Disorder, Inhomogeneities, Average structure, local structure

In Materials with Competing Interactions

Importance ?
Characterization ?

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OUTLINE

Introduction

Cases of disorder/inhomogeneities in MICo oxides
Influence on material properties

Experimental methods to investigate local structure and disorder
  electron microscopy
  EXAFS
  Total scattering/pair distribution function

Examples
  ferroelectric relaxors
  CMR manganites
  multiferroic perovskites
  frustrated ANiO₂

Conclusion
Complexity of phase diagrams & competing interactions

=> disorder, inhomogeneities

Ferrofluid between glass plates

$\lambda \sim 1 \text{cm}$

Ferromagnetic garnet film

$\lambda \sim 10\mu\text{m}$

Block copolymers film

$\lambda \sim 400\text{Å}$

J. Tranquada

Dagotto E., Science 309, 257, 2005
If disorder, inhomogeneities are important for physical properties 
\textit{(phase separations, polarons, stripes, ...)}

They must be characterized structurally

⇒ Necessity for a multi-scale description of the structure
⇒ use of complementary techniques
⇒ use of non-standard crystallographic tools
Effects of substitution disorder in perovskites
(CMR manganites, High-Tc cuprates, relaxor ferroelectrics...)

Perovskite: ABO$_3$

A, large, 12-coord.
B, small, 6 coord.

Local effects drive the crystal structure

J-T distortion
F-E. Distortion

\[ t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \]  
tolerance factor; 0.8 < t < 1

\[ t \approx 1 \Rightarrow \text{cubic / rhombohedral} \]

\[ t \approx 0.8 \Rightarrow \text{distorted perovskite (ex: orthorhombic, GdFeO}_3\text{ type)} \]
Phase Diagram of $La_{1-x}Ca_xMnO_3$

Uehara, Kim and Cheong

R: Rombohedral
O: Orthorhombic (Jahn-Teller distorted)
O*: Orthorhombic (Octahedron rotated)
CAF canted anti ferromagnet
FI ferromagnetic insulator
FM ferromagnetic metal
CO charge ordered
AF antiferromagnetic

But not a thermodynamic phase diagram !!
La$_{2-x}$Ca$_x$MnO$_3$

When $x$ changes

- $<r_A>$ changes
- Valence of Mn changes 3+ -> 4+
- $<r_B>$ changes
- Mn$^{3+}$ is JT, Mn$^{4+}$ is not

<table>
<thead>
<tr>
<th>Ion</th>
<th>Coord.</th>
<th>Charge</th>
<th>Ionic radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>XII</td>
<td>3+</td>
<td>1.36</td>
</tr>
<tr>
<td>Ca</td>
<td>XII</td>
<td>2+</td>
<td>1.34</td>
</tr>
<tr>
<td>Sr</td>
<td>XII</td>
<td>2+</td>
<td>1.44</td>
</tr>
<tr>
<td>Ba</td>
<td>XII</td>
<td>2+</td>
<td>1.61</td>
</tr>
<tr>
<td>Mn</td>
<td>VI</td>
<td>3+</td>
<td>0.64</td>
</tr>
<tr>
<td>Mn</td>
<td>VI</td>
<td>4+</td>
<td>0.53</td>
</tr>
<tr>
<td>Cu</td>
<td>VI</td>
<td>2+</td>
<td>0.73</td>
</tr>
</tbody>
</table>

Which one is the good parameter?
Let us fix all these parameters (same $x$, same $<r_A>$), and vary the degree of disorder

$$\sigma^2 = <r_A^2> - <r_A>^2 = x(1-x)(\Delta A)^2$$

$\sigma$: variance of A-site size distribution

$\Delta A$: difference between Ln$^{3+}$ and M$^{2+}$ radii
"Good" samples, "normal" aver. Struct.

Figure 4. Variation of metal–insulator transition temperature $T_m$ with A cation size variance $\sigma^2$ for the (Ln$_{0.7}$M$_{0.3}$)MnO$_3$ perovskites in Table 1, showing a linear fit to data with $\sigma^2 < 0.015$ Å$^2$.

