g. incommensurately modulated $Ni_{6-x}Se_5$

Composite modulated structures

At first glance EDP's looks like conventional modulated structure EDP's but … composite modulated structures exhibit characteristic intensity asymmetries. Why? Two or more intergrown mutually incommensurable sub-structures.



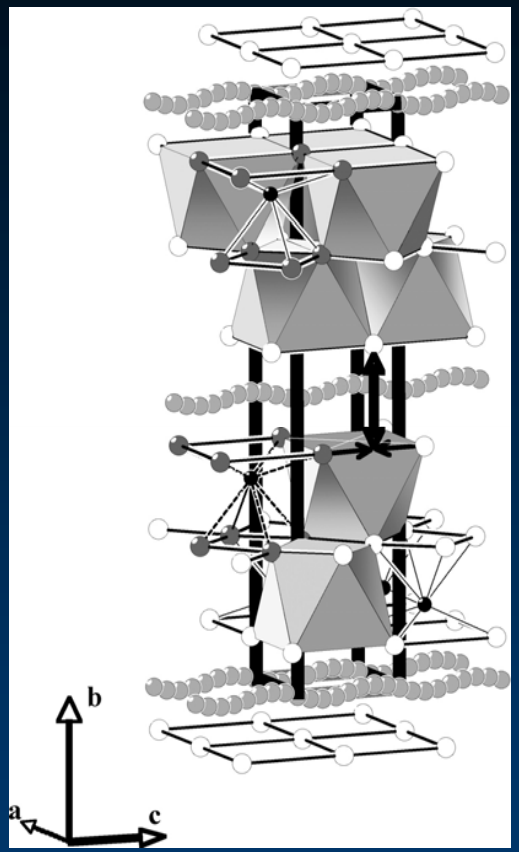


e.g $Ba_xM_yTi_{8-y}O_{16}$, *M* = Zn, Co, Mg, Fe and Mn, ~1.0 < x < ~ 1.4, hollandites.

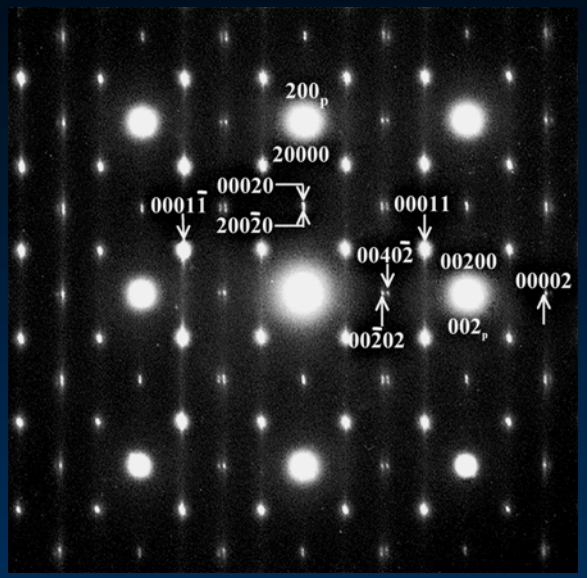
Mutually intergrown *I*2/*m* framework and Ba sub-structures with $\mathbf{b}_{Ba} = {}^{2}/_{x}\ \mathbf{b}_f$, $\mathbf{b}_{Ba}^* = {}^{x}/_{2}\ \mathbf{b}_f^*$ and *I'*2/*m* (0,x/2,0)1, $\mathbf{b}_{Ba}^* = {}^{x}/_{2}\ \mathbf{b}_f^*$.

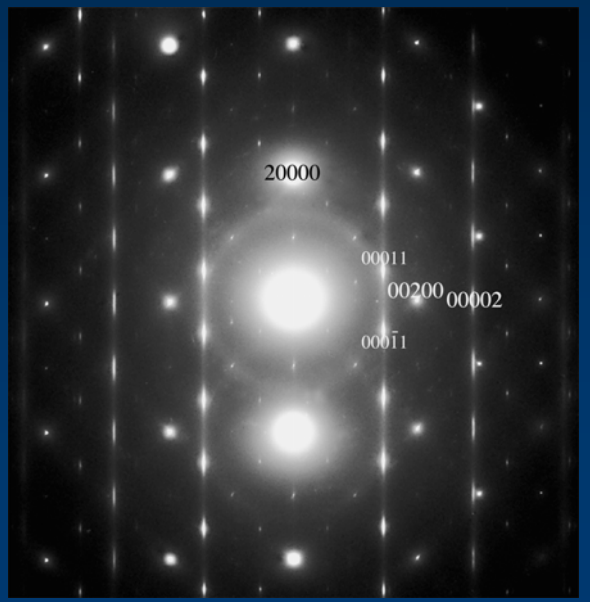
2110 = 211 of the framework sub-structure, 2011 = 211 of the Ba sub-structure *etc.*

Where are the Sn atoms in $LaSb_2Sn_x$, $0.1 \leq x \leq 0.75$?



Well-defined *Cmcm* average structure for the $LaSb_2$ (L) sub-structure but where are the Sn (S) atoms?

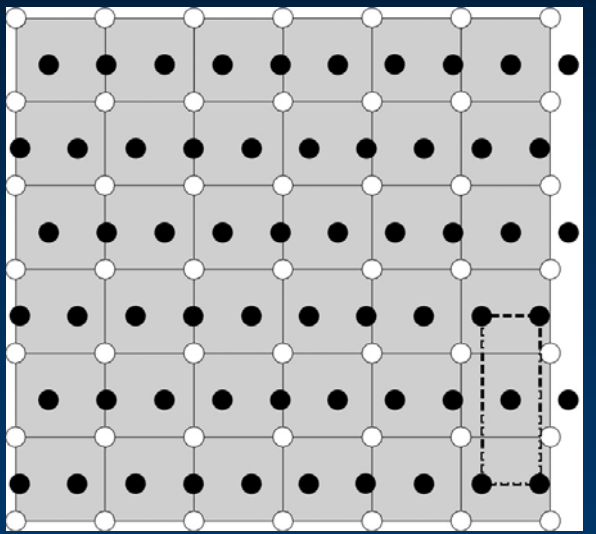


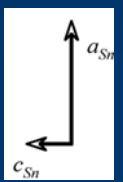


$M^* = \{\mathbf{a}_L^*, \mathbf{b}_L^*, c_L^*, \mathbf{a}_S^*, c_S^* \sim {}^3/_2\, c_L^*\}$

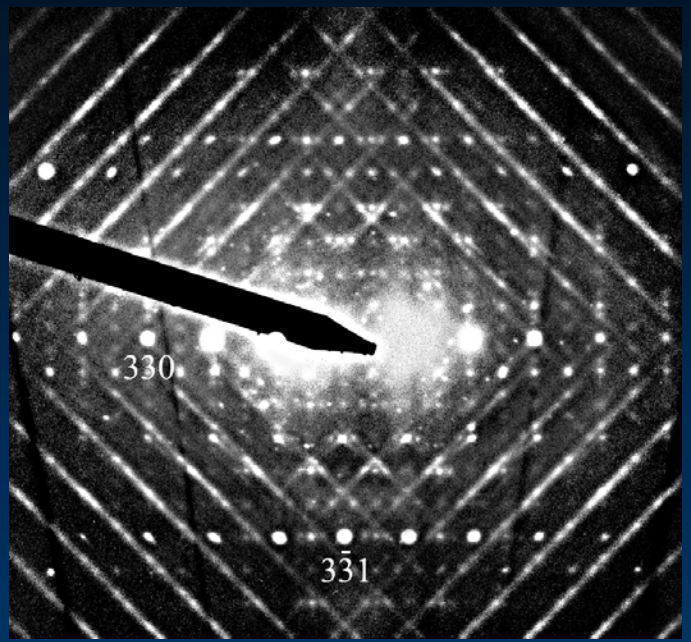
$0K0MN^*$ *reflns.* correspond to MKN^* reflections of the Sn sub-structure.

