Solving and refining crystal structures using symmetry modes: FullProf + AMPLIMODES.

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Overview of the Symmetry Analysis in phase transitions

How is implemented the use of symmetry modes in FullProf

Detailed examples: Janh-Teller transition in LaMnO$_3$
In a displacive phase transition the symmetry-breaking distortion (with respect to the high symmetry phase) is mainly caused by the freezing of the primary mode, associated with the order parameter.

In general, secondary modes are also triggered at the transition and can have non-zero amplitudes in the distorted structure.

The symmetry-mode analysis of a structural phase transition consists on the calculation of the amplitudes of the symmetry modes frozen in the distortion characterized by the eigenvectors of both primary and secondary modes present in the distortion.
Modes are collective correlated atomic displacements fulfilling certain symmetry properties. Structural distortions can be decomposed into contributions from different modes with symmetries given by irreducible representations of the parent space group.

In general, the use of symmetry-adapted modes in the description of distorted structures introduces a natural physical hierarchy among the structural parameters. This can be useful not only for investigating the physical mechanisms that stabilize these phases, but also for pure crystallographic purposes.
The team of the Bilbao Crystallographic Server has developed the computer program: AMPLIMODES, that allows an easy calculation of the decomposition in modes of a distorted crystal structure with respect to a (virtual) high symmetry structure.

The originality of this approach with respect to more classical ones (e.g. BasIreps, MODY, Sarah, ...) is that the polarization vectors are referred to the basis of the low symmetry phase, allowing to use conventional crystallographic approaches (asymmetric unit and space group operators) to the crystal structure analysis.

Let \( r(\mu) \) be the positions of the atoms \( \mu (\mu = 1, \ldots, s) \) within an asymmetric unit of the parent structure with space group \( H \). The asymmetric unit of the observed distorted structure with lower space group \( L \), subgroup of \( H \), will in general have a larger number of atoms due to the splitting of the Wyckoff orbits in \( H \).

\[
\mathbf{r}(\mu, i) = \mathbf{r}_0(\mu, i) + \mathbf{u}(\mu, i) \quad \mu = 1, 2, \ldots, s, \quad i = 1, 2, \ldots, n_\mu
\]

\[
\mathbf{u}(\mu, i) = \sum_{\tau, m} A_{\tau, m} \, \mathbf{e}(\tau, m \mid \mu, i)
\]

The indices \( \tau \) and \( m \) label all possible distinct allowed symmetry-adapted distortion modes. \( \tau \) stands for the possible different mode symmetries, while \( m \) (\( m = 1, \ldots, n_\tau \)) enumerates the possible different independent modes of a given symmetry.
Distorted structures in terms of modes

\[ u(\mu, i) = \sum_{\tau, m} A_{\tau, m} \varepsilon(\tau, m | \mu, i) \]
\[ \mu = 1, 2, \ldots s, \quad i = 1, 2, \ldots n_\mu \]

The mode \((\tau, m)\) is defined by the polarisation vectors:

\[ \varepsilon(\tau, m | \mu, i) \]

One can refer to the global polarization vector \(\varepsilon(\tau, m)\), taking all atoms simultaneously, of the mode \((\tau, m)\)

The displacements of an atom \((\mu', i')\) related by the symmetry operator \(\{R|t\}\) to the atom \((\mu, i)\) are given directly by:

\[ R \varepsilon(\tau, m | \mu, i) \]
Distorted structures in terms of modes

The normalization of the polarisation vectors is chosen to verify:

\[ \sum_{\mu,i} \text{mult}_{\mu,i} |\varepsilon(\tau, m | \mu, i)|^2 = 1 \]

“\text{mult}_{\mu,i}” represents the multiplicity in a primitive cell of the space group \( L \) for the Wyckoff position \((\mu, i)\).

The following orthogonality relation is verified by the polarization vectors:

\[ \sum_{\mu,i} \text{mult}_{\mu,i} \varepsilon(\tau, m | \mu, i) \varepsilon(\tau', m' | \mu, i) = \delta_{\tau\tau'} \delta_{mm'} \]
Distorted structures in terms of modes

The distortion modes of the phase with group $H$ having isotropy group equal to $L$ can be called primary, while those with isotropy groups given by subgroups of $H$ which are distinct supergroups of $L$, are usually termed secondary.