The linear correlation between $T_e (= T_m)$ and $\sigma^2$ is fitted as

$$T_e = T_e^0 - p_1\sigma^2$$  \hspace{1cm} (5)

where the negative slope $p_1$ quantifies the size variance dependence of $T_e$ and the intercept $T_e^0 (= T_m^0)$ is an experimental estimate of the ideal transition temperature that would be observed if cation size disorder were not present.
The variation is not seen in cell or atomic position parameters. Only in the atomic displacement parameters, a.d.p. = statistical average over locally different distances due to distribution of $r_A$, $r_B$, Mn valence, JT distortion...
Relaxor ferroelectrics

Classical PZT ferroelectric
Conventional Ferroelectric
(ex. BaTiO$_3$)

Dielectric constant $\varepsilon$

Ferroelectric tetragonal

Paraelectric cubic

Temperature $T_c$

Response independent on frequency
Well defined $T_c$
Para-ferro =
Cubic/centro – non cubic/non centro

Relaxor Ferroelectric
(ex. PbMg$_{1/3}$Nb$_{2/3}$O$_3$)

Dielectric constant $\varepsilon$

Temperature

$\Delta T \approx 100K$

Response dependent on $f$
Diffuse transition
Cubic - cubic
Relaxor ferroelectrics
= heterovalent substitution on A or B site of perovskite
=> Disorder / inhomogeneities / importance of local structure

\[ \text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3 \]

Raman signal

⇒ Local Structure is not cubic/centro

Local polar nano-regions in non polar matrix

Doping $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ with 3d metal decreases $T_c$

Where does it go (chains vs planes); what mechanism?

J.M. Tarascon et al., PRB 37, 7458, 1988
Neutron powder diffraction + electron diffraction
\[ \Rightarrow \text{Average structure + diffuse scattering} \]
= twinning + clustering of Fe
O content, O-T phase boundary... depends on clustering

Fig. 1: The crystal structure of orthorhombic YBa$_2$Cu$_3$O$_7$. The squares represent the unoccupied sites at (1/2 0 0) positions.

Table 2: Refined structural parameters for YBa$_2$Cu$_2$Cu$_{1.77}$Fe$_{1.23}$O$_{13}$

<table>
<thead>
<tr>
<th>Atom</th>
<th>pos.</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>n</th>
<th>B/β$_{11}$</th>
<th>β$_{22}$</th>
<th>β$_{33}$</th>
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</thead>
<tbody>
<tr>
<td>Y</td>
<td>1d</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
<td>0.62(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>2h</td>
<td>0.5</td>
<td>0.5</td>
<td>0.1855(1)</td>
<td>1</td>
<td>0.96(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu1</td>
<td>1a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.77(3)</td>
<td>0.99(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe1</td>
<td>1a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.23(3)</td>
<td>0.99(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu2</td>
<td>2g</td>
<td>0</td>
<td>0</td>
<td>0.35565(9)</td>
<td>1</td>
<td>0.53(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O1</td>
<td>2g</td>
<td>0</td>
<td>0</td>
<td>0.1575(2)</td>
<td>1</td>
<td>0.029(1)</td>
<td>0.029(1)</td>
<td>0.0022(2)</td>
</tr>
<tr>
<td>O2</td>
<td>4i</td>
<td>0.5</td>
<td>0</td>
<td>0.37803(8)</td>
<td>1</td>
<td>0.69(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O4</td>
<td>2f</td>
<td>0</td>
<td>0.5</td>
<td>0</td>
<td>0.564(6)</td>
<td>0.079(4)</td>
<td>0.026(3)</td>
<td>0.024(3)</td>
</tr>
</tbody>
</table>

Space group P4/mmm, a = b = 3.8674(0)Å, c = 11.6687(2)Å, V = 174.53(1)Å$^3$
R$_{p}$ = 4.44, R$_{wp}$ = 5.96, R$_{b}$ = 2.85, R$_{e}$ = 4.26

Fig. 4: Basal plane showing a model of the linear cluster arrangement in YBa$_2$Cu$_{2.77}$Fe$_{2.23}$O$_{13}$. The ordering is not correlated along the c axis and domain crossing along the same axis occurs.