Implies *B*-centred Sn sub-structure with $c_S \sim {}^2/_3\, c_L$



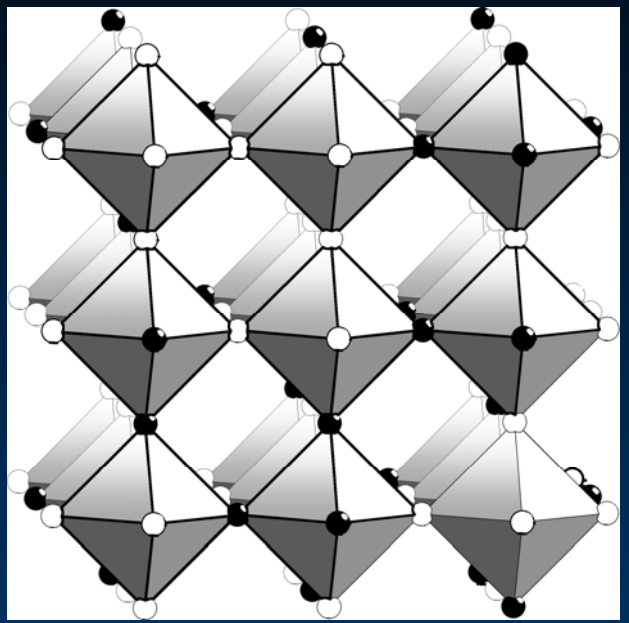


Displacively modulated structures induced by compositional ordering



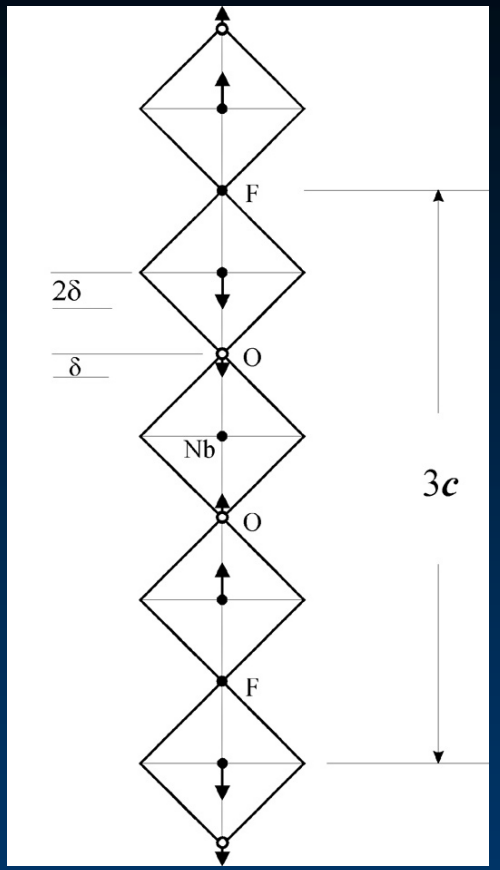
Strong azimuthal intensity variation is characteristic of a displacive modulation.

$F_{\mu}(\mathbf{G}\pm\mathbf{q}) \sim 2\pi(\mathbf{G}\pm\mathbf{q}).\mathbf{e}_{\mu}(\mathbf{q})$



NbO_2F of ReO_3 average structure type. 1-d O/F ordering along <001> strings.

Gives rise to transverse polarized $\mathbf{G}\pm\langle hk^1/_3\rangle^*$ sheets of diffuse and diffuse streaking along all $\langle h0l\rangle^*$ directions of reciprocal space.

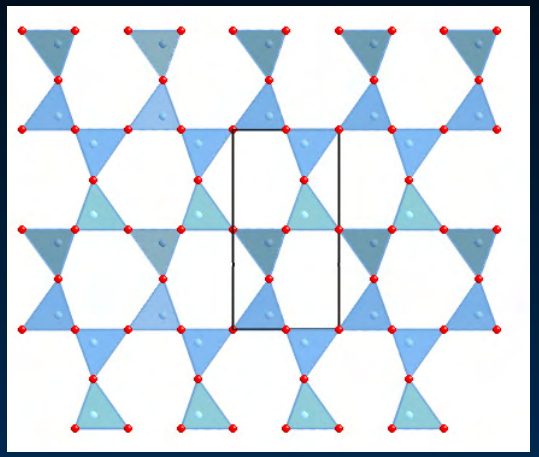


Just because the scattering is dominated by displacive effects doesn't mean there isn't an underlying compositional origin!

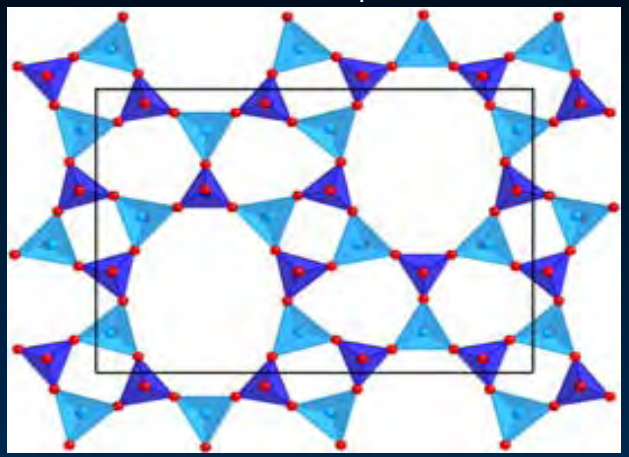
Pure displacively flexible framework structures

e.g silicas, perovskites, zeolites, fresnoites *etc.*

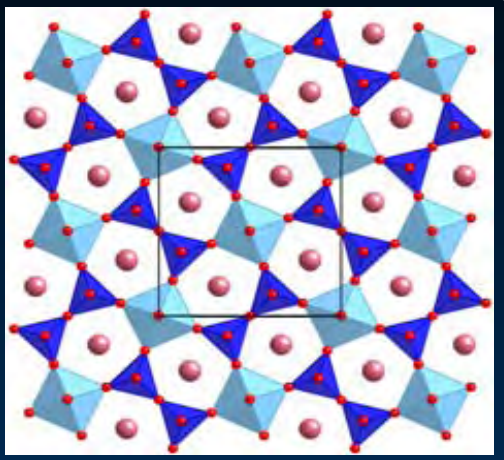
SiO_2-tridymite



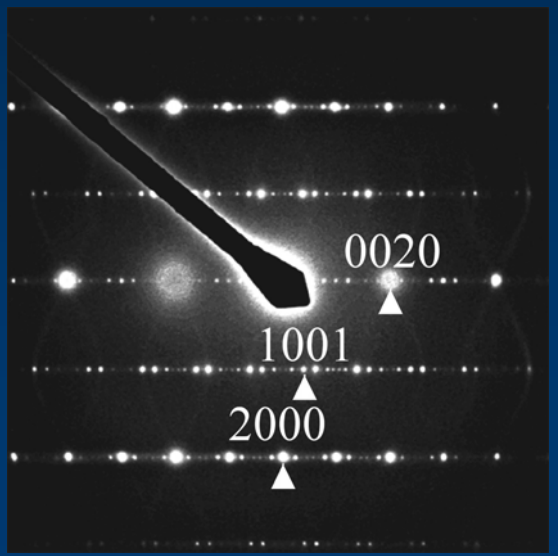
$AlPO_4$-11

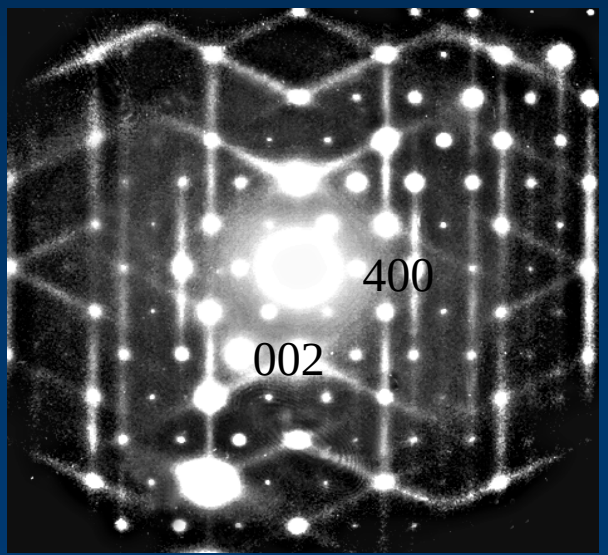


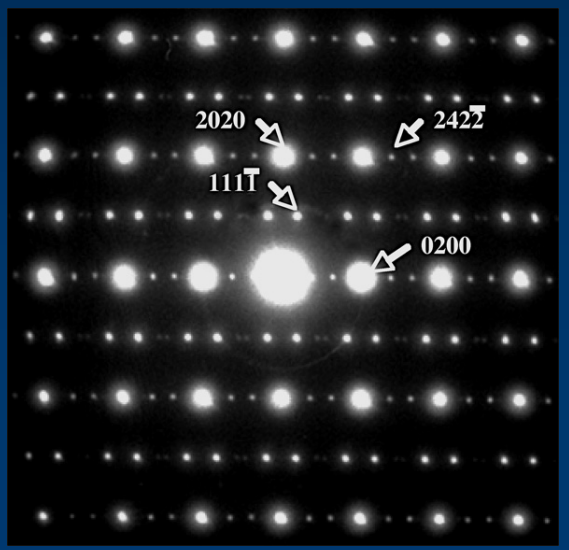
Fresnoite *e.g* $Ba_2TiGe_2O_8$



Polyhedra are rigid but their relative orientation is not - often gives rise to incommensurately modulated structures at lower temperatures arising from condensed RUM modes of distortion.