A primary distortion mode is sufficient to produce the observed symmetry breaking between the parent and the observed structure, while secondary distortion modes alone would yield a higher symmetry.
Distorted perovskite: structure type $\text{GdFeO}_3$

Space group: $\text{Pnma}$, parent structure $\text{Pm3m}$
Group-subgroup chains relating \textit{Pm3m} and \textit{Pnma}
Distorted structures in terms of modes

It is also in general very convenient to express the global distortion in terms of the different symmetry components (this is done in AMPLIMODES):

\[
\mathbf{u}(\mu, i) = \sum_{\tau,m} A_{\tau,m} \mathbf{e}(\tau, m \mid \mu, i) = \sum_{\tau} A_{\tau} \mathbf{e}(\tau \mid \mu, i)
\]

\[
A_{\tau} = \left( \sum_{m} A_{\tau,m}^2 \right)^{1/2}
\]

\[
\mathbf{e}(\tau \mid \mu, i) = \sum_{m} a_{\tau,m} \mathbf{e}(\tau, m \mid \mu, i); \quad a_{\tau,m} = \frac{A_{\tau,m}}{\left( \sum_{m} A_{\tau,m}^2 \right)^{1/2}}
\]
Overview of the Symmetry Analysis in phase transitions

How is implemented the use of symmetry modes in FullProf

Detailed examples: Janh-Teller transition in LaMnO$_3$
In **FullProf** the refinement of a crystal structure can be done in terms of symmetry adapted modes.

http://www.ill.eu/sites/fullprof/

**FullProf** uses the polarisation vectors obtained from the output of the program **AMPLIMODES** from the Bilbao Crystallographic Server

http://www.cryst.ehu.es/cryst/amplimodes.html

A low symmetry (LS) crystal structure (Space Group L) is supposed to derive (from a phase transition) from a high symmetry (HS) structure (Space Group H) with $L \subset H$.

The free parameters, instead of atom positions, are the amplitudes of a combination of allowed symmetry modes.
FullProf Suite

Access to all programs and documentation
Magnetic structures

Magnetic moment of each atom: Fourier series

\[ \mathbf{m}_{ljs} = \sum_{\mathbf{k}} S_{kjs} \exp \left\{ i2\pi \mathbf{k} \cdot \mathbf{R}_l \right\} \]

The program \texttt{Fp_Studio} performs the above sum and represents graphically the magnetic structure. This program can help to learn about this formalism because the user can write manually the Fourier coefficients and see what is the corresponding magnetic structure immediately.

Web site: http://www.ill.eu/sites/fullprof/
Fourier coefficients as linear combinations of the basis functions of the irreducible representation of the propagation vector group $G_k$

$$S_{kjs} = \sum_{n\lambda} C_{n\lambda}^\nu S_{n\lambda}^k \ js$$

$$M \ h = p \sum_{j=1}^{n} O_j f_j \ h \ T_j \sum_{n\lambda} C_{n\lambda}^\nu \sum_{s} S_{n\lambda}^k \ js \ \exp \ 2\pi i h_s r_j$$
Figure 6. Thermodiffractogram of HoGe$_3$: (a) in a 2D projection on heating and cooling showing the succession of magnetic phase transitions below $T_N = 11$ K at $T^H_2 = 8.1$ K and $T^H_3 = 4.8$ K (temperatures given on heating) and (b) in a 3D view on cooling.
Refinement of crystal structures using amplitudes of symmetry modes instead of atom positions in FullProf

The atoms position are calculated from the following formula:

\[ \mathbf{r}_{j}^{LS} = \mathbf{r}_{j}^{HS} + \sum_{m} c_{m} Q_{m} \varepsilon(m \mid j) \]

Where \( j \) runs over the atoms in the asymmetric unit of the LS phase.
The index \( m \) runs over all contributing modes. It may content modes corresponding to different representations and wave vectors of the H space group (Isotropy subgroups) that are compatible with the L space group.

