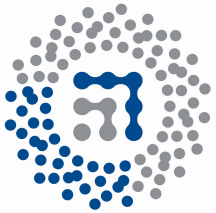

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Facultad de Ciencia y Tecnología

Universidad del País Vasco
Euskal Herriko Unibertsitatea

Introduction to symmetry mode analysis:

J. Manuel Perez-Mato
Facultad de Ciencia y Tecnología
Universidad del País Vasco, UPV-EHU
BILBAO, SPAIN

A detailed review with many examples:

"Mode crystallography of distorted structure", Acta Cryst. (2010). A66, 558-590
J.M. Perez-Mato, D. Orobengoa and M.I. Aroyo
Acta Cryst. (2010). A66, 558–590 (open access)

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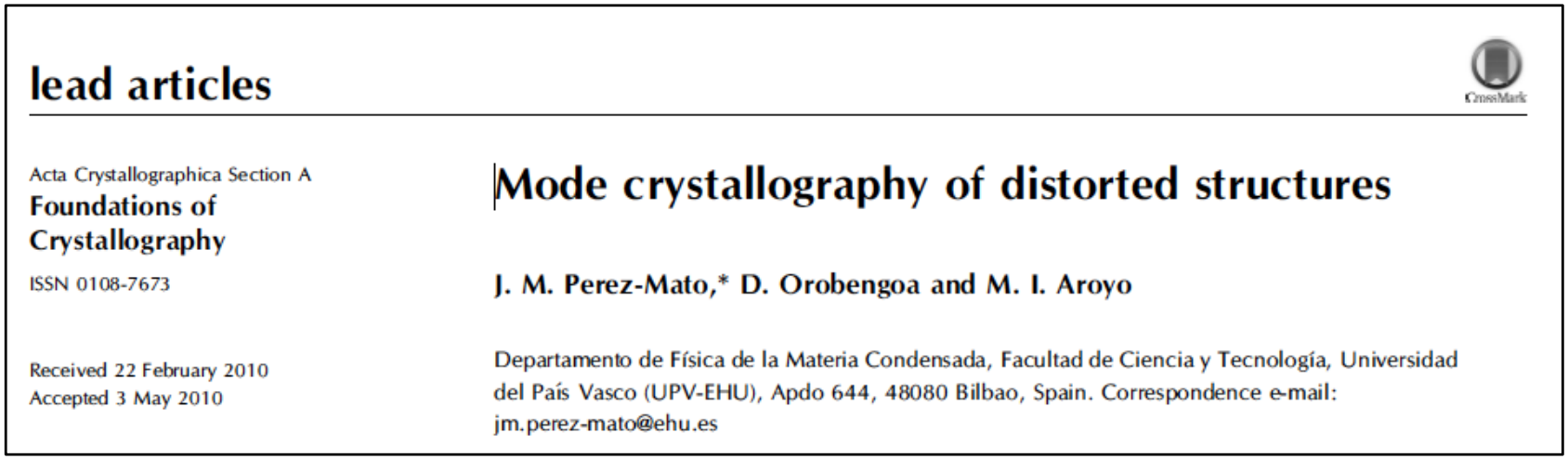

lead articles

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Mode crystallography of distorted structures

J. M. Perez-Mato,* D. Orobengoa and M. I. Aroyo

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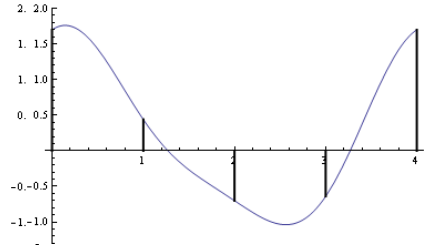
What is a mode decomposition?

Fourier decomposition:



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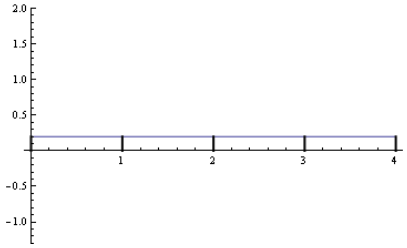

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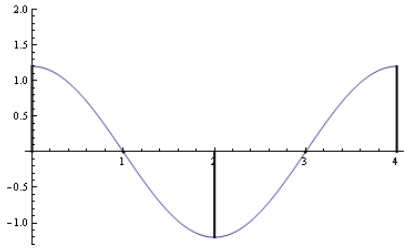

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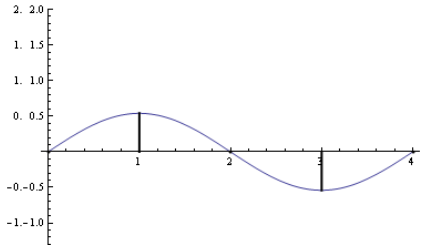

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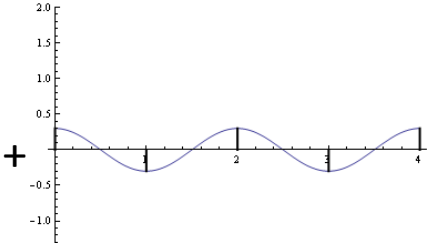
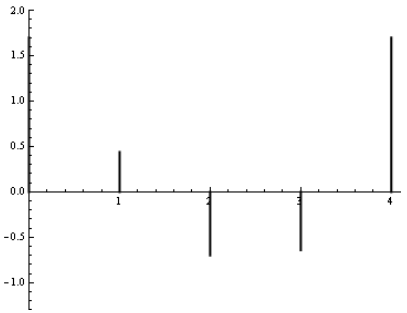


mode decomposition:



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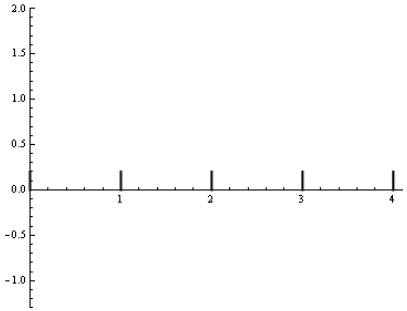

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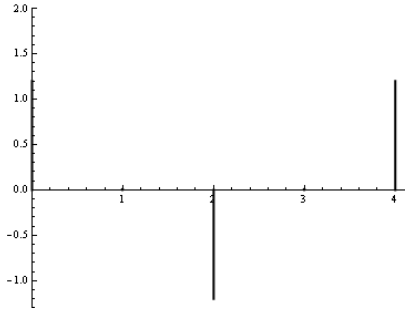

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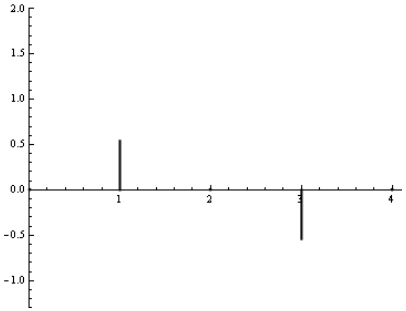

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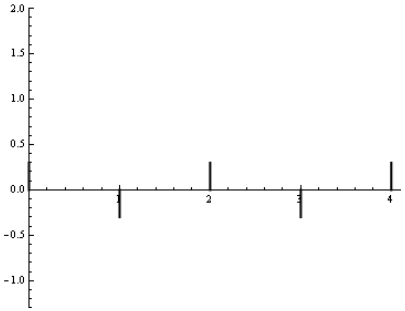
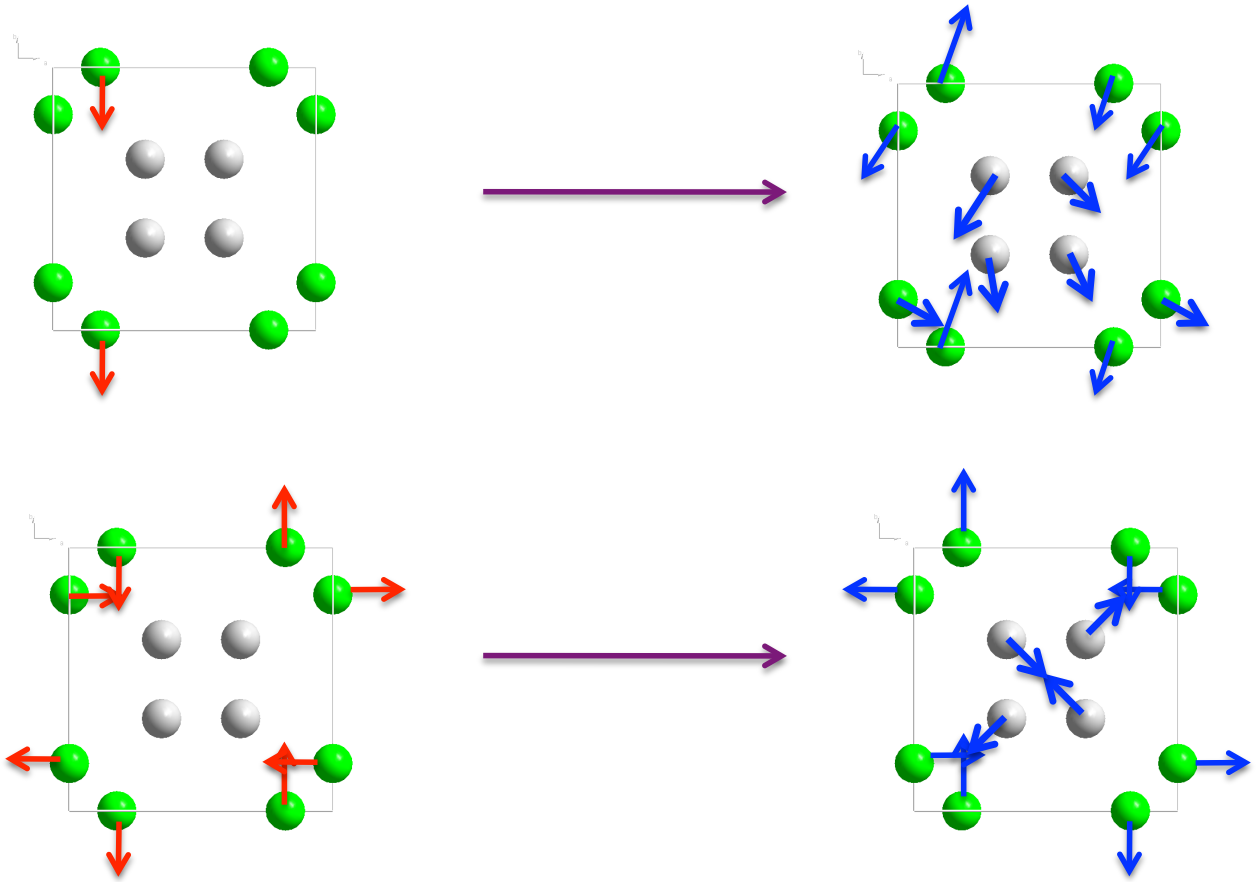