Detect & quantify local (i.e. non periodic) structural effects ??

Crystallography studies and makes use of crystals to investigate the structure of materials.

Crystals are periodic and symmetric. Periodicity is what makes diffraction so efficient to study the structure.
The structure obtained by diffraction is time- and space averaged

Time is infinite vs atomic vibrations

Coherence length for diffraction is $\approx$ few 100 Å

*We are not sensitive to disorder using Bragg diffraction only*
How can we study the structure of disordered, inhomogeneous materials?

<table>
<thead>
<tr>
<th>Local scale</th>
<th>Global scale</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>spectroscopies</strong></td>
<td><strong>Small Angle Scattering</strong></td>
</tr>
<tr>
<td>Raman, IR, NMR….</td>
<td>size and shape of particles</td>
</tr>
<tr>
<td><strong>EXAFS</strong></td>
<td>no internal structure</td>
</tr>
<tr>
<td>element specific (abs. edge)</td>
<td></td>
</tr>
<tr>
<td>rdf about given atom type,</td>
<td></td>
</tr>
<tr>
<td>limited to a few spheres,</td>
<td></td>
</tr>
<tr>
<td><strong>Electron microscopy</strong></td>
<td></td>
</tr>
<tr>
<td>single grain analysis</td>
<td><strong>Diffraction (x-rays, neutron, electrons)</strong></td>
</tr>
<tr>
<td>particle size</td>
<td>use of Bragg peaks only</td>
</tr>
<tr>
<td>internal structure</td>
<td>crystal. site specific</td>
</tr>
<tr>
<td></td>
<td>average structure</td>
</tr>
<tr>
<td></td>
<td>microstructure (peak shape/position)</td>
</tr>
<tr>
<td></td>
<td><strong>Diffuse Scattering (x-rays, electrons)</strong></td>
</tr>
<tr>
<td></td>
<td>evidence of disorder, involved sublattices</td>
</tr>
<tr>
<td></td>
<td>measure &amp; interpretation difficult (3D)</td>
</tr>
</tbody>
</table>

Total scattering studies + pair distribution function = multi-scale

diffraction + pdf analysis = average + micro + local structures
Defects => diffuse scattering

Example: stacking faults in close packed structure

http://www.pa.msue.edu/cmp/billinge-group/teaching/teaching.html

<table>
<thead>
<tr>
<th>ALPHA</th>
<th>probability of &quot;ab&quot; followed by &quot;a&quot;</th>
<th>1 - ALPHA</th>
<th>probability of &quot;ab&quot; followed by &quot;c&quot;</th>
<th>BETA</th>
<th>probability of &quot;ba&quot; followed by &quot;b&quot;</th>
<th>1 - BETA</th>
<th>probability of &quot;ba&quot; followed by &quot;c&quot;</th>
<th>ALPHA BETA</th>
<th>resulting structure</th>
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</thead>
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<tr>
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<td>0.0</td>
<td>0.05</td>
<td>0.05</td>
<td>0.5</td>
<td>0.5</td>
<td>1.0</td>
<td>1.0</td>
<td>0.0</td>
<td>pure cubic sequence</td>
</tr>
<tr>
<td>0.05</td>
<td>0.05</td>
<td></td>
<td></td>
<td>0.5</td>
<td>0.5</td>
<td>1.0</td>
<td>1.0</td>
<td>0.05</td>
<td>Sequence of cubic twins</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
<td></td>
<td></td>
<td>1.0</td>
<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
<td>random stacking</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
<td></td>
<td></td>
<td>0.0</td>
<td>0.0</td>
<td>0.05</td>
<td>0.05</td>
<td>1.0</td>
<td>pure hexagonal sequence</td>
</tr>
</tbody>
</table>