The polarisation vectors \( \varepsilon(m \mid j) \) have normalized components referred to the conventional cell of the LS phase and are provided by AMPLIMODES. The refined parameters are the amplitudes \( Q_{m} \). \( c_{m} \) are normalisation coefficients.

A representation of the modes using arrows and the HS phase can be visualised using FullProf Studio.
Example of PCR file for FullProf corresponding to the compound LaMnO$_3$

LaMnO$_3$

Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth ATZ Nvk Npr More
4 0 0 0.0 0.0 1.0 6 0 0 0 7 967.370 0 7 1

Space group symbol

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</tr>
<tr>
<td>1 O2</td>
<td>R4+</td>
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<tr>
<td>2 La</td>
<td>R5+</td>
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<tr>
<td>3 O1</td>
<td>R5+</td>
</tr>
<tr>
<td>7 O2</td>
<td>M3+</td>
</tr>
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</table>

Amplitudes of Symmetry Modes
Example of PCR file for *FullProf* corresponding to the compound LaMnO$_3$

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**Indices of the modes**

```
! Polarisation Vectors of Symmetry Modes for each atom
V_MODES 12
! Nm Atm Irrep Vx Vy Vz Coeff
1  O1  R4+ 0.000000 0.000000 0.031721 1.000000
1  O2  R4+ 0.063442 0.000000 0.000000 1.000000
2  La  R5+ 0.089721 0.000000 0.000000 1.000000
3  O1  R5+ 0.000000 0.000000 -0.031721 1.000000
. . . . . . . . . . . .
7  O2  M3+ 0.000000 0.000000 0.000000 1.000000
```

**Symbols of the Irreducible representations**

```
! Amplitudes of Symmetry Modes
A_MODES 7 1 1 1 1 1 1 1
Q1_R4+ -1.189680 181.0000
Q2_R5+ -0.086467 191.0000
Q3_R5+ 0.018171 201.0000
Q4_X5+ -0.546082 211.0000
Q5_X5+ -0.139910 221.0000
Q6_M2+ 0.355652 231.0000
Q7_M3+ 0.901264 241.0000
```

**Keywords, # of modes, output for FST**

```
!-------> Profile Parameters for Pattern # 1
! Scale  Scale  Bov  Str1  Str2  Str3  Strain-Model
0.86919E-01 0.00000 0.00000 0.00000 0.00000 0.00000 0
```

**Polarisation vectors components**

**Names of amplitudes, values and refinement codes (allowing constraints)**
Outline

- Overview of the Symmetry Analysis in phase transitions
- How is implemented the use of symmetry modes in FullProf
- Detailed example: Janh-Teller transition in LaMnO$_3$
Example: The Jahn-Teller transition in LaMnO$_3$

Neutron-diffraction study of the Jahn-Teller transition in stoichiometric LaMnO$_3$

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L. Pinsard and A. Revcolevschi

Laboratoire de Chimie des Solides, Université Paris Sud, 91405 Orsay Cedex, France

(Received 2 September 1997)

The parent compound of the giant magnetoresistance Mn-perovskite, LaMnO$_3$, has been studied by thermal analysis and high-resolution neutron-powder diffraction. The orthorhombic $Pbnm$ structure at room temperature is characterized by an antiferrodistorsive orbital ordering due to the Jahn-Teller effect. This ordering is evidenced by the spatial distribution of the observed Mn-O bond lengths. LaMnO$_3$ undergoes a structural phase transition at $T_J \approx 750$ K, above which the orbital ordering disappears. There is no change in symmetry although the lattice becomes metrically cubic on the high-temperature side. The MnO$_6$ octahedra become nearly regular above $T_J$ and the thermal parameter of oxygen atoms increases significantly. The observed average cubic lattice is probably the result of dynamic spatial fluctuations of the underlying orthorhombic distortion. [S0163-1829(98)51706-7]
Example: The Janh-Teller transition in LaMnO$_3$
AMPLIMODES: Bilbao Crystallographic Server