Why symmetry-adapted modes?

to first-order, these modes only couple with modes of the same symmetry

atomic displacements:

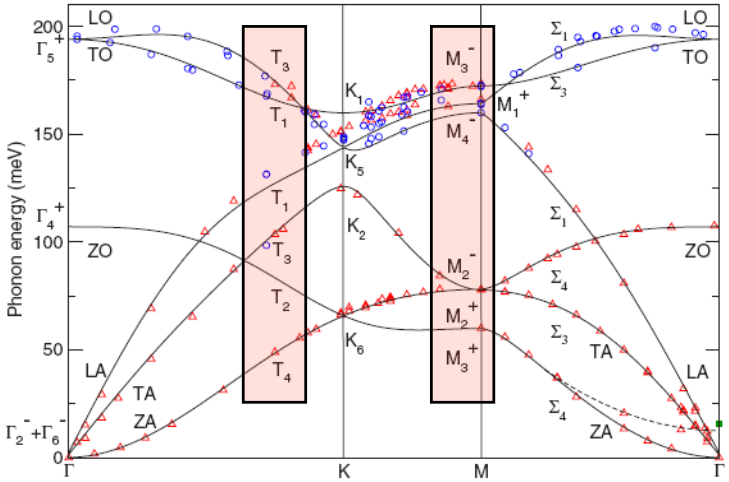
resultant atomic forces:



MODES OF DIFFERENT SYMMETRY ARE UNCOUPLED TO FIRST ORDER

Modes in the dynamics of solids:

$\hbar\omega_j(k)$



Mohr et al. PRB 2007

Energy as a function of the normal (dynamic) coordinates:

$$E = Eo + 1/2 \sum \omega^2_j(k)\, Q_j^{dyn\,2}(k) + \ldots$$

$$\omega^2_j(k) > 0$$

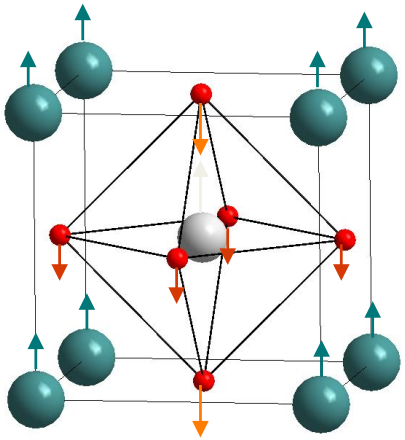
Zero mean value of mode coordinates : $< Q_i^{dyn} >= 0$

Symmetry of vibrational modes: **irreducible representations** (group theory)

irrep modes....

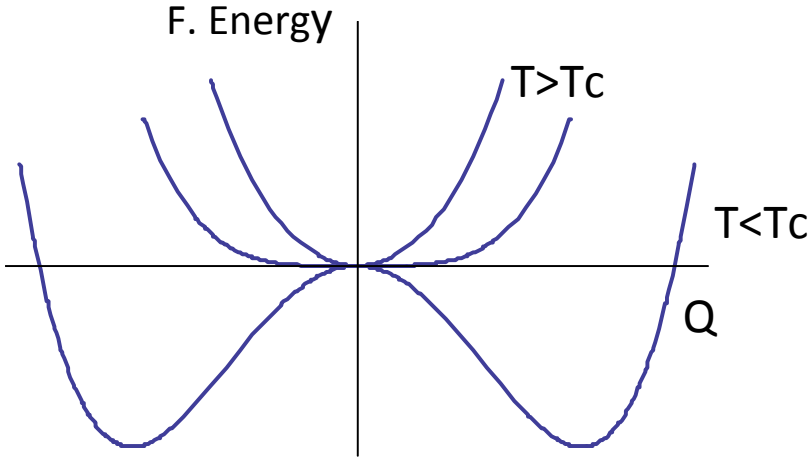
Modes in the statics of low-symmetry distorted phases:

The natural language to describe a symmetry break/phase transition (Landau Theory)



primary distortion mode – order parameter

Unstable collective degree of freedom:



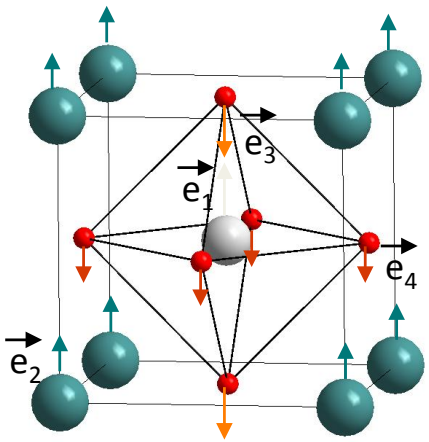
$$E = Eo + 1/2\ \kappa(T)\ Q^2 + \ldots$$

$\kappa(T)<0$ $T<Tc$

Modes in the statics of solids:

Distorted Structure = High-symmetry Struct + "frozen" modes

distortion mode = Amplitude x polarization vector



Description of a "mode":

$\vec{u}(\text{atoms}) = Q\ \vec{e}$

amplitude | polarization vector

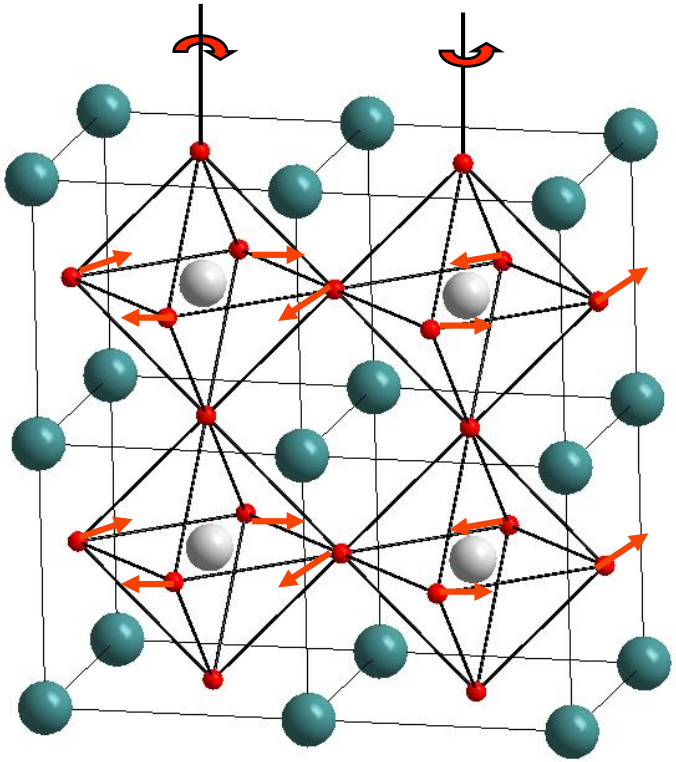
$\mathbf{e} = (\ \vec{e}_1\ ,\vec{e}_2\ ,\vec{e}_3\ ,\vec{e}_4\ )$

normalization: $|\vec{e}_1|^2 + |\vec{e}_2|^2 + |\vec{e}_3|^2 + 2\ |\vec{e}_4|^2 = 1$
(within a unit cell)

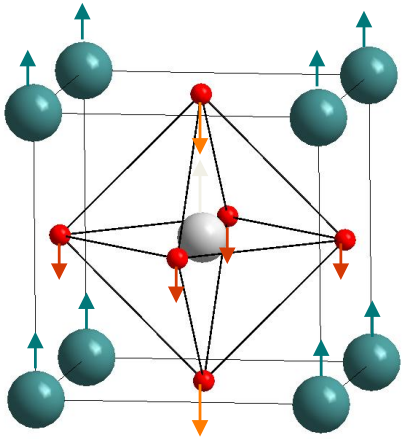
distortion modes:

- displacive type: local variable =atomic displacements
- order-disorder type: local variable: site occupation probabilities
- magnetic type: local variable: atomic magnetic moments

We can compare the amplitudes of different frozen distortion modes:



$Q_2 \vec{e}_2$



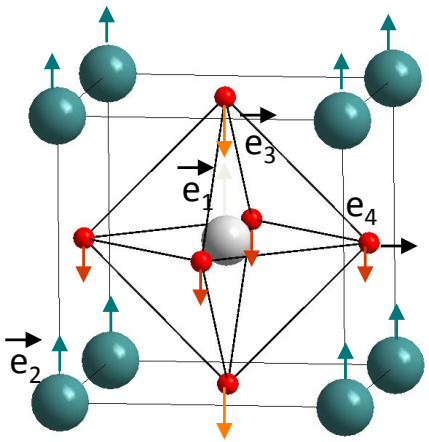
$Q_1 \vec{e}_1$

Q_1 and Q_2 have the same dimensions and their values can be compared

Modes in the statics of low-symmetry distorted phases:

Distorted Structure = High-symmetry Struct + "frozen" modes

distortion mode = Amplitude x polarization vector



Description of a "mode":

$\vec{u}(\text{atoms}) = Q\ \vec{e}$

amplitude | polarization vector

$\mathbf{e} = (\ \vec{e}_1\ ,\vec{e}_2\ ,\vec{e}_3\ ,\vec{e}_4\ )$

normalization: $|\vec{e}_1|^2 + |\vec{e}_2|^2 + |\vec{e}_3|^2 + 2\ |\vec{e}_4|^2 = 1$
(within a unit cell)

AMPLIMODES calculates the amplitudes and polarization vectors of all distortion modes with different symmetries (irreps) frozen in a distorted structure.

Phase Transition / Symmetry break / Order Parameter

High symmetry group $G = \{g\}$

Irreducible representation of G (irrep) (matrices)

$T(g)\,Q = Q$

g belongs to F

$T(g)\,Q = Q' \neq Q$

g does not belong to F: Q′ equivalent but distinguishable state

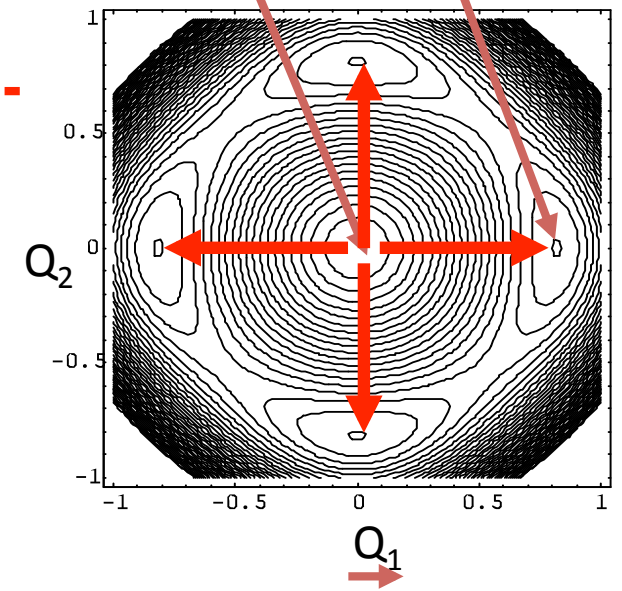
group-subgroup relation:

$G \rightarrow F$

F: isotropy subgroup

High symmetry

Low symmetry



amplitude

Order parameter $Q = (Q_1,Q_2) = \rho\,(a_1,a_2)$

$a_1^2+a_2^2 = 1$

Key concept of Landau theory:
It defines the type of symmetry break

Collective irrep modes is the natural language to describe the structure of distorted phases:

Hierarchy of modes:

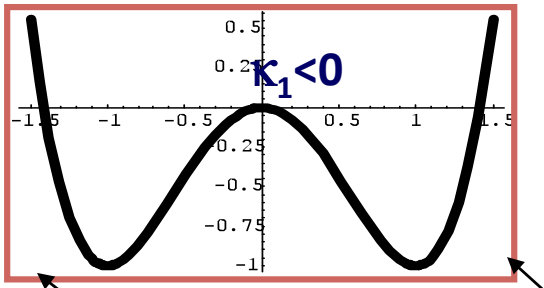
Von Neumann principle:
all modes compatible with the symmetry will be present in the total distortion ….

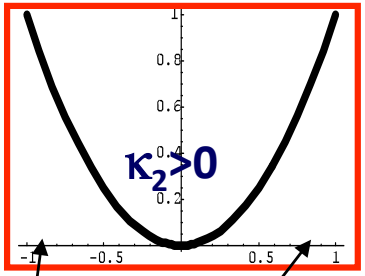
But not all with the same weight!:

primary mode(s): unstable ⟶ the origin of the distortion

secondary modes: induced by the presence of the primary one(s)

Hierarchy of modes



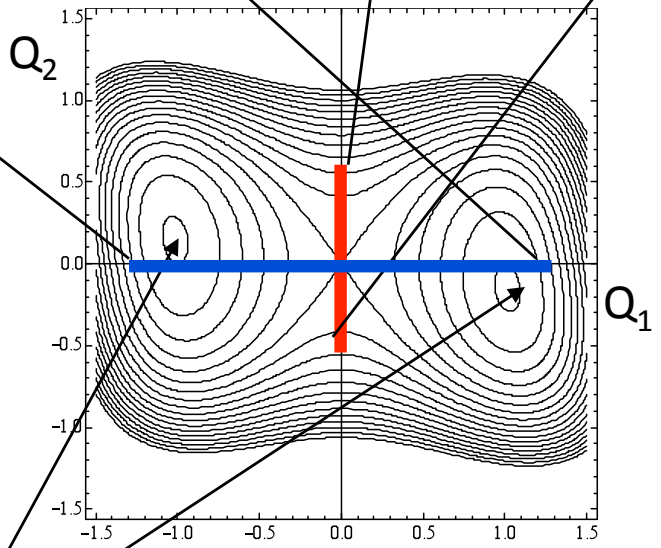


Example of a (free) energy map with primary (Q_1) and secondary (Q_2) distortion modes:

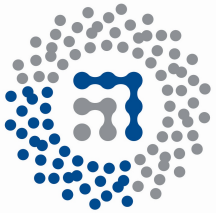
$$E = E_o + \tfrac{1}{2}\,\kappa_1 Q_1^2 + \tfrac{1}{2}\,\kappa_2 Q_2^2 + \gamma Q_1 Q_2^3 +$$

($\kappa_1<0$, $\kappa_2>0$)

Anharmonic allowed coupling



Equivalent ferroic stable structures



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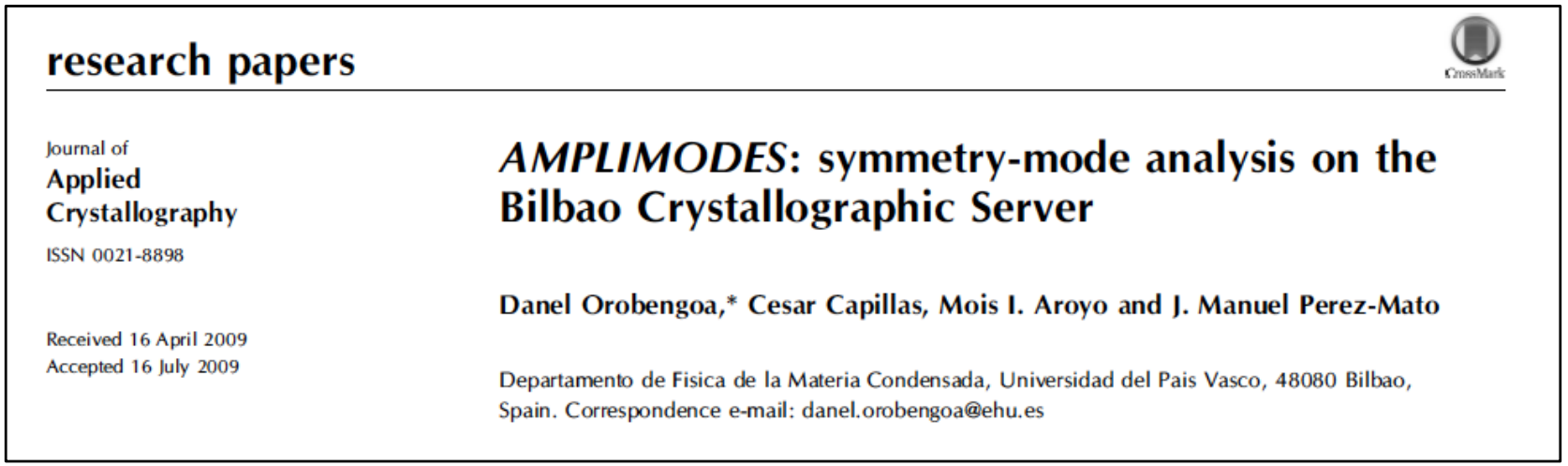
Facultad de Ciencia y Tecnología

Universidad del País Vasco
Euskal Herriko Unibertsitatea

Using AMPLIMODES

An introduction to the program:

"AMPLIMODES: symmetry-mode analysis on the Bilbao Crystallographic Server",
J. Appl. Cryst. (2009). 42, 820-833
D. Orobengoa, C. Capillas, M. I. Aroyo and J. M. Perez-Mato



research papers

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***AMPLIMODES*: symmetry-mode analysis on the Bilbao Crystallographic Server**