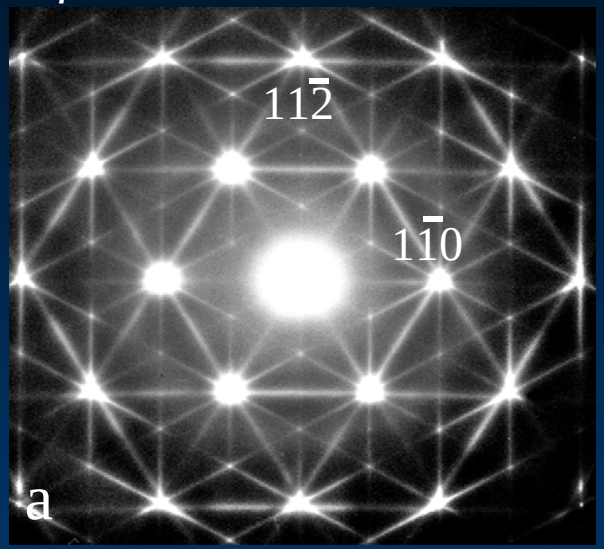




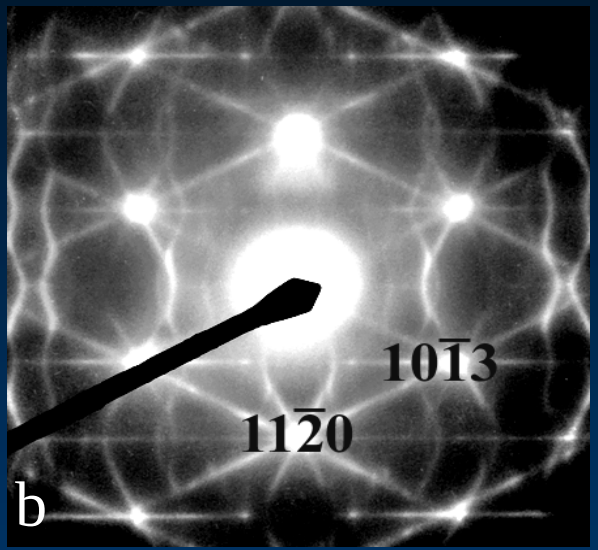


Evidence for inherent orientational flexibility at higher temperatures

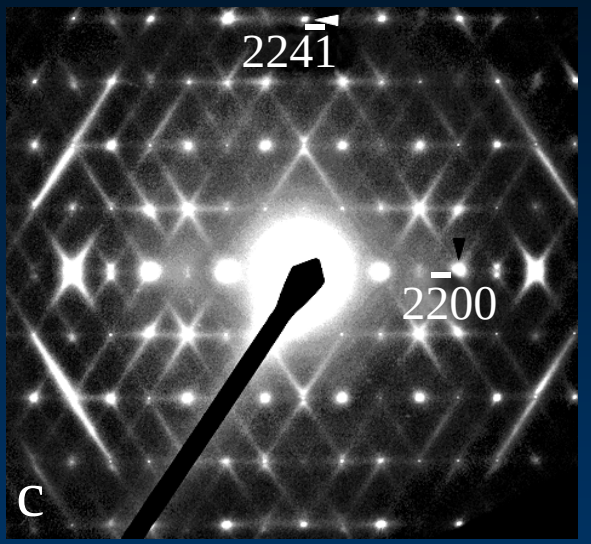
β-Cristobalite >270°C



Tridymite >250°C



β-Hexacelsian >310°C

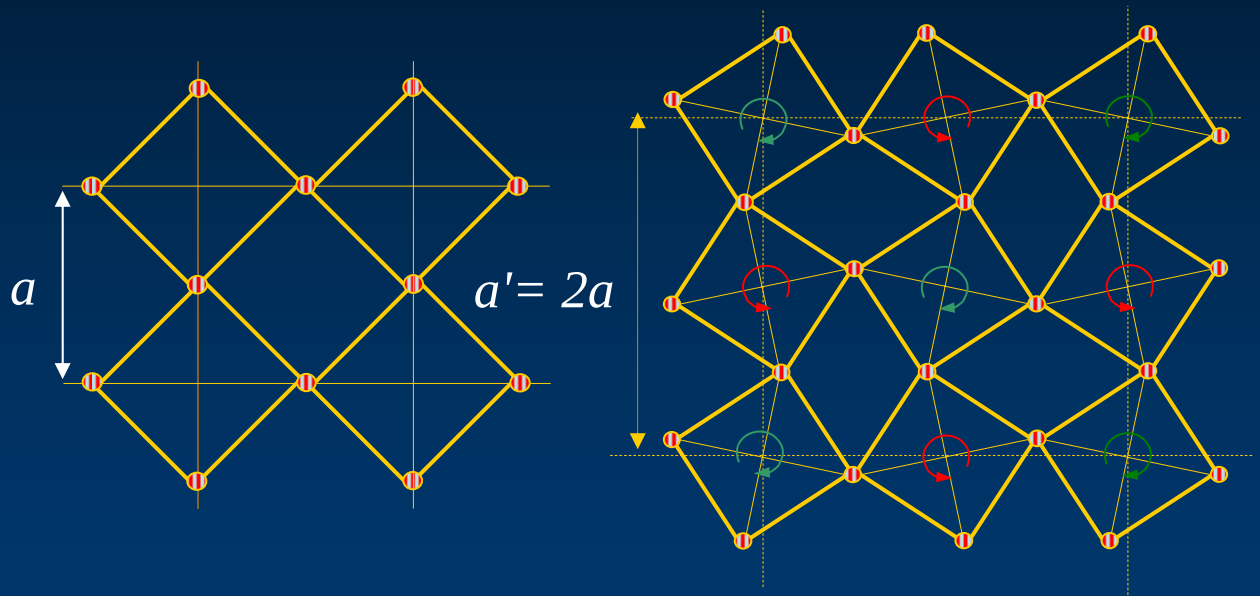


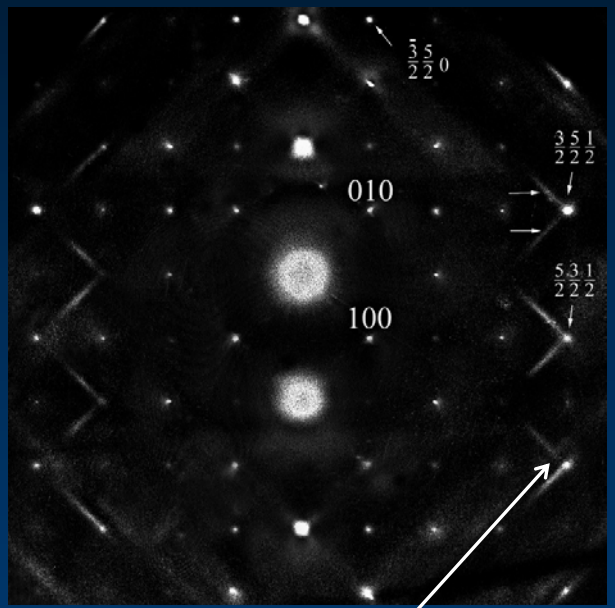
These sharp, continuous diffuse intensity distributions map out the zero energy cost, or ‘zero frequency’, Rigid Unit Mode (RUM) phonon modes of distortion of these various inherently flexible framework structures.

Real space origin.

Rigid Unit Mode (RUM) modes of distortion?

Co-operative ‘zero frequency’ modes of distortion that do not distort the individual polyhedral units





often only occur for very specific modulation wave-vectors
e.g. **q** = <$^1/_2$,$^1/_2$, ξ>* in ReO_3’s *e.g.* NbO_2F.