[ The crystallographic site at the Condensed Matter Physics Dept. of the University of the Basque Country ]

[ Space Groups ] [ Layer Groups ] [ Rod Groups ] [ Frieze Groups ] [ Wyckoff Sets ]

Space Groups Retrieval Tools

- GENPOS: Generators and General Positions of Space Groups
- WYCKPOS: Wyckoff Positions of Space Groups
- HKLCOND: Reflection conditions of Space Groups
- MAXSUB: Maximal Subgroups of Space Groups
- SERIES: Series of Maximal Isomorphic Subgroups of Space Groups
- WYCKSETS: Equivalent Sets of Wyckoff Positions
- NORMALIZER: Normalizers of Space Groups
- KVEC: The k-vector types and Brillouin zones of Space Groups

Group - Subgroup Relations of Space Groups

- SUBGROUPGRAPH: Lattice of Maximal Subgroups
- HERMANN: Distribution of subgroups in conjugated classes
- COSETS: Coset decomposition for a group-subgroup pair
- WYCKSPLIT: The splitting of the Wyckoff Positions
- MINSUP: Minimal Supergroups of Space Groups
- SUPERGROUPS: Supergroups of Space Groups

PhD Studentship

REGISTRATION OPEN
AMPLIMODES: Bilbao Crystallographic Server

**Point Group Tables**
- **POINT**
- **SITESYM**

**Site-symmetry induced representations of Space Groups**

**Solid State Theory Applications**
- **SAM**
- **NEUTRON**
- **SYMMODES**
- **AMPLIMODES**
- **PSUEDO**
- **DOPE**
- **BPLOT**
- **TRANPATH**

**Transition Paths (Group not subgroup relations)**

**Structure Utilities**
- **CELLTRAN**
- **STRAIN**
- **WPASSIGN**
- **TRANSTRU**
- **SETSTRU**
- **EQUIVSTRU**

**Transform Unit Cells**
- **Strain Tensor Calculation**
- **Assignment of Wyckoff Positions**
- **Transform structures to lower symmetry Space Group basis.**
- **Alternative Settings for a given Crystal Structure**
- **Equivalent Descriptions for a given Crystal Structure**

**Subperiodic Groups: Layer, Rod and Frieze Groups Retrieval Tools**
AMPLIMODES carries out symmetry-mode analysis of a displacive phase transition. Starting from the experimental structures of the high- and low symmetry phases, the program determines the global structural distortion that relates the two phases. The symmetry modes compatible with the symmetry break are then calculated. Their orthogonality permits the decomposition of the global distortion obtaining the amplitude of each symmetry mode as well as the corresponding eigenvectors.

The input of the program consists of:

- The information about the structures of the high- and low symmetry phases: Space group number, lattice parameters and relative atomic coordinates of the asymmetric unit.
- The transformation matrix that relates the basis of the two space groups.

### Structure data

<table>
<thead>
<tr>
<th>HINT: [Upload the structure as a CIF file (default), or as a text in the window below]</th>
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<tbody>
<tr>
<td># Space Group IIA number</td>
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<tr>
<td># Lattice parameters</td>
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<td>3.8 3.8 90 90 90</td>
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<td># [atom type] [number] [MP] [L] [x] [y] [z]</td>
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<tr>
<td>Ca 1 1b 0.8 0.5 0.8</td>
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<tr>
<td>O 1 3d 0.5 0.0 0.0</td>
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</table>

For the low symmetry structure, only the space group and the lattice parameters are necessary, the structure is optional, if given, the program will return the amplitudes of the modes.

<table>
<thead>
<tr>
<th>HINT: [Upload the structure as a CIF file (default), or as a text in the window below]</th>
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<tbody>
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### Maximum Δ Transformation

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The input of the program consists of:

- The information about the structures of the high- and low-symmetry phases: Space group number, lattice parameters and relative atomic coordinates of the asymmetric unit.
- The transformation matrix that relates the basis of the two space groups.