Danel Orobengoa,* Cesar Capillas, Mois I. Aroyo and J. Manuel Perez-Mato

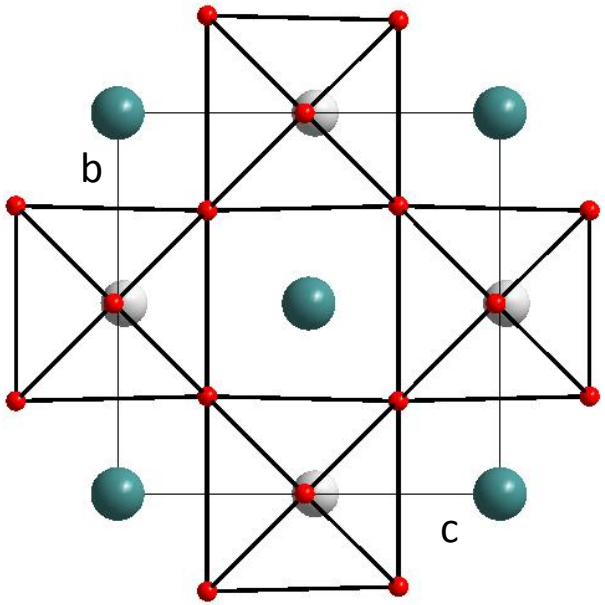
Departamento de Fisica de la Materia Condensada, Universidad del Pais Vasco, 48080 Bilbao, Spain. Correspondence e-mail: danel.orobengoa@ehu.es

A Tutorial is in the download material for this workshop and in the
Bilbao Crystallographic server (not updated!, the most recent features not included…):

site address: www.cryst.ehu.es

Example of input of AMPLIMODES:

Amm2 phase of $BaTiO_3$



High symmetry structure Pm-3m

```
221
4.006 4.006 4.006 90 90 90
3
Ba      1    1a      0.0 0.0 0
Ti      1    1b      0.5 0.5 0.5
O       1    3c      0.5 0.0 0.5
```

Low symmetry structure Amm2

```
38
3.9828 5.6745 5.6916 90 90 90
4
Ba      1    2a      0.0 0.0 0.0
Ti      1    2b      0.5 0.0 0.5170
O       1    2a      0.0 0.0 0.4890
O       2    4e      0.5 0.2561 0.2343
```

4 parameters

Transformation matrix Transf.

```
[      0      1      1 ]  [      0]
[      0     -1      1 ]  [      0]
[      1      0      0 ]  [      0]
```

Example of output of AMPLIMODES:

Reference structure:

Transformed high symmetry structure in the subgroup basis

```
038
4.006000 5.665339 5.665339 90.000000 90.000000 90.000000
4
Ba      1       2a      0.000000        0.000000        0.000000
Ti      1       2b      0.500000        0.000000        0.500000
O       1       4e      0.500000        0.250000        0.250000
O       1_2     2a      0.000000        0.000000        0.500000
```

Atom pairings and distances

Atom Mappings					
WP		Atom	Coordinates in S_1	Atom	Coordinates in S_2
2a	(0,0,z)	Ba1	(0,0,0)	Ba1	(0,0,0)
2b	(1/2,0,z)	Ti1	(1/2,0,1/2)	Ti1	(1/2,0,0.51700)
4e	(1/2,y,z)	O1	(1/2,1/4,1/4)	O2	(1/2,0.25610,0.23430)
2a	(0,0,z)	O1_2	(0,0,1/2)	O1	(0,0,0.48900)

WP		Atom	Atomic Distances			
			u_x	u_y	u_z	|d|
2a	(0,0,z)	Ba1	0.0000	0.0000	0.0000	0.0000
2b	(1/2,0,z)	Ti1	0.0000	0.0000	0.0170	0.0963
4e	(1/2,y,z)	O1	0.0000	0.0061	-0.0157	0.0954
2a	(0,0,z)	O1_2	0.0000	0.0000	-0.0110	0.0623

NOTE: d_x, d_y and d_z are given in relative units. |d| is the absolute distance given in Å

Maximum atomic displacement in the distortion, Δ: 0.0963 Å
Total distortion amplitude: 0.1771 Å

After origin shift

Relative origin shift to eliminate a global displacement: (0.00000, 0.00000, -0.00508)

Atom Mappings					
WP		Atom	Coordinates in S_1	Atom	Coordinates in S_2
2a	(0,0,z)	Ba1	(0,0,0)	Ba1	(0,0,0.00508)
2b	(1/2,0,z)	Ti1	(1/2,0,1/2)	Ti1	(1/2,0,0.52208)
4e	(1/2,y,z)	O1	(1/2,1/4,1/4)	O2	(1/2,0.25610,0.23938)
2a	(0,0,z)	O1_2	(0,0,1/2)	O1	(0,0,0.49408)

WP		Atom	Atomic Distances			
			u_x	u_y	u_z	|d|
2a	(0,0,z)	Ba1	0.0000	0.0000	0.0051	0.0288
2b	(1/2,0,z)	Ti1	0.0000	0.0000	0.0221	0.1251
4e	(1/2,y,z)	O1	0.0000	0.0061	-0.0106	0.0694
2a	(0,0,z)	O1_2	0.0000	0.0000	-0.0059	0.0335

NOTE: d_x, d_y and d_z are given in relative units. |d| is the absolute distance given in Å
Maximum atomic displacement in the distortion, Δ: 0.1251 Å
Total distortion amplitude: 0.1650 Å

Symmetry Modes Summary

Atoms	WP	Modes
O1	3*c*	**GM4-(2) GM5-(1)**
Ti1	1*b*	**GM4-(1)**
Ba1	1*a*	**GM4-(1)**

Note: The primary mode is written in bold letters

Summary of Amplitudes

K-vector	Irrep	Direction	Isotropy Subgroup	Dimension	Amplitude (Å)
(0,0,0)	GM4-	(a,a,0)	Amm2 (38)	4	0.1649
(0,0,0)	GM5-	(0,a,-a)	Amm2 (38)	1	0.0056

Global distortion: 0.1650 Å

Example of output of AMPLIMODES:

Normalized Symmetry modes

The modes are normalized to the low symmetry unit c
cell and are given as relative displacements in this cell.

Irrep GM4-

GM4- Mode Ba1 1

Atom	δx	δy	δz
Ba1	0.000000	0.000000	0.176512

GM4- Mode Ti1 1

Atom	δx	δy	δz
Ti1	0.000000	0.000000	0.176512

GM4- Mode O1 1

Atom	δx	δy	δz
O1	0.000000	0.062406	0.062406
O1_2	0.000000	0.000000	0.124813

GM4- Mode O1 2

Atom	δx	δy	δz
O1	0.000000	-0.088256	0.088256
O1_2	0.000000	0.000000	0.000000

basis for this 4dim vector

Irrep GM5-

GM5- Mode O1 1

Atom	δx	δy	δz
O1	0.000000	-0.062406	-0.062406
O1_2	0.000000	0.000000	0.124813

K-vector: GM = (0,0,0)

Irrep: GM4-

Direction: (a,a,0)

Isotropy Subgroup: 38 Amm2 C2v-14

Transformation matrix:

```
[     0     1     1 ] [     0]
[     0    -1     1 ] [     0]
[     1     0     0 ] [     0]
```

amplitude of the GM4- distortion

The amplitude of this distortion is:
A_{GM4-} = 0.1649 Å

Normalized polarization vector: (in terms of the amplitudes of the (normalized)

Ba1 1	Ti1 1	O1 1	O1 2
0.1745	0.7585	-0.2536	-0.5744

as a vector (norm 1) with 4 components

NOTE: A second number next to the label counts the different symmetry modes that

Normalized polarization vector expressed as displacements (in cell relative un
Ångström)

Atom	δx	δy	δz
Ba1	0.0000	0.0000	0.0308
Ti1	0.0000	0.0000	0.1339
O1	0.0000	0.0349	-0.0665
O1_2	0.0000	0.0000	-0.0317

polarization vector in two forms

crystallographic form

Virtual structure with only this symmetry component of the distortion frozen.

Example of output of AMPLIMODES:

O1	0.0000	0.0349	-0.0665
O1_2	0.0000	0.0000	-0.0317

= -0.2536 x

GM4- Mode O1 1

Atom	δx	δy	δz
O1	0.000000	0.062406	0.062406
O1_2	0.000000	0.000000	0.124813

+ (-0.5744)x

GM4- Mode O1 2

Atom	δx	δy	δz
O1	0.000000	-0.088256	0.088256
O1_2	0.000000	0.000000	0.000000

4dim vector

GM4- Mode O1 1

Atom	δx	δy	δz
O1	0.000000	0.062406	0.062406
O1_2	0.000000	0.000000	0.124813

GM4- Mode O1 2

Atom	δx	δy	δz
O1	0.000000	-0.088256	0.088256
O1_2	0.000000	0.000000	0.000000

Normalized polarization vector: (in terms of the amplitudes of the (normalized)

Ba1 1	Ti1 1	O1 1	O1 2
0.1745	0.7585	-0.2536	-0.5744

as a vector (norm 1) with 4 components

NOTE: A second number next to the label counts the different symmetry modes that

Normalized polarization vector expressed as displacements (in cell relative un
Ångström)

Atom	δx	δy	δz
Ba1	0.0000	0.0000	0.0308
Ti1	0.0000	0.0000	0.1339
O1	0.0000	0.0349	-0.0665
O1_2	0.0000	0.0000	-0.0317

polarization vector in two forms

crystallographic form

Irrep GM5-

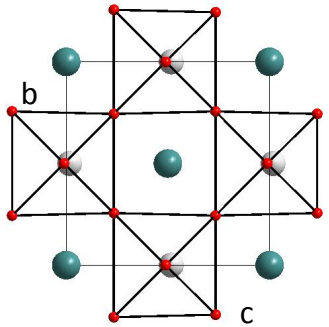
GM5- Mode O1 1

Atom	δx	δy	δz
O1	0.000000	-0.062406	-0.062406
O1_2	0.000000	0.000000	0.124813

Virtual structure with only this symmetry component of the distortion frozen.