Intersect at **G** ± $^1/_2$ <111>*

$Pb_2Fe_2O_5$

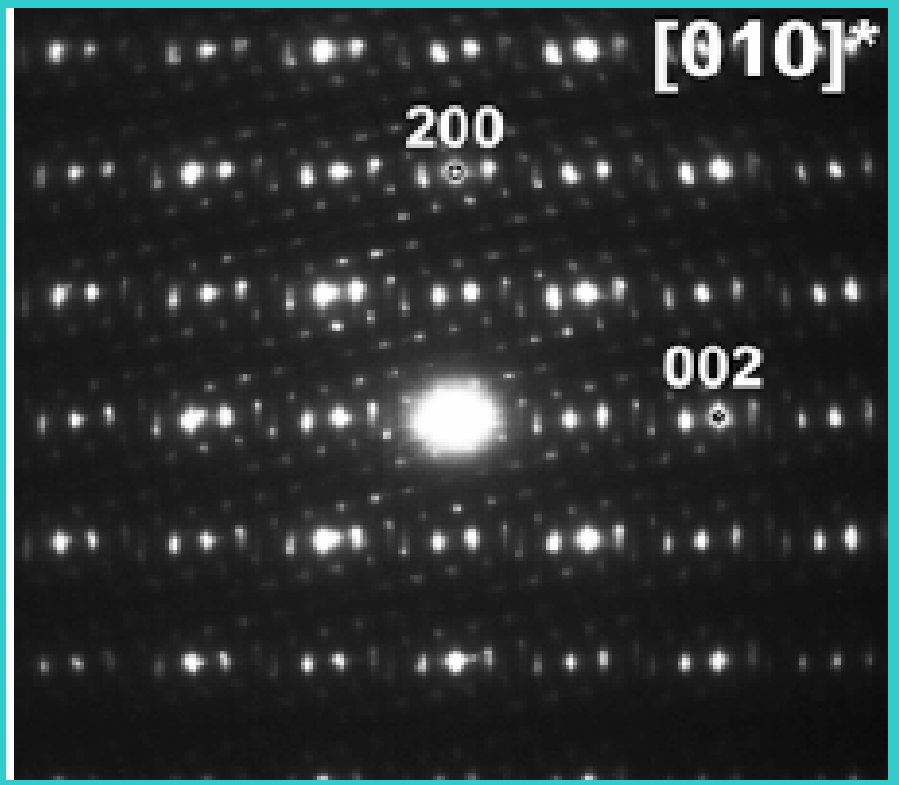
Courtesy of Staf Van Tenderloo
Abakumov et al. Angewandte Chemie (2006)

Different Example

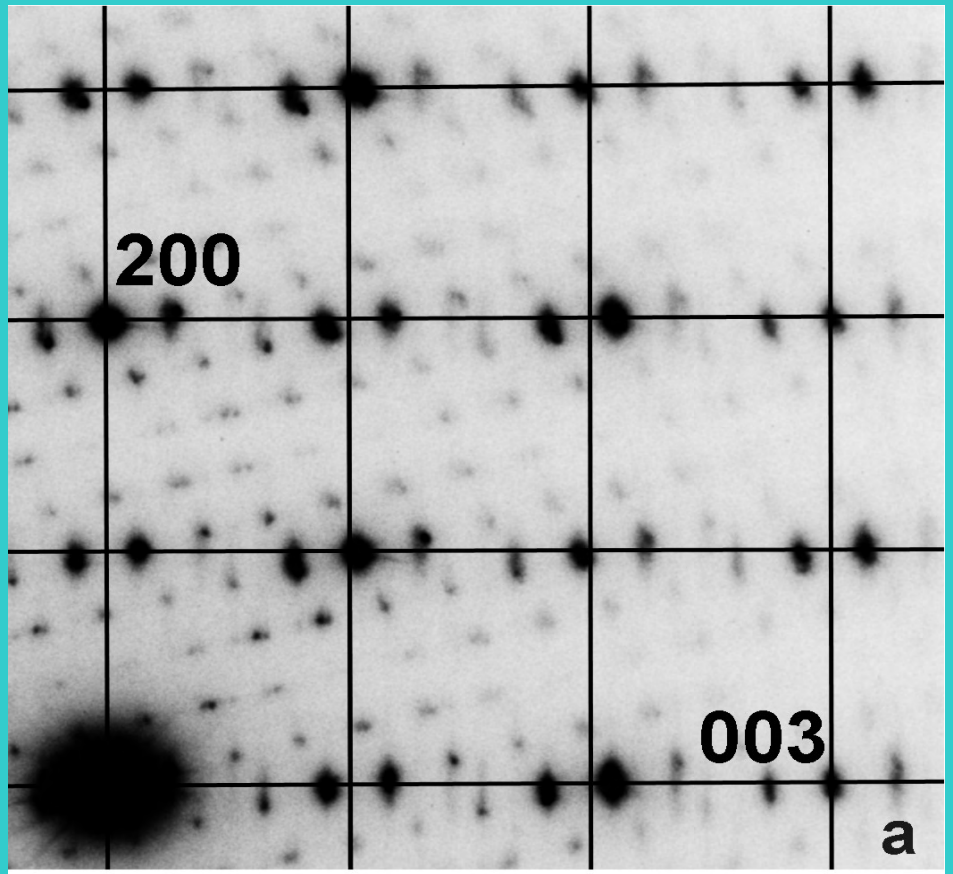
$Pb_2Fe_2O_5$

◊ perovskite based material

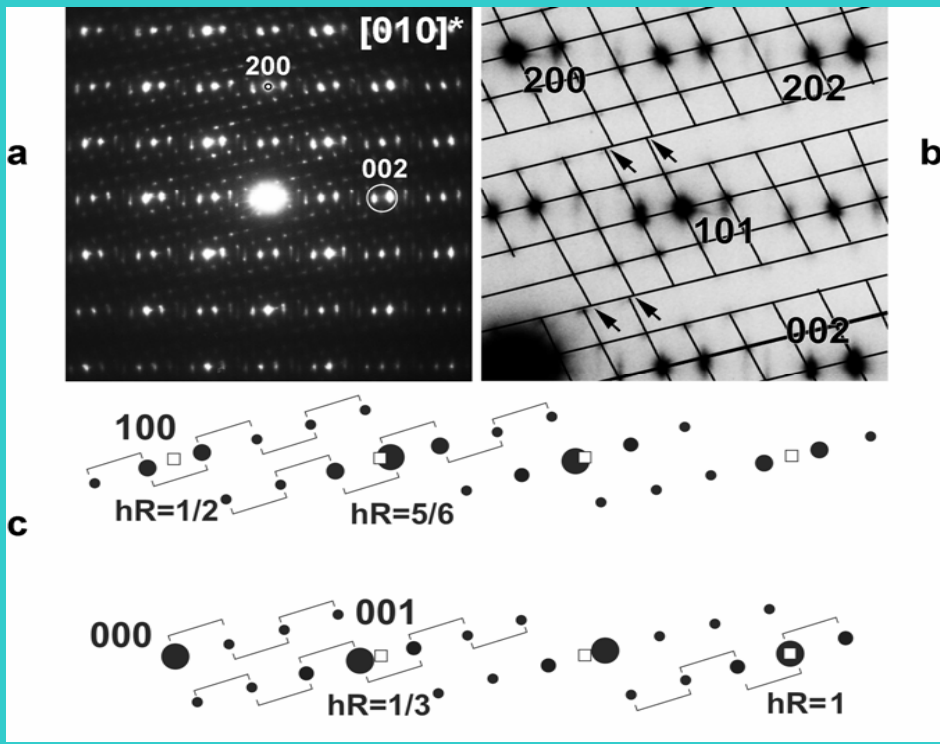
◊ complex incommensurate unknown superstructure

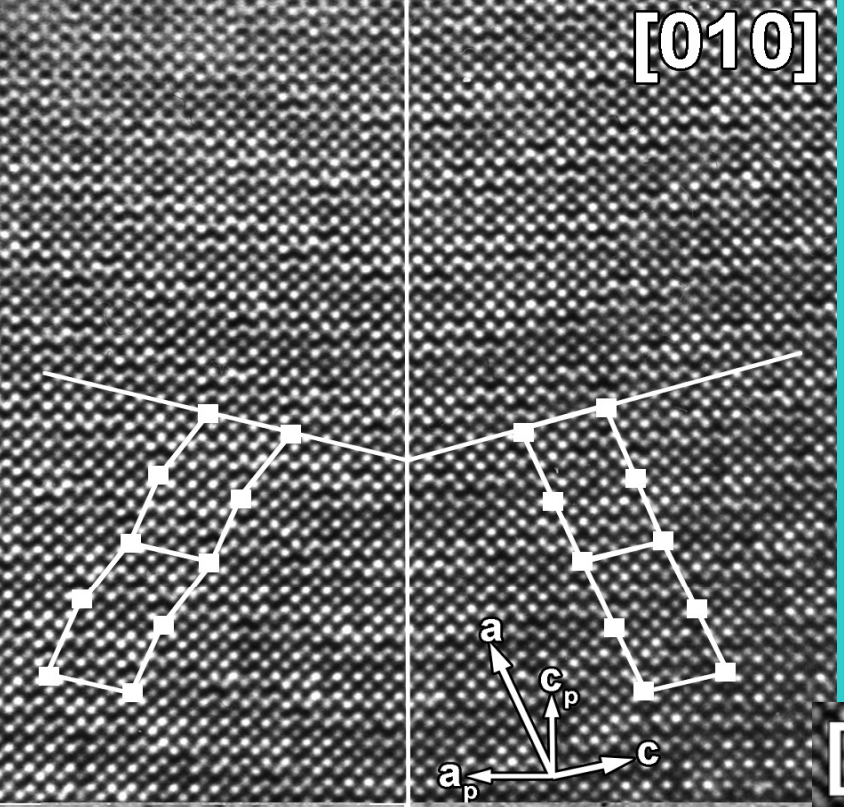


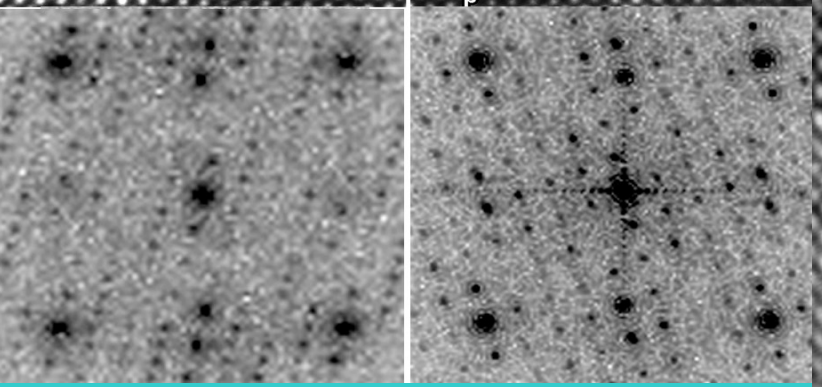
Abakumov, Hadermann et al.
Angewandte Chemie (2006)