For the low symmetry structure, only the space group and the lattice parameters are necessary, the structure is optional, if given, the program will return the amplitudes of the modes.

HINT: [Upload the structure as a CIF file (default), or as a text in the window below]

# Space Group ITA number
62
# Lattice parameters
5.374012 7.400000 5.374012 90.0 90.0 90.0

Low Symmetry Structure

Maximum δ 1 [Maximum distance allowed]

Transformation Matrix

Rotational part

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Origin Shift

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AMPLIMODES: Bilbao Crystallographic Server

Transformed high symmetry structure in the subgroup basis

062
5 3740 12 7.600000 5 3740 12 90.000000 90.000000 90.000000

4
Ca 1 4c 0.000000 0.250000 0.000000
Tl 1 4b 0.500000 0.000000 0.000000
O 1 8d 0.750000 0.000000 0.750000
O 1 2 4c 0.500000 0.250000 0.000000

Symmetry Modes Summary

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You can copy and paste the following text on your .pcr file

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| Polarisation Vectors of Symmetry Modes for each atom |

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<td>0.000000</td>
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<td>1.00</td>
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<tr>
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<td>-0.04652</td>
<td>0.000000</td>
<td>0.000000</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Example of **FullProf** running a refinement of LaMnO$_3$ using symmetry modes

```
Example of FullProf running a refinement of LaMnO3 using symmetry modes

=> Bragg R-factor: 4.651
=> RF-factor : 3.019

=> Convergence reached at this CYCLE !!!!: CYCLE No. 15
=> R-Factors: 4.94  5.79  Chi2: 2.11  DW-Stat.: 1.0292  Patt#: 1
=> Expected : 3.98  1.0768
=> Conventional Rietveld R-factors for Pattern: 1
=> Global user-weighted Chi2 (Bragg contrib.): 2.150
=> Pattern# 1
=> Phase: 1
=> Bragg R-factor: 4.651
=> RF-factor : 3.019
=> Normal end, final calculations and writing...

=> CPU Time: 9.453 seconds
=> 0.158 minutes

=> END Date:19/08/2008 Time => 01:44:25.133
```
Rietveld, Profile Matching & Integrated Intensity
Refinement of X-ray and/or Neutron Data
(Multi_Pattern: Windows-version)

START Date: 20/09/2008 Time => 15:37:17.640
Reading control file *.PCR ...
End of preliminary calculations!

**** SIMULATED ANNEALING SEARCH FOR STARTING CONFIGURATION ****

Initial configuration cost: 107.15
Initial configuration state vector:
Q1_R4+ Q2_R5+ Q3_R5+ Q4_X5+ Q5_X5+ Q6_M2+ Q7_M3+
1 2 3 4 5 6 7
0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
NT: 1 Temp: 6.00 (%Acc): 42.04 <Step>: 4.0000 <Rp-factor>: 85.4356

Function evaluations: 491 lamn_san.int

Intensity (arb. units) vs. 2Theta
START Date: 20/09/2008  Time => 15:33:20.281
Reading control file *.PCR ...
End of preliminary calculations!

**** SIMULATED ANNEALING SEARCH FOR STARTING CONFIGURATION ****

Initial configuration cost: 107.15
Initial configuration state vector:
Q1_R4+ Q2_R5+ Q3_R5+ Q4_X5+ Q5_X5+ Q6_M2+ Q7_M3+
1 2 3 4 5 6 7
0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
NT: 1 Temp: 6.00 (%Acc): 42.04 <Step>: 4.0000 <Rp-factor>: 85.4356
NT: 2 Temp: 5.70 (%Acc): 56.12 <Step>: 3.7571 <Rp-factor>: 86.7607
NT: 3 Temp: 5.41 (%Acc): 24.49 <Step>: 3.8286 <Rp-factor>: 65.8903
NT: 4 Temp: 5.14 (%Acc): 32.04 <Step>: 2.2809 <Rp-factor>: 56.3059

Function evaluations: 1961
lamn_san.int

Intensity (arb. units) vs 2Theta
**** SIMULATED ANNEALING SEARCH FOR STARTING CONFIGURATION ****