The orthorhombic Amm2 structure of $BaTiO_3$

(Kwei et al. (1993) neutron-powder 190 K)



Perovskite in Amm2 setting

	δx	δy	δz
Ba1	0.0	0.0	0.0
Ti1	0.5	0.0	0.5
O1	0.5	0.25	0.25
O12	0.0	0.0	0.5

+

polarization vector GM4-

	δx	δy	δz
Ba1	0.0	0.0000	0.0308
Ti1	0.0	0.0000	0.1339
O1	0.0	0.0349	-0.0665
O12	0.0	0.0000	-0.0317

+ Q_{GM4-}

polarization vector GM5-

	δx	δy	δz
Ba1	0.0	0.0000	0.0000
Ti1	0.0	0.0000	0.0000
O1	0.0	0.0624	0.0624
O12	0.0	0.0000	-0.1248

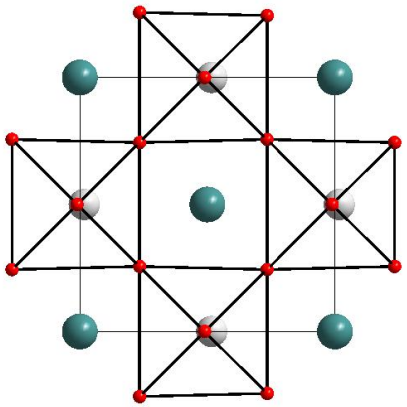
+ Q_{GM5-}

Q_{GM4-} = 0.165 Å

Q_{GM5-} = 0.006 Å

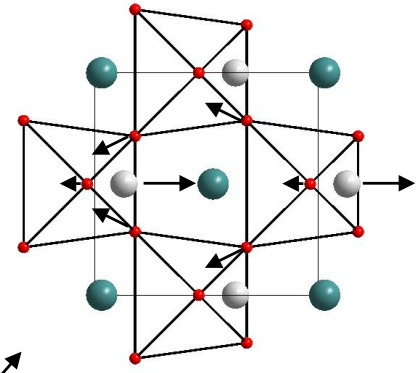
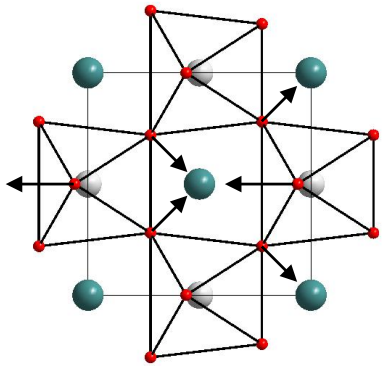
The orthorhombic Amm2 structure of $BaTiO_3$

(Kwei et al. (1993) neutron-powder 190 K)



max. atomic displ. : 0.13 Å

Mode decomposition of distortion:

Q_{GM4-} x  + Q_{GM5-} x 

GM4- mode

GM5- mode

polar ferroelectric mode

$Q_{GM4-} >> Q_{GM5-}$

Applications of symmetry mode analysis of distorted structures:

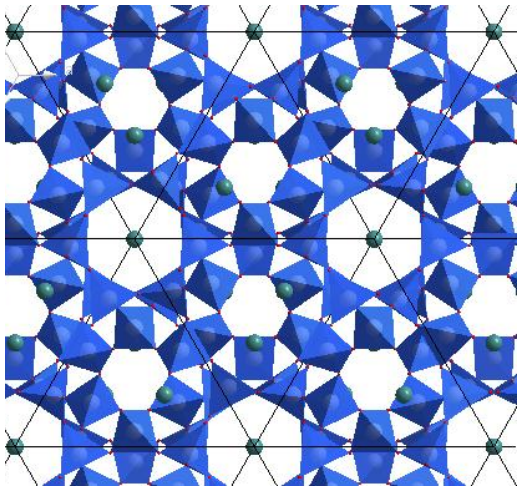
- identification of fundamental and marginal degrees of freedom
- reduction of the effective number of crystallographic parameters
- detection of false refinement minima
- quantitative comparison of structures with the same or different space group
- detection of hidden structural correlations (specially for low symmetry distortions)
- systematic characterization of variation of the structure with temperature
- rationalization of phase diagrams and various symmetries in families of compounds.

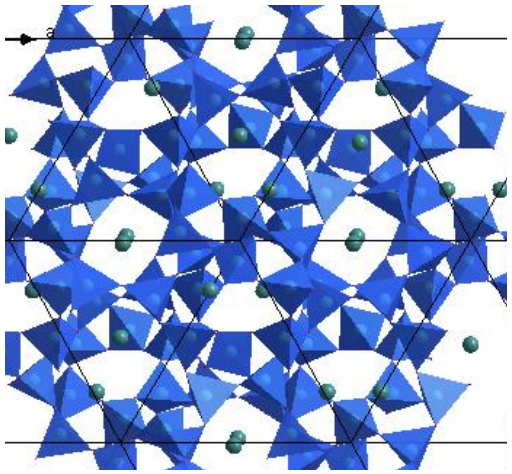
Leucite

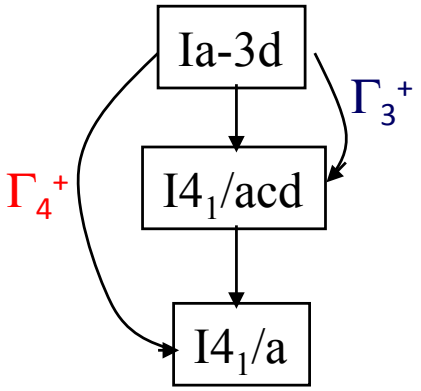
$KAlSi_2O_6$

$I4_1/a$ Palmer et. (Amer. Miner. 82 (1997) 16

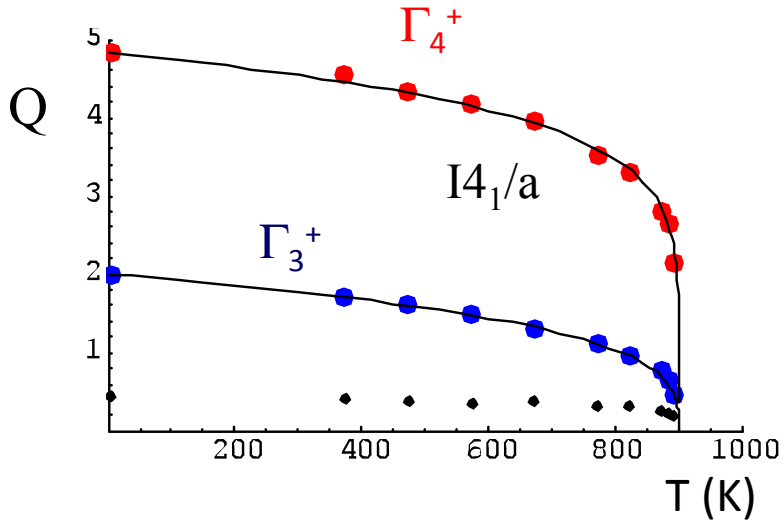
max. atomic displ. : 1.04Å







DISTORTION AMPLITUDES VS. TEMPERATURE:

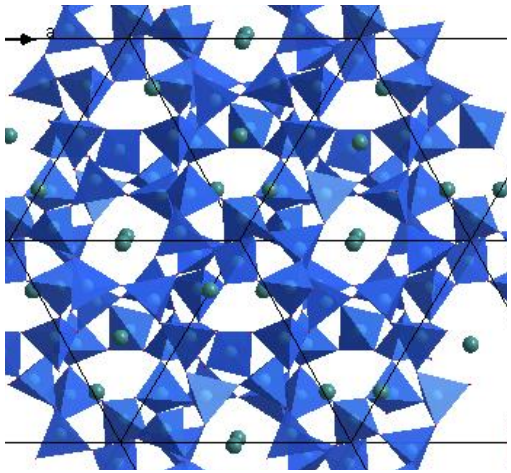


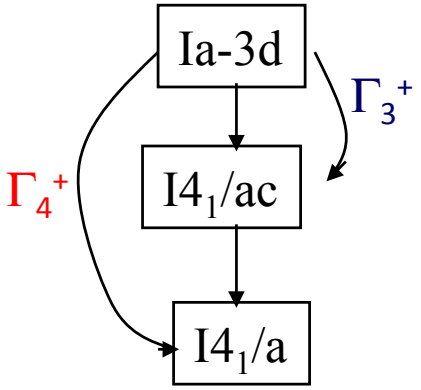
Induced effect : $Q_{\Gamma 3+} = \alpha\, Q^2_{\Gamma 4+}$

