Electron Diffraction and the Structural Characterization of Modulated and Aperiodic Structures

Courtesy of Ray Withers
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!
An average structure plus a modulation e.g. a displacive modulation
\[ u_\mu(r_\mu + t) = e_\mu(q) \exp 2\pi i q \cdot (r_\mu + t) \]
with \[ e_\mu(q) = e_\mu(-q)^* \]

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
\[ \delta f_\mu(r_\mu + t) = a_\mu(q) \exp 2\pi i q \cdot (r_\mu + t) \]

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

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 \( q \cdot (r_\mu + t) \).

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$_3$Ti$_4$O$_{12}$

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 $P-3m1$, 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. \((\text{Ba}_{1-x}\text{La}_x\text{In}_2\text{O}_{5+x}, x = 0.2\) for imaging a disordered Brownmillerite.

Imaging strongly suggests 1x1x2?
Ni$_6$Se$_{5-x}$Te$_x$, $x \sim 0.5$, $Bmmb$ parent structure

Ordering of partially occupied Ni sites gives rise to a $\mathbf{q} \sim \frac{1}{2}[-101]_p^*$ (or $\frac{1}{2}[101]_p^*$) modulation which is twinned perpendicular to $\mathbf{c}^*$ 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.

\[ e.g. \text{ incommensurately modulated Ni}_{6-x}\text{Se}_5 \]
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 \( Ba_x M_y Ti_{8-y} O_{16} \), \( M = \) Zn, Co, Mg, Fe and Mn, \( \sim 1.0 < x < \sim 1.4 \), hollandites.

Mutually intergrown \( \text{i}2/\text{m} \) framework and Ba sub-structures with \( \mathbf{b}_{Ba} = \frac{2}{x} \mathbf{b}_f \), \( \mathbf{b}_{Ba}^* = \frac{x}{2} \mathbf{b}_f^* \) and \( \text{i}2/\text{m} \) (0,\( x/2 \),0), \( \mathbf{b}_{Ba}^* = \frac{x}{2} \mathbf{b}_f^* \). \( 2110 = 211 \) of the framework sub-structure, \( 2011 = 211 \) of the Ba sub-structure etc.
Where are the Sn atoms in LaSb$_2$Sn$_x$, 0.1$\leq x \leq$0.75?

Well-defined \textit{Cmcm} average structure for the LaSb$_2$ (L) sub-structure but where are the Sn (S) atoms?

\[ M^* = \{a_L^*, b_L^*, c_L^*, a_S^*, c_S^* \sim \frac{3}{2} c_L^*\} \]

0K0MN$^*$ reflns. correspond to MKN$^*$ reflections of the Sn sub-structure. Implies $B$-centred Sn sub-structure with c$_S \sim \frac{2}{3} c_L$
Displacively modulated structures induced by compositional ordering

Strong azimuthal intensity variation is characteristic of a displacive modulation. $F_\mu(G \pm q) \sim 2\pi (G \pm q) \cdot e_\mu(q)$

$\text{NbO}_2\text{F of ReO}_3$ average structure type. 1-d O/F ordering along <001> strings.

Gives rise to transverse polarized $G \pm \langle h k^{1/3} \rangle*$ sheets of diffuse and diffuse streaking along all $\langle h 0 l \rangle*$ 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.

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. $\mathbf{q} = \langle 1/2, 1/2, \xi \rangle^*$ in ReO$_3$’s e.g. NbO$_2$F.

Intersect at $\mathbf{G} \pm 1/2 <111>^*$
Pb$_2$Fe$_2$O$_5$

Courtesy of Staf Van Tenderloo
Pb$_2$Fe$_2$O$_5$

◊ 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.
Pb₂Fe₂O₅ - HRTEM

... but which atoms are where ???
\[ I = \beta Z^n \]

\[ Z_O = 8 \]
\[ Z_{Fe} = 26 \]
\[ Z_{Pb} = 82 \]

\[ \text{Pb}_2\text{Fe}_2\text{O}_5 - \text{HAADF} \]

\[ \text{Pb}_2\text{Fe}_2\text{O}_5 - \text{HRTEM} \]

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$_3$CaRu$_2$O$_9$

(Courtesy of Ken Poeppelmeier)

Neutron Diffraction: suggests large cell – is this right?
Yes -- Electron Diffraction

From ED:

\[ \text{\(P2_1/c\)} \]
\[ a = 17.1 \text{ Å} \]
\[ b = 5.7 \text{ Å} \]
\[ c = 9.8 \text{ Å} \]
\[ \beta = 125^\circ \]
\[ V = 786 \text{ Å}^3 \]

- 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 \(\text{Sr}_3\text{CaRu}_2\text{O}_9\) ratios
A New Manganite With An Original Composite Tunnel Structure $\text{Ba}_6\text{Mn}_{24}\text{O}_{48}$
Ph. BOULLAY, M. HERVIEU and B. RAVEAU

$\text{Ba}_{0.25}\text{MnO}_2$

Chemical composition
- cationic ratio by EDS analyses
- oxygen content by chemical analyses

**X-ray powder diffraction**
- tetragonal lattice - $I$ centring
- $a \approx 1.8$ nm and $c \approx 0.28$ nm
1) Basic cell: I-4/m or 4/mmm  
\( a \approx 1.8 \text{ nm}, \ c \approx 0.28 \text{ nm} \)  

2) Extra reflections:  
an incommensurate structure  

3) Diffuse scattering:  
a disordered structure
Modulated Structure
\[ s^* = h\alpha^* + k\beta^* + l\gamma^* + m\eta^*, \]
q = 0.36c

A composite structure with a disordered subsystem

+ Diffuse Scattering (Disorder)
Intergrowth of rutile and hollandite tunnels

Verified by HREM