Initial configuration cost:  107.15
Initial configuration state vector:
Q1_R4+  Q2_R5+  Q3_R5+  Q4_X5+  Q5_X5+  Q6_M2+  Q7_M3+
1  2  3  4  5  6  7
0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000

NT: 1 Temp: 6.00 (%Acc): 42.04 <Step>: 4.0000 <Rp-factor>: 85.4356
NT: 2 Temp: 5.70 (%Acc): 56.12 <Step>: 3.7571 <Rp-factor>: 86.7607
NT: 3 Temp: 5.41 (%Acc): 24.49 <Step>: 3.8286 <Rp-factor>: 65.8903
NT: 4 Temp: 5.14 (%Acc): 32.04 <Step>: 2.2809 <Rp-factor>: 56.3059
NT: 5 Temp: 4.89 (%Acc): 31.02 <Step>: 1.6271 <Rp-factor>: 49.8507
NT: 6 Temp: 4.64 (%Acc): 47.76 <Step>: 1.1245 <Rp-factor>: 48.1753
NT: 7 Temp: 4.41 (%Acc): 34.29 <Step>: 1.1456 <Rp-factor>: 33.1074
NT: 8 Temp: 4.19 (%Acc): 42.24 <Step>: 0.8090 <Rp-factor>: 35.1309

Function evaluations: 3921 lamn_san.int
**** SIMULATED ANNEALING SEARCH FOR STARTING CONFIGURATION ****

Initial configuration cost: 107.15

Initial configuration state vector:

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<tr>
<th></th>
<th>Q1_R4+</th>
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<th>Q3_R5+</th>
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<th>Q5_X5+</th>
<th>Q6_M2+</th>
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NT: 1 Temp: 6.00 (%Acc): 42.04 <Step>: 4.0000 <Rp-factor>: 85.4356

NT: 2 Temp: 5.70 (%Acc): 56.12 <Step>: 3.7571 <Rp-factor>: 86.7607

NT: 3 Temp: 5.41 (%Acc): 24.49 <Step>: 3.8286 <Rp-factor>: 65.8903

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NT: 7 Temp: 4.41 (%Acc): 34.29 <Step>: 1.1456 <Rp-factor>: 33.1074

NT: 8 Temp: 4.19 (%Acc): 42.24 <Step>: 0.8090 <Rp-factor>: 35.1309

NT: 9 Temp: 3.98 (%Acc): 42.04 <Step>: 0.7418 <Rp-factor>: 28.3311

Function evaluations: 4411 lamn_san.int

[Graph showing intensity vs. 2Theta]
Initial configuration cost: 107.15

Initial configuration state vector:

Q1_R4+  Q2_R5+  Q3_R5+  Q4_X5+  Q5_X5+  Q6_M2+  Q7_M3+

1  2  3  4  5  6  7

0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000

NT: 1 Temp: 6.00 (%Acc): 42.04 <Step>: 4.0000 <Rp-factor>: 85.4356
NT: 2 Temp: 5.70 (%Acc): 56.12 <Step>: 3.7571 <Rp-factor>: 86.7607
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NT: 4 Temp: 5.14 (%Acc): 32.04 <Step>: 2.2809 <Rp-factor>: 56.3059
NT: 5 Temp: 4.89 (%Acc): 31.02 <Step>: 1.6271 <Rp-factor>: 49.8507
NT: 6 Temp: 4.64 (%Acc): 47.76 <Step>: 1.1245 <Rp-factor>: 48.1753
NT: 7 Temp: 4.41 (%Acc): 34.29 <Step>: 1.1456 <Rp-factor>: 33.1074
NT: 8 Temp: 4.19 (%Acc): 42.24 <Step>: 0.8090 <Rp-factor>: 35.1309
NT: 9 Temp: 3.98 (%Acc): 42.04 <Step>: 0.7418 <Rp-factor>: 28.3311
NT: 10 Temp: 3.78 (%Acc): 49.39 <Step>: 0.6986 <Rp-factor>: 38.8114

Function evaluations: 4901

lamn_san.int

Intensity (arb. units)