ALPHA=BETA=0.00
ALPHA=BETA=0.05
ALPHA=BETA=0.2
ALPHA=BETA=0.5
ALPHA=BETA=0.8
ALPHA=BETA=0.1
Transmission electron Microscopy

Energy of electrons: few 100 keV
Size studied: few Å

Complementary infos on same nano-object
- HRTEM: direct space image
- Diffraction image
- EDX chemical analysis

HR image
Indirect interpretation
Projection of atomic columns

Single crystal diffraction on a nano-object
Yields symmetry, cell, etc...
Strong e-/matter interactions
dynamic interactions
detect weak effects (diffuse scatt.)
Electron diffraction in precession mode

=> decrease dynamical effects
=> more kinematical Bragg intensities can be used to solve (not yet refine) the local structure
EXAFS (Extended X-ray Absorption Fine Structure)

Sweep E across absorption edge => chemical selectivity

X-ray absorption edge (copper K edge)

Photoelectron mean free path increases with E

**XANES**: near edge (E<20eV above edge) electronic structure

**EXAFS**: E>20ev-> few 100 eV above edge local atomic arrangement
Starting from a local structure model, the data are fit in direct or k space.

Element specific (choice of abs. edge)
(very) local structure (few atomic shells)
Independent of long range order
Liquid, amorphous, etc...
Diffuse Scattering using “single crystals” : relaxor ferroelectric

\[ \text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3 \text{ (PMN)} \]

The cubic phase is Short Range Ordered

Applied pressure shows the origin of SRO is structural, not chemical

\[ \begin{array}{cccccc}
0.1 \text{ GPa} & 1.5 \text{ Gpa} & 2.5 \text{ GPa} & 3.6 \text{ GPa} & 5.6 \text{ GPa} & 9.0 \text{ GPa} \\
\end{array} \]

Na$_{1/2}$Bi$_{1/2}$TiO$_3$

Broad diffuse scattering:
Chemical order Na/Bi
(not sensitive to pressure)

Structural order
Guinier-Preston zones
Disappears at high pressure

Total Scattering for multiscale structural analysis

Measure of powder diffraction data up to high $Q = 4\pi \cdot \sin \theta / \lambda$

Reciprocal space

Direct space

Rietveld analysis
Average + microstructure

PDF analysis
Local structure

Total Scattering for multiscale structural analysis

Measure of powder diffraction data up to high $Q = 4\pi \cdot \sin \theta / \lambda$
Crystallographic powder diffraction: Rietveld method

\[ y_{ci} = y_{bi} + \sum_{\Phi=1}^{N} S_{\Phi} \sum_{k=k1}^{k2} j_{\Phi k} \cdot Lp_{\Phi k} \cdot O_{\Phi k} \cdot M \cdot |F_{\Phi k}|^2 \cdot \Omega_{i\Phi k} \]

\[ F_{hkl} = \sum_{j\subset cell} f_j T_j \exp(2i\pi(hx_j + ky_j + lz_j)) \]

Only Bragg peaks are used.

Diffuse scattering from disorder is discarded: « bruit de fond »

To study the real material, describe the whole diagram including diffuse background
Use of pair distribution function (pdf) in the study of partly disordered crystal structures and nano-crystalline powders

Experimentally, from powder diffraction data:

$$G(r) = 4\pi r [\rho(r) - \rho_0] = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1] \sin(Qr) dQ$$

- $r =$ interatomic distance
- $\rho(r) =$ pair density, $\rho_0 :$ average numerical density
- $S(Q) =$ normalised coherent scattered intensity,
- $Q = 4\pi \sin(\theta)/\lambda$

From a structural model:

$$G_{calc}(r) = \frac{1}{r} \sum_i \sum_j \left[ \frac{b_i b_j}{\langle b \rangle^2} \delta(r - r_{ij}) \right] - 4\pi r \rho_0 ,$$

- $r_{ij} =$ interatomic distance
- $b_i =$ scattering power

=> Fit using « direct space Rietveld » (PDFFIT Proffen et al., Appl. Cryst., 1999)