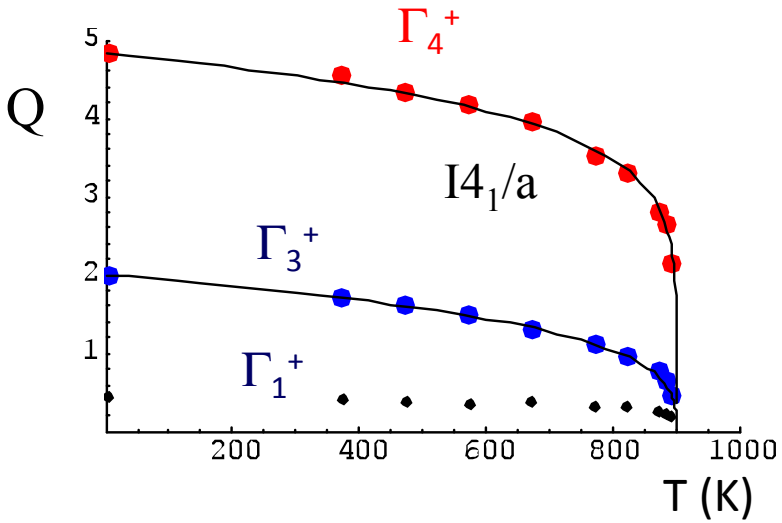
Polarization vectors in Leucite

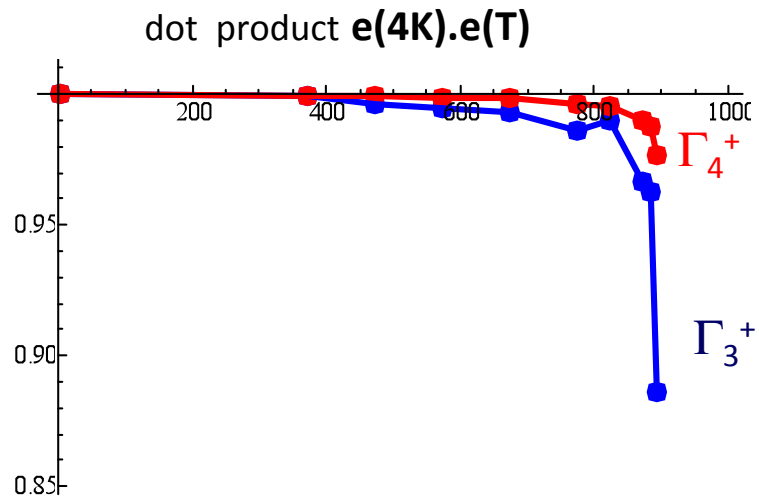
$I4_1/a$ Palmer et. (Amer. Miner. 82 (1997) 16

$KAlSi_2O_6$









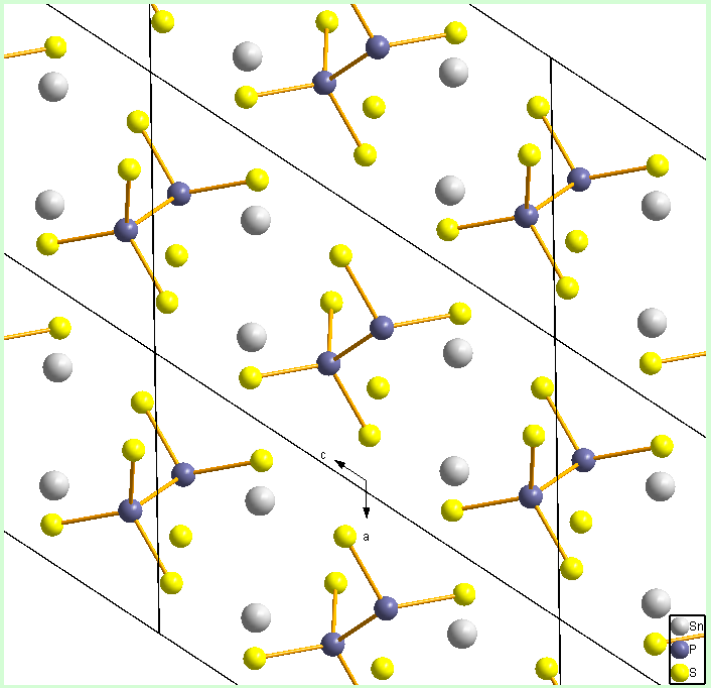
Induced effect : $Q_{\Gamma 3+} = \alpha\, Q^2_{\Gamma 4+}$

Exercise A1

Ferroelectric phase of $S_2Sn_2P_6$

How does the symmetry mode decomposition depends on the parent structure?

Exercise A1: $S_2Sn_2P_6$



Summary of Amplitudes

K-vector	Irrep	Direction	Isotropy Subgroup	Dimension	Amplitude (Å)
(0,0,0)	GM1+	(a)	P2_1/c (14)	15	0.1714
(0,0,0)	GM2-	(a)	Pc (7)	15	0.4883

changing the parent structure:

K-vector	Irrep	Direction	Isotropy Subgroup	Dimension	Amplitude (Å)
(0,0,0)	GM1+	(a)	P2_1/c (14)	15	4.1205
(0,0,0)	GM2-	(a)	Pc (7)	15	0.4883

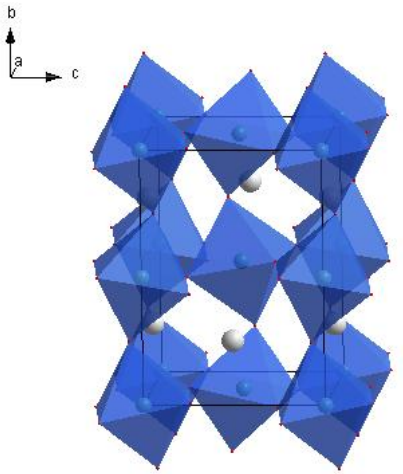
using the option for FullProf (and the "good" parent):

K-vector	Irrep	Direction	Isotropy Subgroup	Dimension	Amplitude (Å)
(0,0,0)	GM1+	(a)	P2_1/c (14)	15	0.1713
(0,0,0)	GM2-	(a)	Pc (7)	15	0.5372

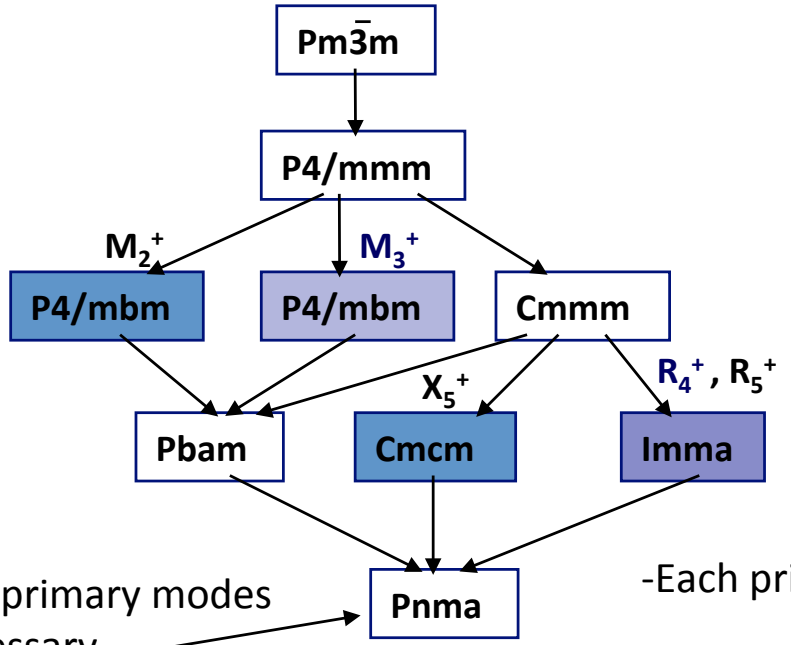
Sequence of transitions in $SrZrO_3$

20 C

Pnma



(Howard et al. 2000 & data from B. Kennedy)



two primary modes necessary

-Each primary mode is a different instability mechanism

- each primary mode condenses in general at different temperatures : two phase transitions

Q_{M2+} = 0.007 Å

Q_{M3+} = 0.794 Å

Q_{X5+} = 0.338 Å

Q_{R4+} = 1.185 Å

Q_{R5+} = 0.069 Å

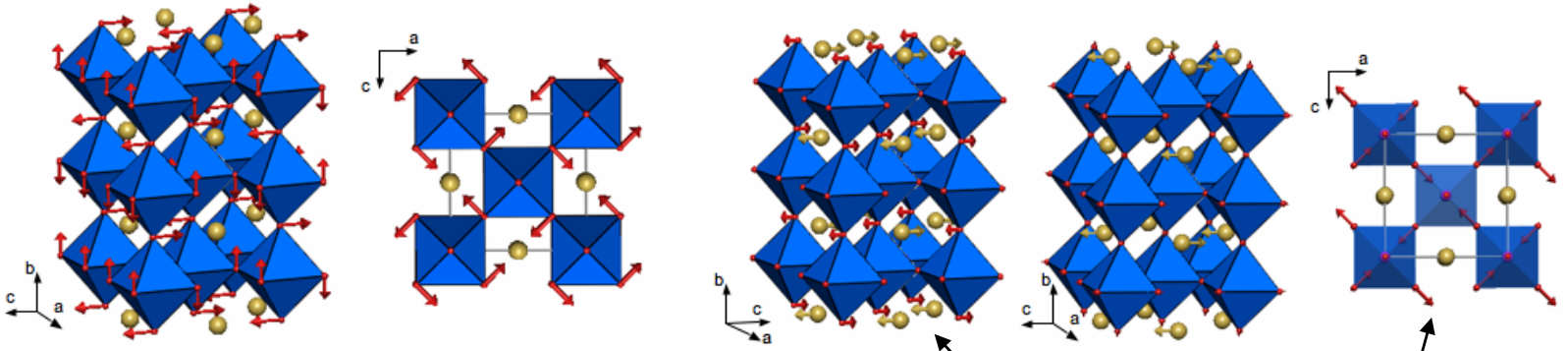
→ Pnma

Expected transition sequence:

T > →

Pnma (M_3^+, R_4^+) → Imma (R_4^+) → Pm3̄m

Sequence of transitions in $SrZrO_3$



R_4^+
1.18 Å

M_3^+
0.79 Å

X_5^+
0.338 Å

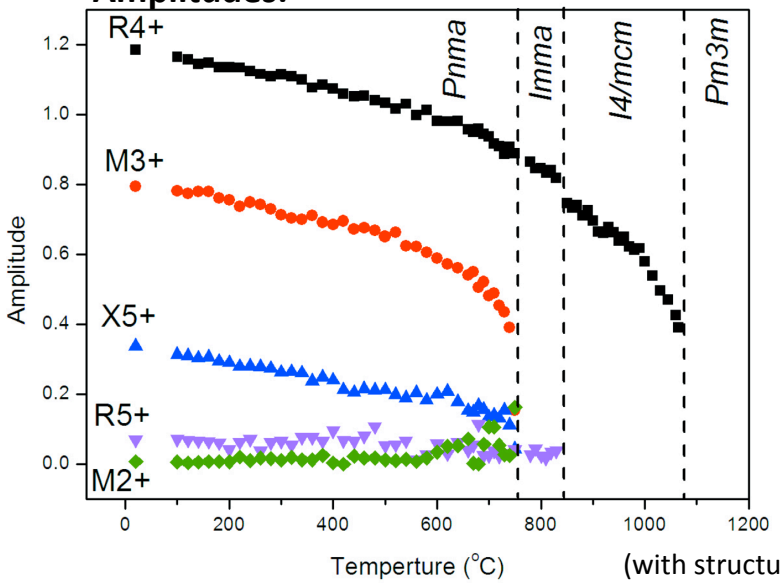
R_5^+
0.07 Å

M_2^+
0.007 Å

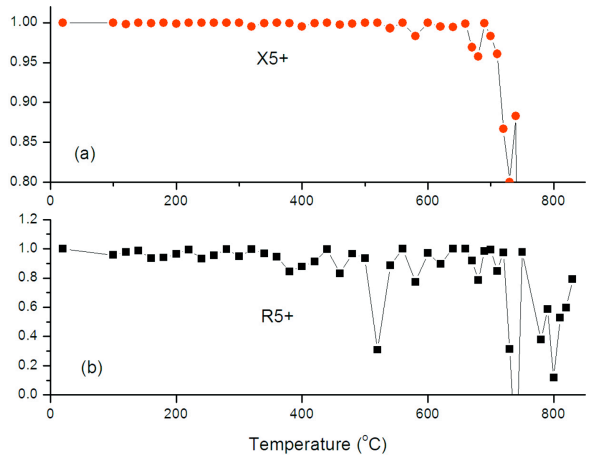
They deform the octahedra.
X_5^+ has significant amplitude

Temperature variation:

Amplitudes:



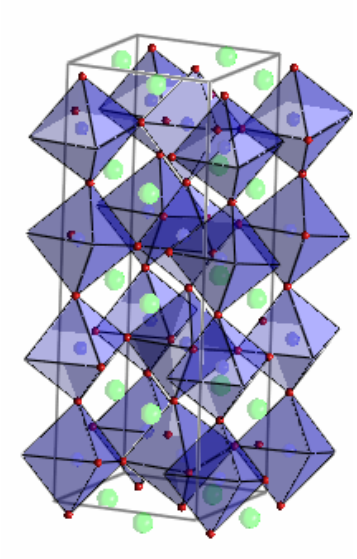
modes polarization vectors:

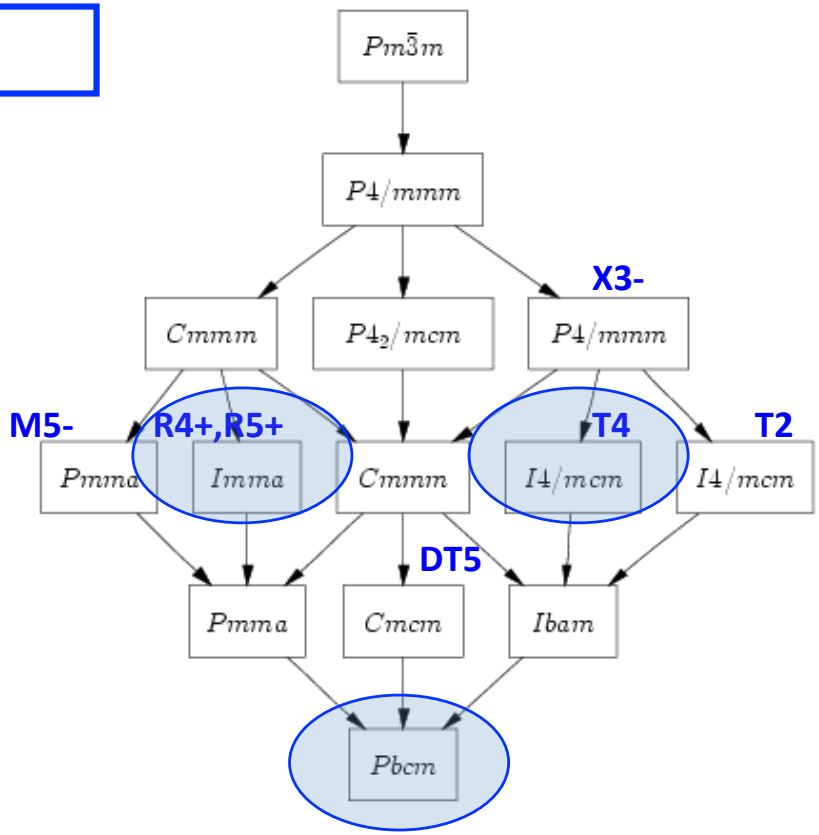


(with structural data from Kennedy, Howard and K.S. Knight, 2010)

Another distorted perovskite. $NaNbO_3$

Pbcm – 15 atomic coordinates





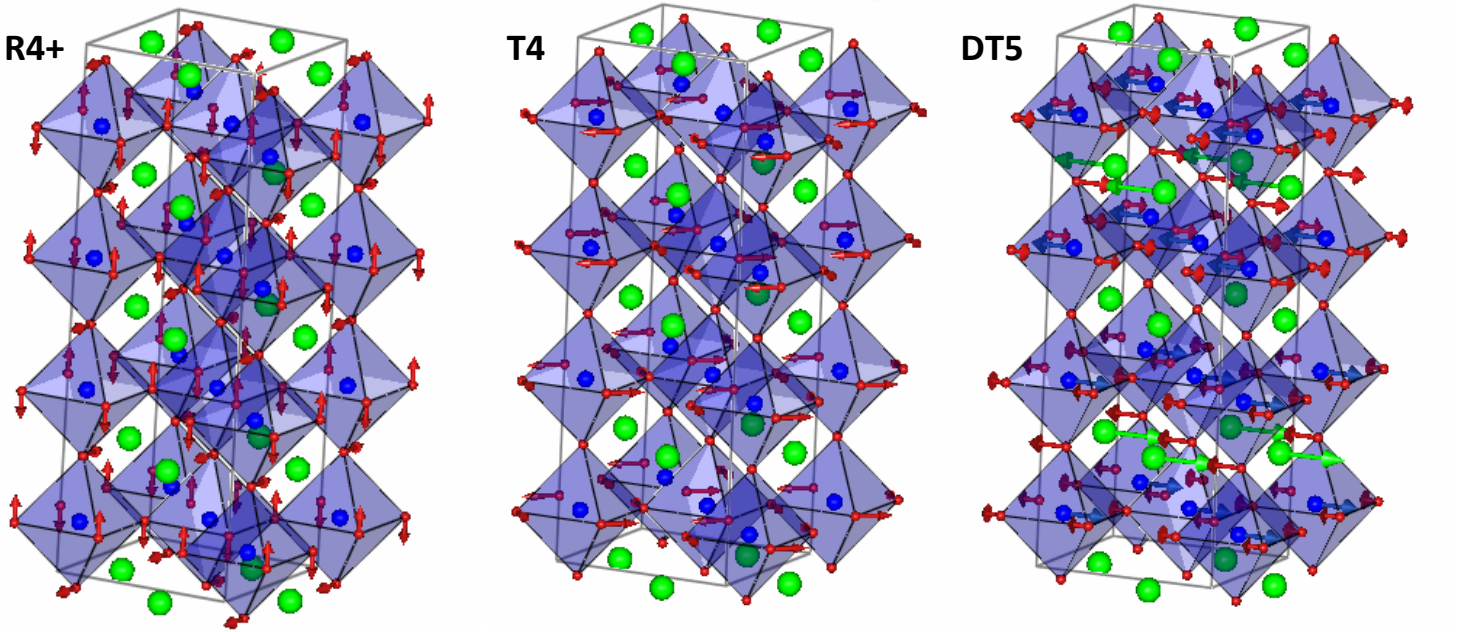
k-vector	irrep	direction	isotropy subgroup	dim.	amplitude (Å)
(0,1/4,0)	**DT5**	**(0,0,0,0,0,0,0,0,a,0,0,-a)**	***Cmcm* (a-b,a+b,4c;0,0,1/2)**	**5**	**0.55**
(1/2,1/2,1/2)	**R4+**	**(0,a,a)**	***Imma* (a+b,2c, a-b,;0,0,0)**	**1**	**1.38**
(1/2,1/2,1/2)	R5+	(0,a,-a)	*Imma* (**a+b**,2**c**, **a-b**,;0,0,0)	2	0.03
(0,1/2,0)	X3-	(0,a,0)	*P4/mmm*(**a**,**b**,2**c**;0,0,1/2)	2	0.08
(1/2,1/2,0)	M5-	(0,0,0,-a,0,0)	*Pmma* (**a+b**,**c**,**a-b**;0,1/2,0)	3	0.16
(1/2,1/2,1/4)	T2	(a,a,0,0,0,0)	*I4/mcm* (**a-b**,**a+b**,4**c**;1/2,1/2,1/2)	1	0.00
(1/2,1/2,1/4)	**T4**	**(a,-a,0,0,0,0)**	***I4/mcm* (a-b,a+b,4c;0,0,1/2)**	**1**	**1.07**