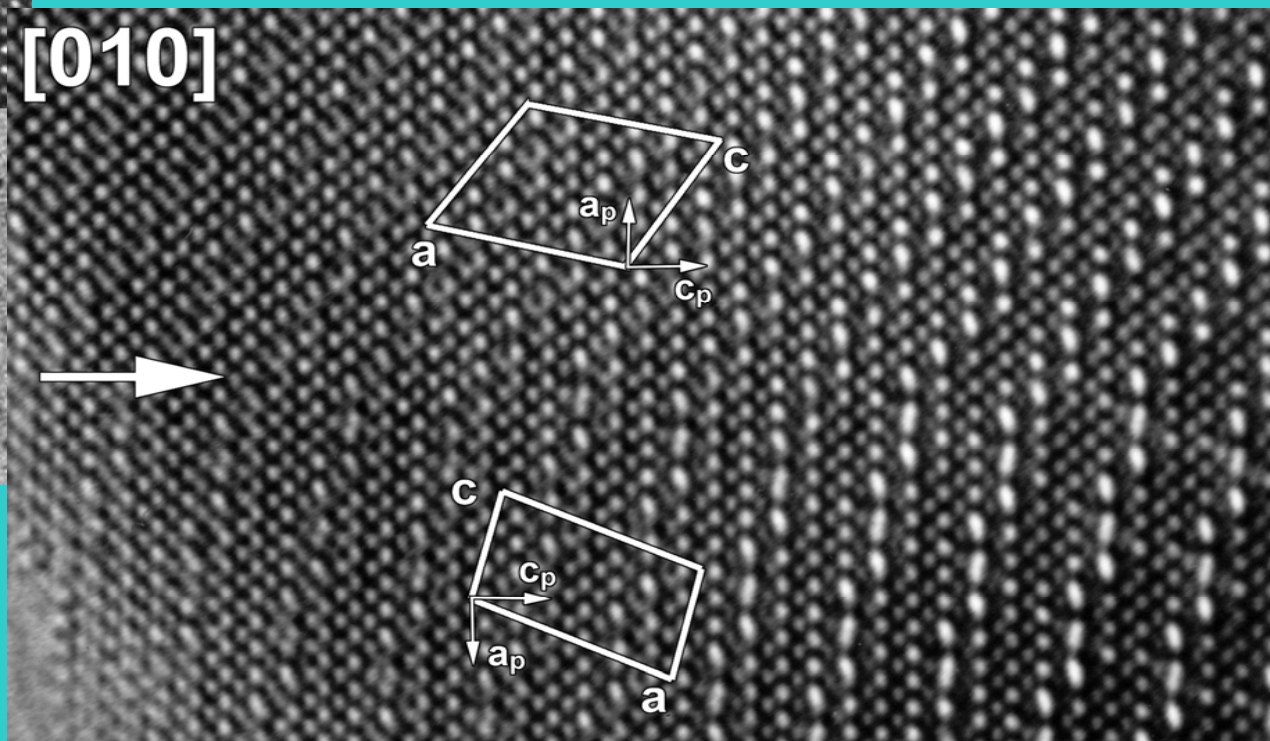
“single crystal” electron diffraction pattern of the modulated Pb-Fe-O structure.