=> RMC fit on PDF (DISCUS, Proffen et al., Appl. Cryst., 1997)

or $S(Q)$ (RMCPow, Mellergard et al., Acta Cryst. A 1999)

or both (RMCPProfile, Keen et al., JPCM 2005)

\[ G(r) = 4\pi r[\rho(r) - \rho_0] = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1] \sin(Qr) dQ, \]

**G(r)**: reduced pair distribution function = \( TF \{F(Q)=Q[S(Q)-1]\} \)

*Centered about 0; amplitude indepdt of r, e.s.d.constant with r*

\[ G(r) = 4\pi r\rho_0(g(r) - 1) \quad g(r) = 1 + G(r)/4\pi r\rho_0 \]

**g(r)**: pair distribution function = \( TF \{S(Q)\} \)

\( \rightarrow 1 \) when \( r \rightarrow \infty \); amplifies low r part, e.s.d.increases with r

\[ R(r) = 4\pi r^2\rho_0 g(r) \]

**R(r)**: radial distribution function

*Increases like \( r^2 \)*

\[ Nc = \int_{r_1}^{r_2} R(r)dr \]
Complementary to “classical crystallographic analysis: independent from Bragg, use total coherent scattering local structure studies (glasses, SRO, nano-grains...)"

Example:

PDF of C60 (neutron powder diffraction)

results:

inter molecular C-C distances

Diameter of the bucky ball

Bucky balls move incoherently

F lattice organization

PDF peak width

Related to the distribution of **interatomic distances** ≠ **diffraction** !!

+ corrections :

\[
\sigma_{ij} = \sigma'_{ij} \sqrt{1 - \frac{\delta_1}{r_{ij}} - \frac{\delta_2}{r_{ij}^2} + Q_{\text{broad}}^2 r_{ij}^2}
\]

\(\delta_1, \delta_2\) effects of displacement correlations (HT, BT)

\(Q_{\text{broad}}\) : broadening due to Q resolution

---

![Graph showing PDF peak width of InAs](image)

**Calculated PDF without “δ” of InAs**

Requires high-Q and high counting statistics

⇒ Available at large facilities

**Neutrons**

constant scatt. factor $b$ ⇒ signal up to higher $Q$

contrast between elements (O, close Z, isotopes...)

steady state reactors (hot neutrons) ex : ILL-D4, $\lambda=0.7, 0.5, 0.35\text{Å}$ ⇒ $Q_{\text{max}} \approx 33\text{Å}^{-1}$,

spallation sources, ex : ISIS-GEM, LANL-NPDF (dedicated), $Q_{\text{max}} > 45\text{Å}^{-1}$

**Synchrotron x-rays**

signal decreases with $f(2\theta)$

very high flux up to very high energies ($\approx 100\text{keV}$)

parallel-beam geometry with analyzer crystal ⇒ suppresses inelastic contributions

in-situ, time dependent experiments possible with 2D detectors
Laboratory instrument

*Lab. powder Diffractometer optimized for high Q, high flux*

\[ \lambda_{\text{MoK} \alpha} \quad (0.71 \text{Å}) \Rightarrow Q_{\text{max}} \approx 17 \text{Å}^{-1} \]

\[ \lambda_{\text{AgK} \alpha} \quad (0.56 \text{Å}) \Rightarrow Q_{\text{max}} \approx 22 \text{Å}^{-1} \]

*Relaxed monochromatization, Position Sensitive Detector*

Ex : BB/DS with primary Mo mirror and PSD

Debye-Scherrer camera with image plate + SSD
Multiscale structural analysis

LaB6 ESRF-ID31, 0.4 A
Example : nano-crystalline TiO$_2$

Lab. X-ray diffraction data

Cluster Structure

Cluster \( \approx 8-9\text{Å} \)

Incoherent Structure

Pair Distribution function

Distance (Å)

Intensity (cts)