2Theta
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<th>Value (Acc)</th>
<th>Step</th>
<th>Rp-factor</th>
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<td>47.76</td>
<td>1.1245</td>
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<td>8</td>
<td>4.19</td>
<td>42.24</td>
<td>0.8090</td>
<td>35.1309</td>
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<tr>
<td>9</td>
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<td>42.04</td>
<td>0.7418</td>
<td>28.3311</td>
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<td>20.1178</td>
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Function evaluations: 10291

Intensity (arb. units) vs. 2Theta
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<td>3.08</td>
<td>57.14</td>
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</table>

Function evaluations: 13231

Int: arb. units

Intensity vs. 2Theta
FullProf Program

Load  Edit PCR  Mode  Run  Exit

NT: 81 Temp: 0.10 (Acc): 45.92  <Step>: 0.0423  <Rp-factor>: 5.7588

NT: 82 Temp: 0.09 (Acc): 49.39  <Step>: 0.0400  <Rp-factor>: 5.7702

BEST CONFIGURATIONS FOUND BY Simulated Annealing FOR PHASE: 1

Configuration parameters (200 reflections):

Sol#: 1 RF2= 5.449 :
Q1_R4+  Q2_R5+  Q3_R5+  Q4_X5+  Q5_X5+  Q6_M2+  Q7_M3+
1 2 3 4 5 6 7
1.2033 0.0830 -0.0167 0.5630 0.1370 0.3626 0.9074

CPU Time: 41.578 seconds
0.693 minutes

END  Date: 20/09/2008  Time => 15:30:28.109

Function evaluations: 40181 lamn_san.int
Visualisation of single modes using FullProf Studio

- A part from the normal FST file generated normally for the final crystal structure, FullProf outputs a series of FST files containing

- The “virtual structures” corresponding to single modes (e.g. A_MODES 7 0 0 0 0 0 0)

- A representation of the high symmetry phase together with arrows indicating the displacement of atoms in the corresponding mode: (e.g. A_MODES 7 1 1 1 1 1 1)

- Both kinds of representations depending on the mode (e.g. A_MODES 7 1 0 0 1 1 0 1)

The items after the number of modes are:

\[ p_{\text{mode}}(i) \quad i=1,..., n_{\text{modes}} \]
Crystal Structure of LaMnO$_3$
Mode 1, Q1_R4+ = -1.18968
O1  R4+  (0.0, 0.0, 0.031721)
O2  R4+  (0.063442, 0.0, 0.0)

Mode 3, Q3_R5+ = 0.018171
O1  R5+  (0.0, 0.0, -0.031721)
O2  R5+  (0.063442, 0.0, 0.0)
Mode 5, $Q_{5 \_X5^+} = -0.139910$
$O2 \_X5^+ (0.0, -0.089721, 0.0)$

Mode 4, $Q_{4 \_X5^+} = -0.546082$
$La \_X5^+ (0.0, -0.089721, 0.0)$
Mode 7, Q7_M3+ = 0.901264
O1  M3+  (-0.04486, -0.04486, 0.0)

Mode 6, Q6_M2+ = 0.355652
O1  M2+  (0.04486, -0.04486, 0.0)
Visualisation of Irreps modes using FullProf Studio

If the value of p_mode(1)=2 (see note of 29 August 2008 in fp2k.inf) the other values are not needed.

The program interprets this value as an indication to output in the FST and OUT files the structures corresponding to single irreducible representations (Irreps).