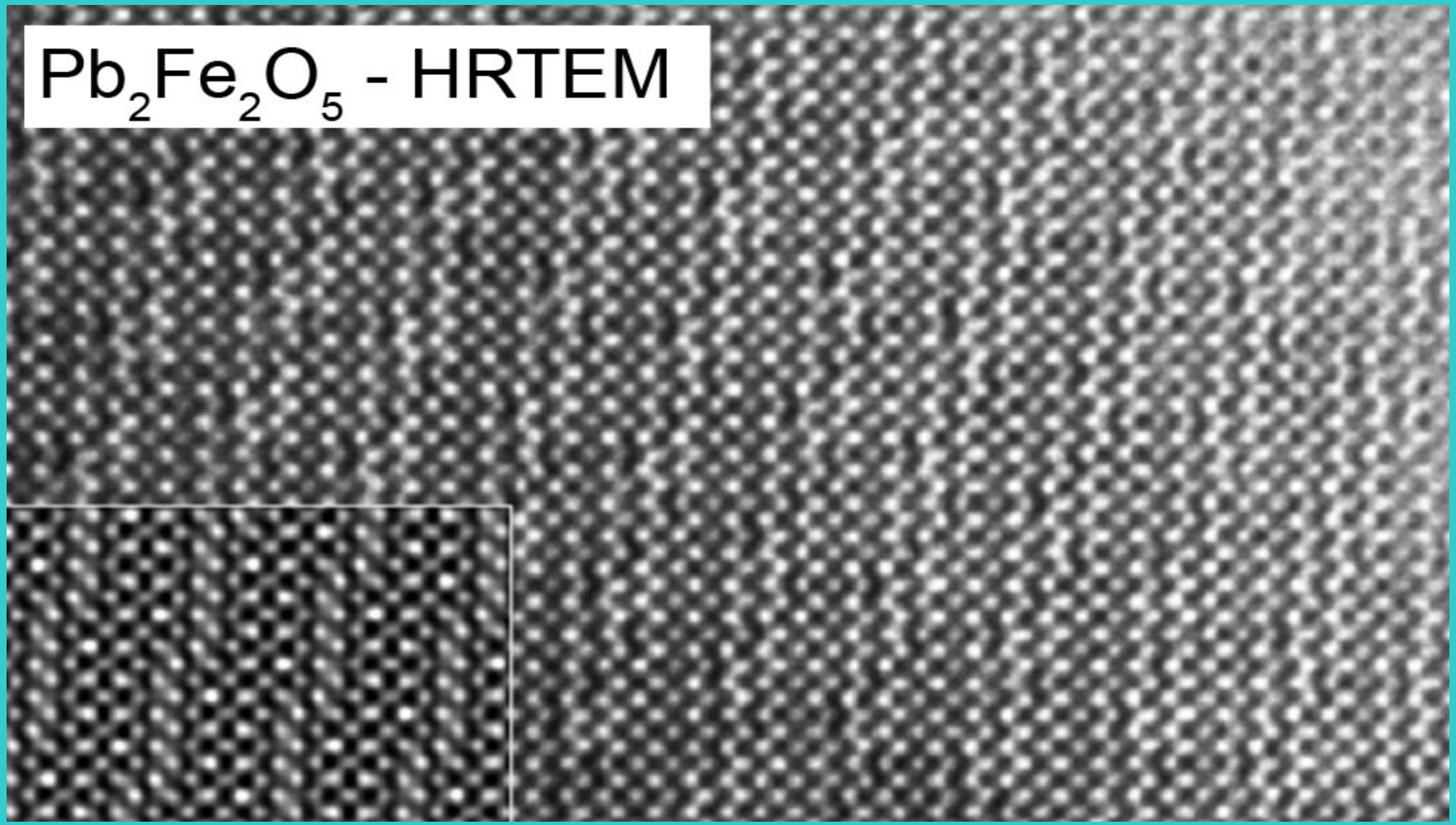






Images

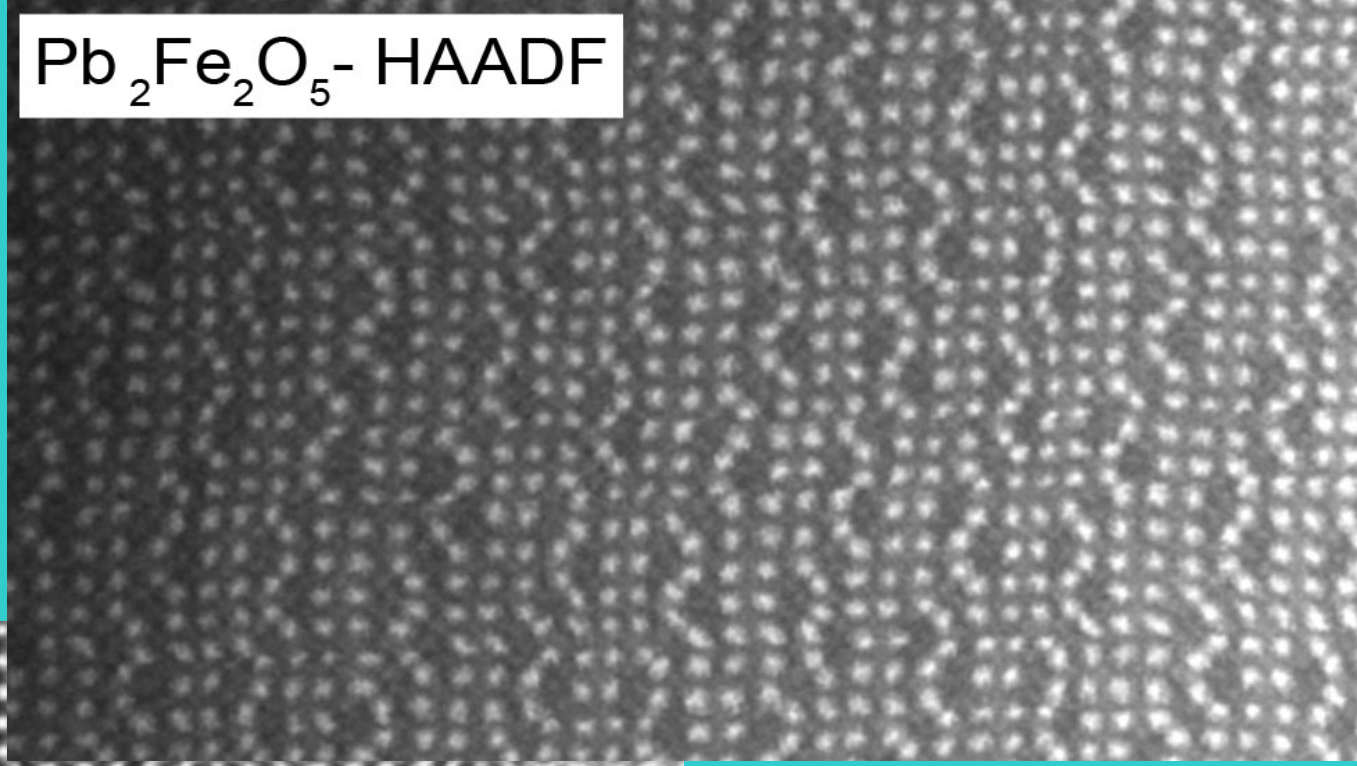


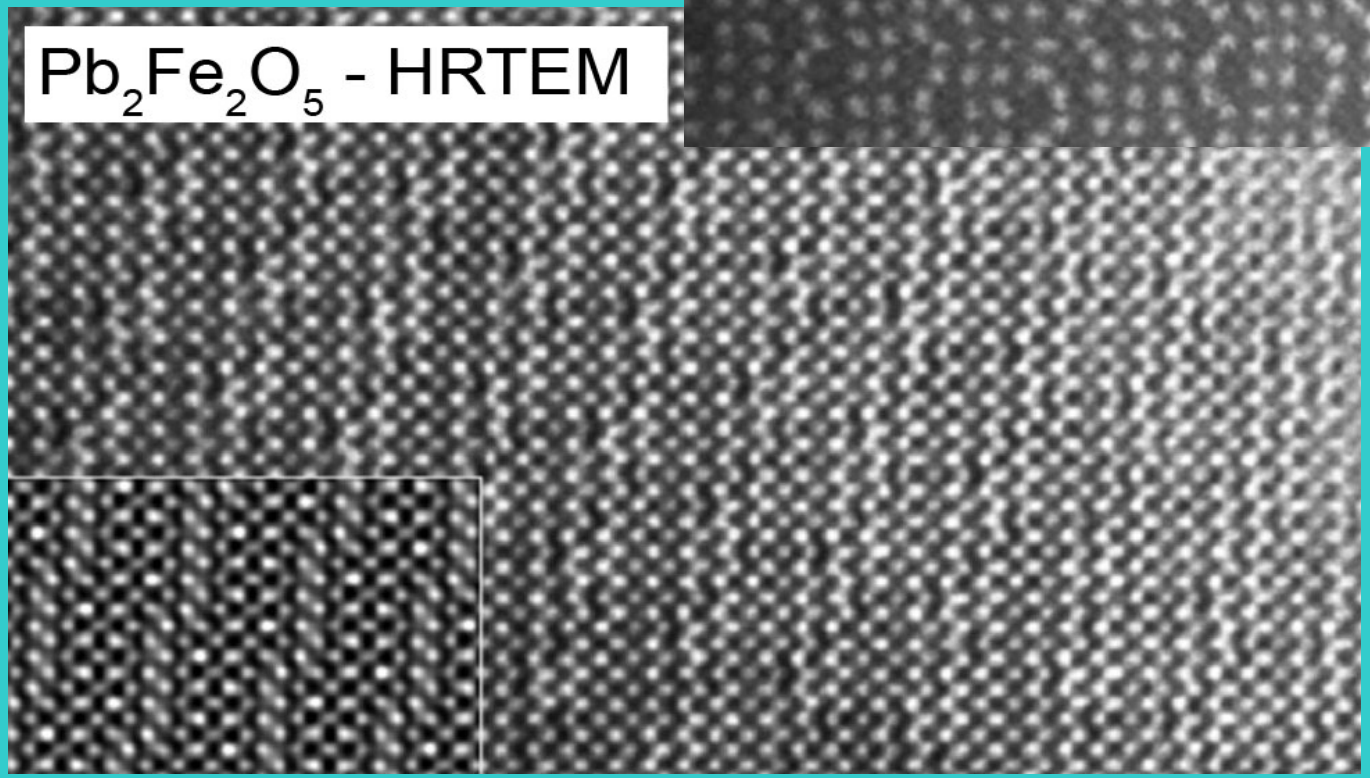


... but which atoms are where ???

$$I = ß\, Z^n$$

$Z_O = 8$
$Z_{Fe} = 26$
$Z_{Pb} = 82$





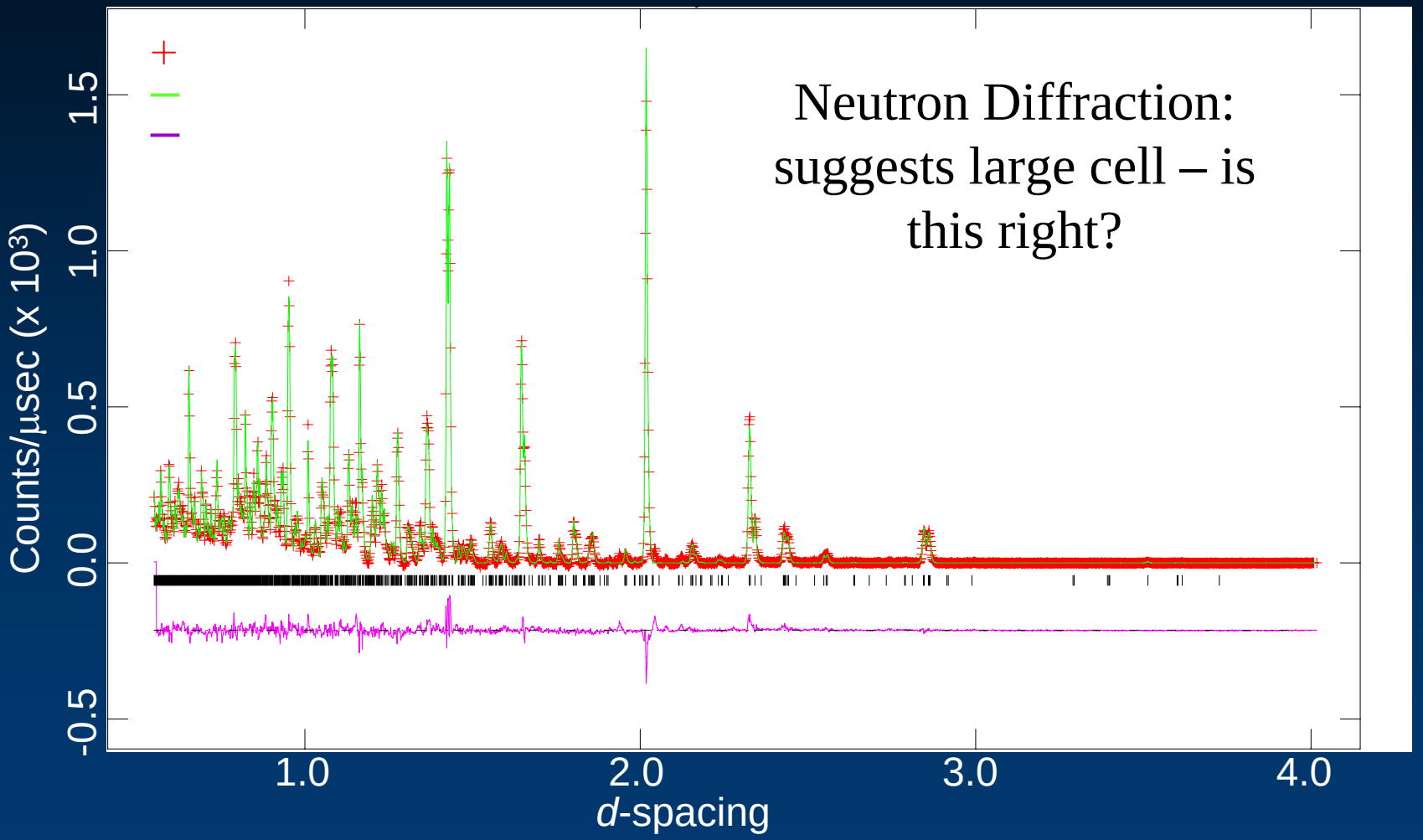
Abakumov et al.
Angewandte Chemie (2006)