2-theta (deg)
Best model
Built from $\text{H}_2\text{Ti}_3\text{O}_7$
Structural disorder in LaCuO$_{2.66}$ delafossite
Refined structural parameters for LaCuO$_{2.66}$

<table>
<thead>
<tr>
<th>Atom</th>
<th>XRPD at RT</th>
<th>NPD at RT</th>
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</thead>
<tbody>
<tr>
<td>$\alpha$ (Å)</td>
<td>6.6941(2)</td>
<td>6.69461(7)</td>
</tr>
<tr>
<td>$\alpha$ (Å)</td>
<td>10.4157(3)</td>
<td>10.3997(2)</td>
</tr>
<tr>
<td>La1 (2h; (0 0 0))</td>
<td>$B$ (Å$^2$)</td>
<td>0.6(3)</td>
</tr>
<tr>
<td></td>
<td>$N$</td>
<td>1/3</td>
</tr>
<tr>
<td>La2 (4f; (1/3 2/3 z))</td>
<td>$z$</td>
<td>0.4902(4)</td>
</tr>
<tr>
<td></td>
<td>$B$ (Å$^2$)</td>
<td>0.5(2)</td>
</tr>
<tr>
<td></td>
<td>$N$</td>
<td>2/3</td>
</tr>
<tr>
<td>Cu1 (6h; (x y 1/4))</td>
<td>$x$</td>
<td>0.830(1)</td>
</tr>
<tr>
<td></td>
<td>$y$</td>
<td>0.169(1)</td>
</tr>
<tr>
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<td>$B$ (Å$^2$)</td>
<td>1.0(2)</td>
</tr>
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<td></td>
<td>$N$</td>
<td>0.56(1)</td>
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<td>Cu2 (6h; (x y 1/4))</td>
<td>$x$</td>
<td>0.169(1)</td>
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<tr>
<td></td>
<td>$y$</td>
<td>0.830(1)</td>
</tr>
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<td></td>
<td>$B$ (Å$^2$)</td>
<td>1.0(2)</td>
</tr>
<tr>
<td></td>
<td>$N$</td>
<td>0.24(1)</td>
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<tr>
<td>Cu3 (6h; (x y, 1/4))</td>
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<td>0.500(4)</td>
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<tr>
<td></td>
<td>$y$</td>
<td>0.499(4)</td>
</tr>
<tr>
<td></td>
<td>$B$ (Å$^2$)</td>
<td>1.0(2)</td>
</tr>
<tr>
<td></td>
<td>$N$</td>
<td>0.19(1)</td>
</tr>
<tr>
<td>O1 (12i; (x y z))</td>
<td>$x$</td>
<td>0.000(6)</td>
</tr>
<tr>
<td></td>
<td>$y$</td>
<td>0.682(5)</td>
</tr>
<tr>
<td></td>
<td>$z$</td>
<td>0.397(1)</td>
</tr>
<tr>
<td></td>
<td>$B$ (Å$^2$)</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>$N$</td>
<td>2.00</td>
</tr>
<tr>
<td>O2 (2a; (2/3 1/3 1/4))</td>
<td>$B$ (Å$^2$)</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>$N$</td>
<td>0.252(6)</td>
</tr>
<tr>
<td>O3 (2a; (0 0 1/4))</td>
<td>$B$ (Å$^2$)</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>$N$</td>
<td>0.263(2)</td>
</tr>
<tr>
<td>O4 (2c; (1/3 2/3 1/4))</td>
<td>$B$ (Å$^2$)</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>$N$</td>
<td>0.053(6)</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>2.39</td>
<td>14.3</td>
</tr>
<tr>
<td>$R_{Bragg}$</td>
<td>7.02</td>
<td>9.71</td>
</tr>
<tr>
<td>$R_{wp}$</td>
<td>31.7</td>
<td>8.35</td>
</tr>
</tbody>
</table>
Back to (LaCa)MnO$_3$ manganites
Compare average & local structure

Does JT distortion persist in metallic phase?
(x,T) results: Rietveld vs PDF (Pbnm)
Length of the Mn-O long bond (=JT distortion)
**Constant T cuts at 10K, 250K, 550K**