All modes corresponding to a single Irrep are combined in the FST file.
Visualisation of modes using FullProf Studio: Summary

Examples:

A_MODES 7 7 \rightarrow All the 7 independent modes are represented by displacement vectors (arrows)

A_MODES 7 -7 \rightarrow All the 7 independent modes are represented by virtual distorted structures

A_MODES 7 -3 \rightarrow No output of independent modes in FST files
Visualisation of single modes using FullProf Studio

Examples:

A_MODES    7    2 → Modes regrouped in an FST file per irreducible representation (arrows)

A_MODES    7    -2 → Modes regrouped in an FST file per irreducible representation (structures)

A_MODES    7    1 1 1 0 1 1 0 → Explicit output of all modes (1: arrows, 0: distorted structure)
Visualisation of single modes using FullProf Studio

Examples:

A_MODES 7 4 1 3 -4 7 → Only the 4 modes 1, 3, 4 and 7 are output in FST files. All of them, except the mode 4, are represented by arrows.
A more complex case:

LiMn$_2$O$_4$
Electronic Crystallization in a Lithium Battery Material: Columnar Ordering of Electrons and Holes in the Spinel LiMn$_2$O$_4$

J. Rodríguez-Carvajal,$^1$ G. Rousse,$^2$ C. Masquelier,$^2$ and M. Hervieu$^3$

$^1$Laboratoire Léon Brillouin (CEA-CNRS), CEA/Saclay, 91191 Gif sur Yvette Cedex, France
$^2$Laboratoire de Chimie des Solides, Université Paris-Sud, 91405 Orsay Cedex, France
$^3$CRISMAT, ISMRA, 6 Boulevard du Maréchal Juin, 14050 Caen Cedex, France

(Received 13 July 1998)

LiMn$_2$O$_4$ presents a first order structural transition at 290 K that was known to perturb the functioning as cathode in rechargeable Li batteries. We have solved the structure at 230 K and deciphered unambiguously the nature of this phase transition. The analysis of valence bond sums shows that the transition results from a partial charge ordering: two of the five Mn sites correspond to well-defined Mn$^{4+}$ and the other three sites are close to Mn$^{3+}$ ions. Charge ordering is accompanied by simultaneous orbital ordering due to the Jahn-Teller effect in Mn$^{3+}$ ions. The microscopic details obtained from the structure are crucial for understanding the electron hopping persisting below the transition. [S0031-9007(98)07667-4]
Electronic crystallization in a Li battery material: columnar ordering of electron and holes in the spinel LiMn$_2$O$_4$

J. Rodríguez-Carvajal, G. Rousse, Ch. Masquelier and M. Hervieu

*Physical Review Letters, 81, 4660 (1998)*

$\text{Li}_{T_d} [\text{Mn}_2]_{\text{Oct.}} \text{O}_4 : \text{Mn}^{3.5+}$

High temperature: mixed valence

Orthorhombic Distortion
Superstructure reflections
LiMn$_2$O$_4$: Electron Diffraction

Cubic Fd$\bar{3}$m
\[ a = 8.248 (1) \text{ Å} \]

Orthorhombic Fddd
\[ a = 24.7435(5) \text{ Å} \]
\[ b = 24.8402(5) \text{ Å} \]
\[ c = 8.1989(1) \text{ Å} \]

J. Rodríguez-Carvajal et al, PRL, 81, 4660 (1998)
Refinement of the charge-ordered phase
LiMn$_2$O$_4$: Partial Charge Ordering

\[
\begin{align*}
\langle \text{Mn-O} \rangle &= 2.003(2) \text{ Å} \\
\text{Mn}(1) &= 3.20^+ \\
\Delta &= 20.6 \\
\langle \text{Mn-O} \rangle &= 1.996(4) \text{ Å} \\
\text{Mn}(2) &= 3.27^+ \\
\Delta &= 19.4 \\
\langle \text{Mn-O} \rangle &= 2.020(5) \text{ Å} \\
\text{Mn}(3) &= 3.12^+ \\
\Delta &= 36.6 \\
\langle \text{Mn-O} \rangle &= 1.903(4) \text{ Å} \\
\text{Mn}(4) &= 4.02^+ \\
\Delta &= 4.6 \\
\langle \text{Mn-O} \rangle &= 1.915(4) \text{ Å} \\
\text{Mn}(5) &= 3.90^+ \\
\Delta &= 6.1
\end{align*}
\]

64 « Mn$^{4+}$ »
80 « Mn$^{3+}$ -like»
8 delocalised holes
Recently a Japanese group has shown, with single X-tals, that Mn(2) are Zener Polarons involving 4Mn.