Two Worked Examples

- Almost no material is phase pure when examined by TEM
- Is:
  - The material not what expected (often true)
  - The TEM data from an anomalous region which is not statistically representative
- Checks
  - Boring… look at many different regions

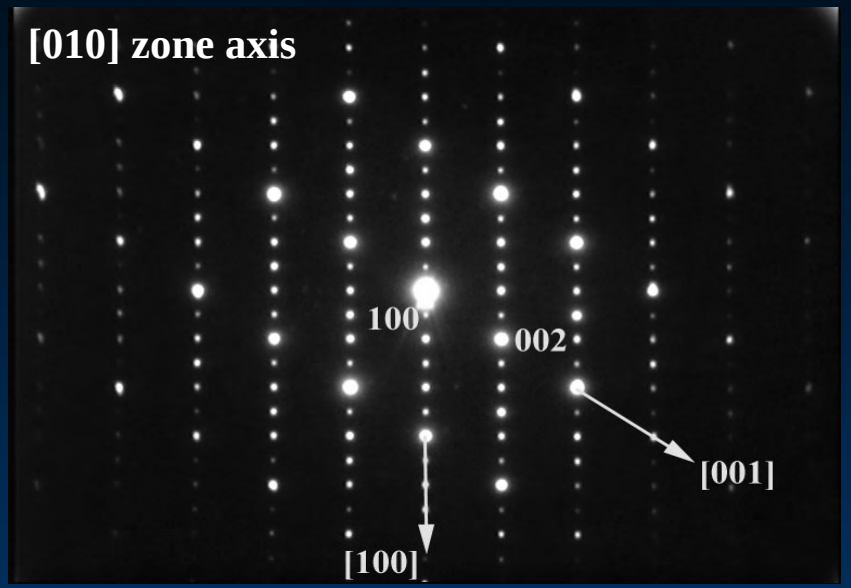
A Simple Example: $Sr_3CaRu_2O_9$

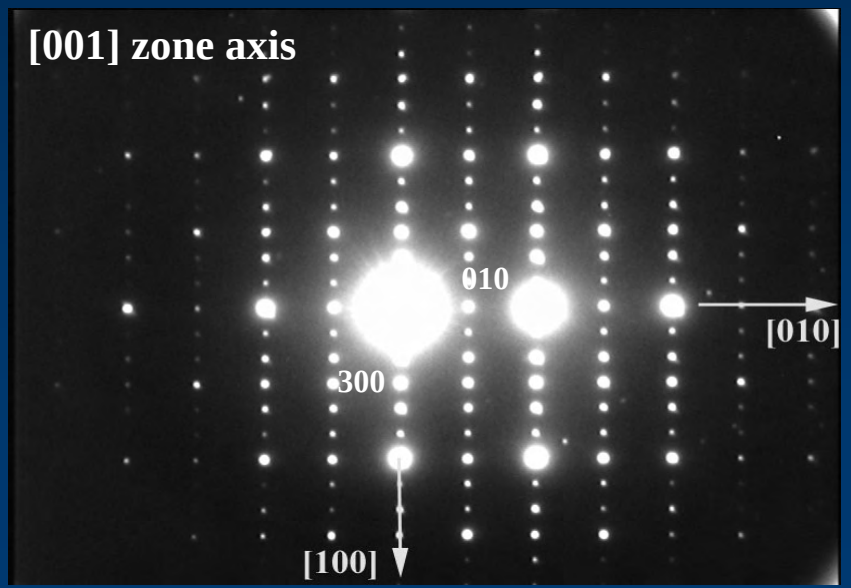
(Courtesy of Ken Poeppelmeier)



Collected on the SEPD at IPNS at Argonne National Laboratory

Yes -- Electron Diffraction





From ED:

$P2_1/c$

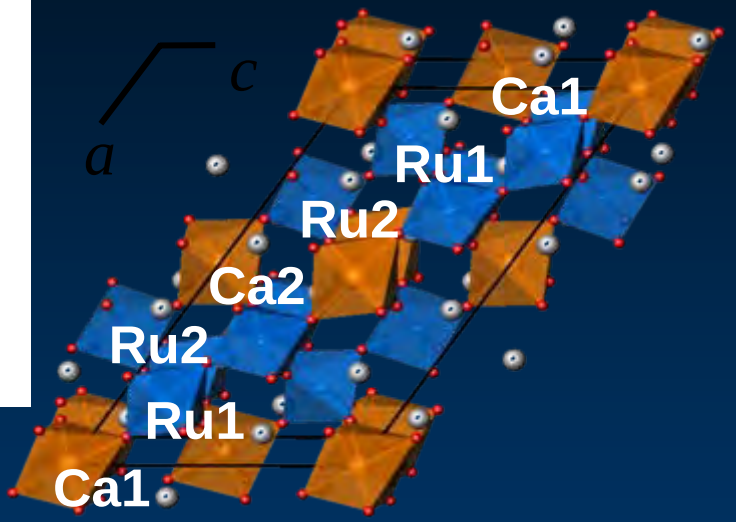
a = 17.1 Å

b = 5.7 Å

c = 9.8 Å

$ß$ = 125°

V = 786 Å^3



- Monoclinic unit cell is four times larger than the trigonal subcell
- Space group $P2_1/c$ (#14)
- Larger cell allows all peaks in the PXD to be indexed
- EDS & TGA confirm $Sr_3CaRu_2O_9$ ratios

A complicated example

A New Manganite With An Original Composite Tunnel Structure $Ba_6Mn_{24}O_{48}$
Journal of Solid State Chem.132, 239 (1997).
Ph. BOULLAY, M. HERVIEU and B. RAVEAU