*Long Mn-O bond vs Ca and T*

- Long bond persists in pseudocubic phase
- Long bond shortens with increasing doping
- Long bond disappears abruptly at IM transition

=> Doped charges are (at least partly) delocalized

---

LaMnO$_3$:
Mn-O bonds are constant up to the R phase
JT distortion persists locally in the ortho and rhombo phases

Varying range refinement
Fix $r_{\text{min}}$, vary $r_{\text{max}}$

Multiferroic perovskites: structure of BiCrO₃

T("FE")=430K, T(AFM)=120K
AF (θ≈360K) “parasitic FM”

Proposed structure: \( Pbnm \Rightarrow C121 \text{ at } 430K \)
\( a=9.47\text{Å}, b=5.48\text{Å}, c=9.59\text{Å}, \beta=108.58^\circ \)

Isostructural to BiMnO₃

Fig. 3. Temperature dependence of dielectric permittivity of BiCrO₃ at 10 kHz, 100 kHz and 1 MHz.

Fig. 4. Temperature dependence of magnetic susceptibility of BiCrO₃ measured at \( H=0.1 \text{ T} \). Open and solid marks represent ZFC and FC measurements, respectively. The inset shows the magnetization curve at 2K.

**BiCrO$_3$ Average Structure**

TEM
Twins, few nanometers

ESRF-ID31
Diffuse scattering
No accurate Rietveld possible

Local structure drives ferroelectric properties (see relaxors)
PDF study of x-ray diffraction data @ ID31-ESRF

$\lambda \approx 40\text{keV} \approx 0.3\ \text{Å},$
Debye-Scherrer + multianalyser,
$2\theta_{\text{max}} = 117^\circ$, $Q_{\text{max}} > 30\ \text{Å}^{-1}$
Refinement for R<20 Å is OK with C2/c centro. C2 non centro no better
Refinement possible because R< twin domain size!
Rw=50% (after refinement, Rmax=100 Å)

structure calculated up to 100 Å

Rw=43% (after refinement, Rmax=100 Å)

Local Structure ≠ long range structure

=> Due to crossing twin boundaries

=> Study the twin orientations
Comparison with BiMnO$_3$ (No twins)
Local Structure $\approx$ long range structure
But still centro!
Why no ordered JT distortion in LiNiO$_2$??

$\text{NaNiO}_2$ C2/m
R-3m -> C2/m
Orbital & AF ordered $T_N=20$K

$\text{LiNiO}_2$ R-3m
Nothing happens...
Ni-KEdge EXAFS shows that NiO$_6$ Octahedra are JT distorted, but disordered

How, Why?

Average structure still R-3m at 10K
Not detectable distortion from Rietveld on NPD


A. Rougier et al., Nucl. Instr. in Phys. Res. 3 97 (1995) 75-77
Double peak at 2 Å => JT at all T !

High R peak height decreases at low T

FIG. 5. The neutron pair density functions of LiNiO₂ (sample 1) measured at 10 and 585 K. The x axis for the 585 K data is scaled considering the lattice constant expansion. The PDF peaks are clearly seen up to as high as 200 Å.

Peak height decrease indicates loss of structural coherence due to strain

FIG. 7. The peak-height ratio for local maxima observed in the PDFs of (a) LiNiO₂ (sample 1), (b) LiNiO₂ (sample 2), (c) LiVO₂, and (d) Na₀.₇₅CoO₂ compared between the lowest temperature and the room temperature. In each plot, the x axis represents the distances at the lower temperature. The dashed lines are fits to the logarithmic equations.
Conclusions

Effects of disorder & non-homogeneities can be important for the correct interpretation of physical / structural measurements.

They are likely to occur in case of:
- structural phase transitions
- atomic substitution
- stress/strain
- ...

They can be detected by observation of diffuse scattering.

The multi-scale structure can be studied and quantified with complementary tools, including analysis of the pdf.
merci de votre attention !