$Ba_{0.25}MnO_2$

Chemical composition

cationic ratio by EDS analyses

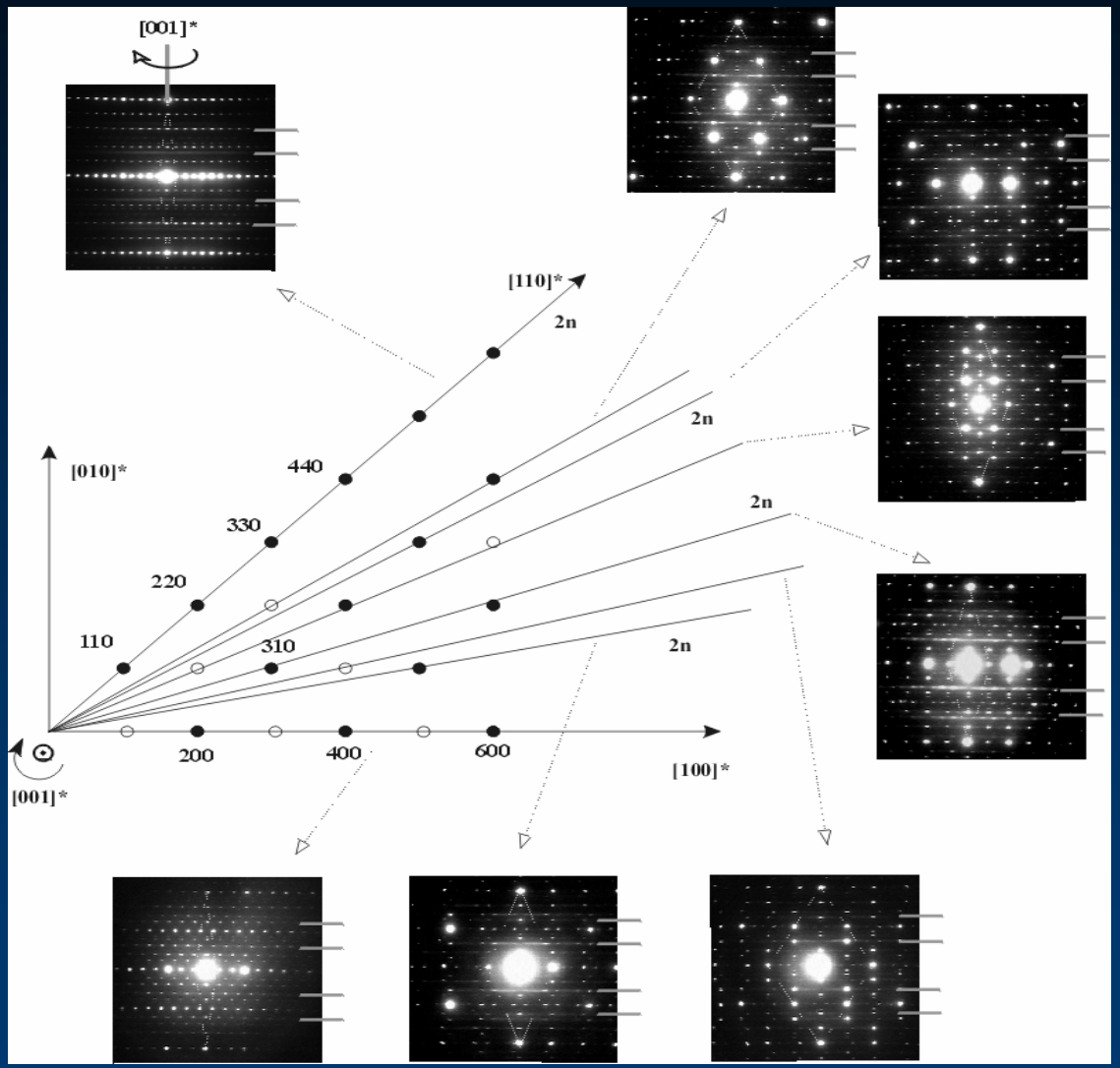
oxygen content by chemical analyses

X-ray powder diffraction

$\Rightarrow$ tetragonal lattice - I centring

$\Rightarrow$ $a \approx 1.8$ nm and $c \approx 0.28$nm

But…. Wrong Cell



1) Basic cell: I-4/m or 4/mmm
a≈1.8 nm, c≈0.28nm

+

2) Extra reflections :
an incommensurate structure

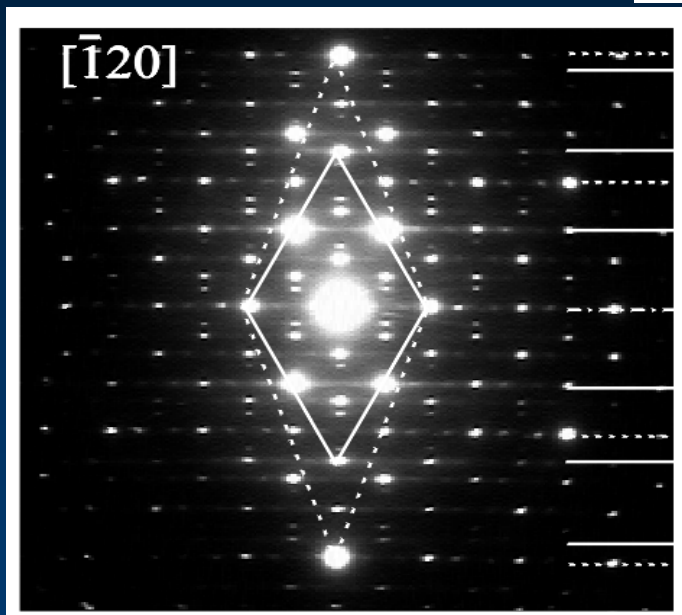
+

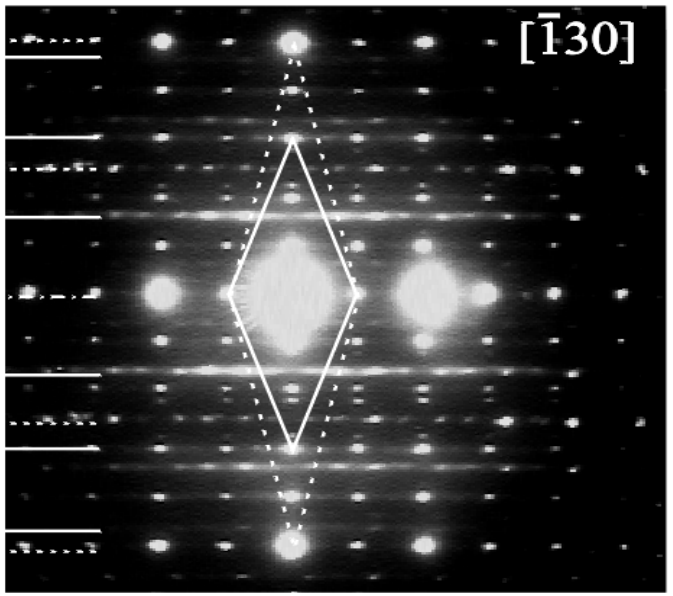
3) Diffuse scattering
a disordered structure

Basic cell seen by x-rays

Modulated Structure

$s^*=ha^*+kb^*+lc^*+mq^*$,
$q=0.36c$

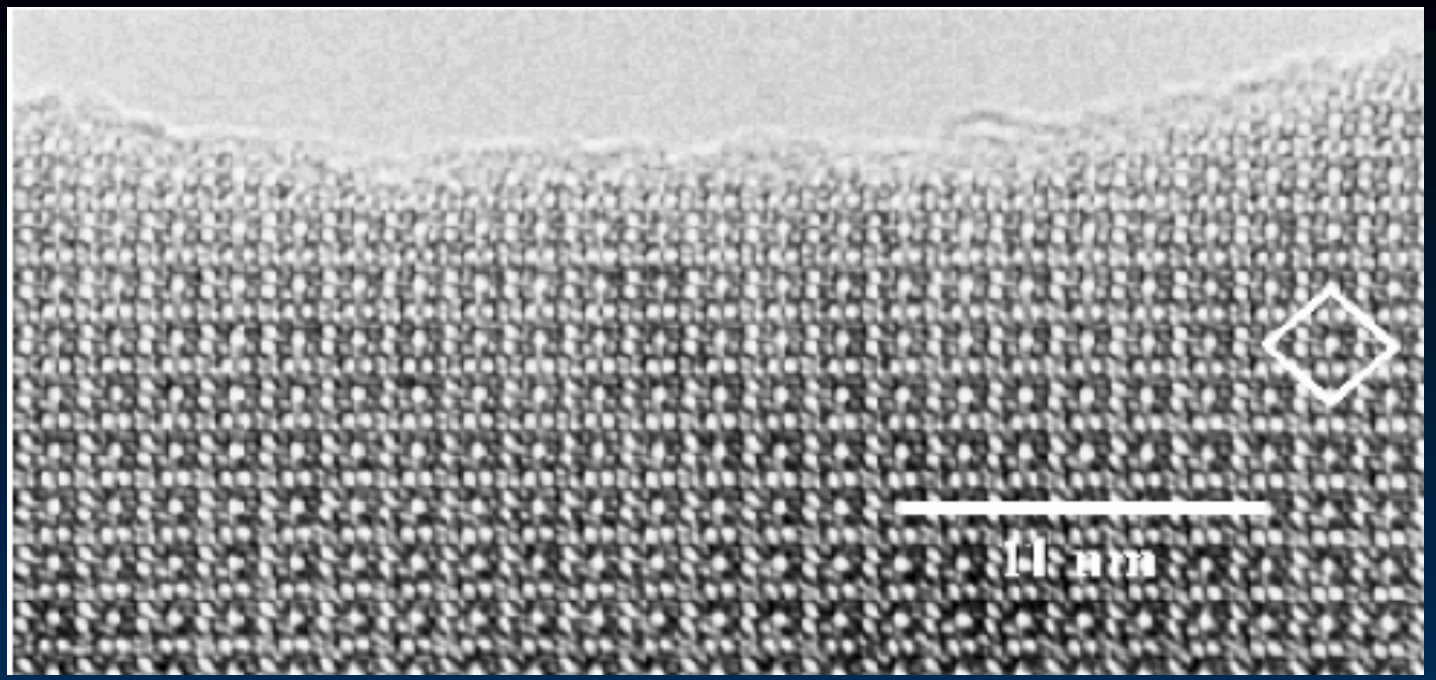




+ Diffuse Scattering (Disorder)

=

A composite structure with a disordered subsystem



Verified by HREM

Intergrowth of rutile and hollandite tunnels