max atom. displ. : 0.40 Å

Predominant irrep distortions in $NaNbO_3$

primary distortions (RUMs)

secondary distortions



1.38 Å

1.07 Å

0.55 Å

$q_1 = (1/2,1/2,1/2)$

$q_2 = (1/2,1/2,1/4)$

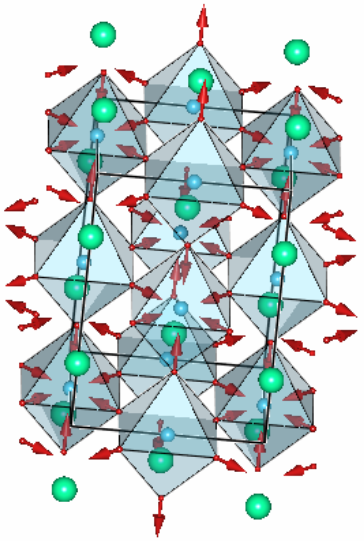
$q_3 = q_1 - q_2 = (0,0,1/4)$

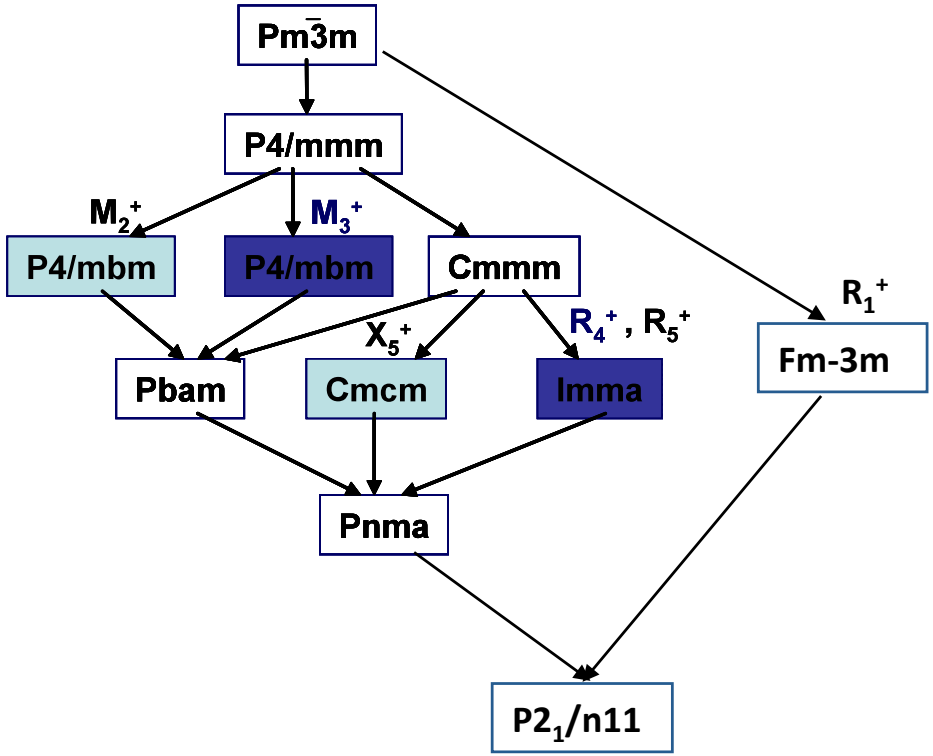
$PrNiO_3$ Charge disproportionation

$P2_1/n$ instead of Pnma

Medarde et al. PRL (2007)

Mode R1+:





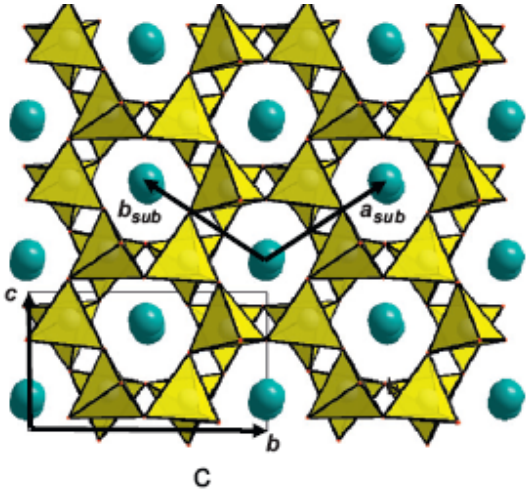
Amplitudes		SrZrO3	PrNiO3
R4+	(Imma)	1.19(1)	1.092(9)
M3+	(P4/mbm)	0.79(1)	0.689(9)
X5+	(Cmcm)	0.34(1)	0.361(4)
R5+		0.07(1) (Imma)	0.06(1) (C2/m)
M2+	(P4/mbm)	0.01(1)	0.004(9)
R1+	**(Fm-3m)**	-	**0.091(9)**
R3+	(I4/mmm)	-	0.012(9)
M5+	(Pmna)	-	0.00(1)

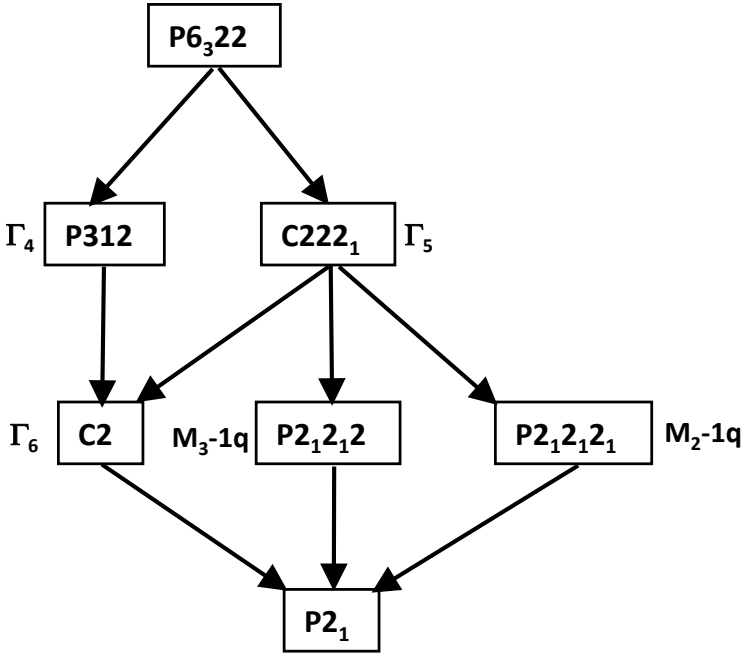
Mode decomposition vs. ab-initio calculations

$SrAl_2O_4$

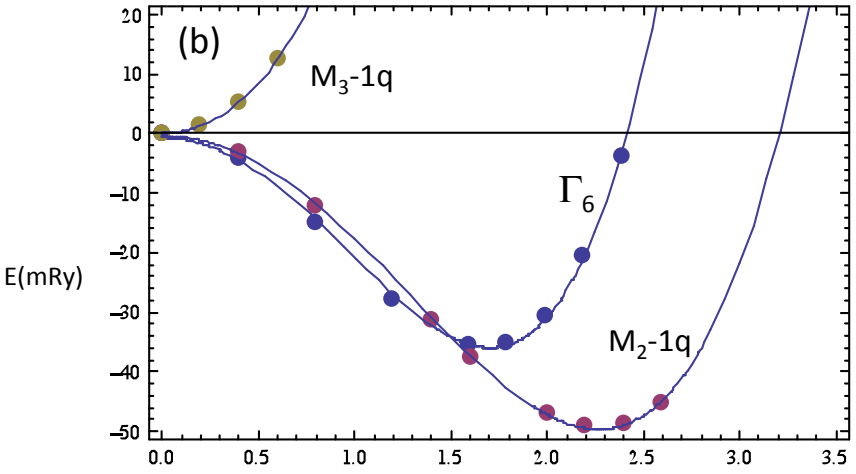
$P6_322 \longrightarrow P2_1$

(Larsson et al. 2008)



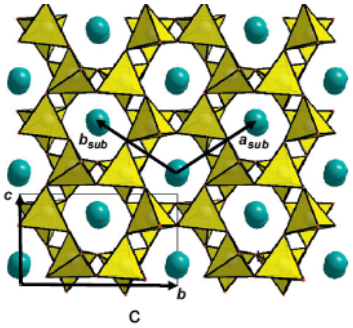


two different displacive instabilities:



$SrAl_2O_4$

Comparison of mode decomposition of experimental and ab-initio structures

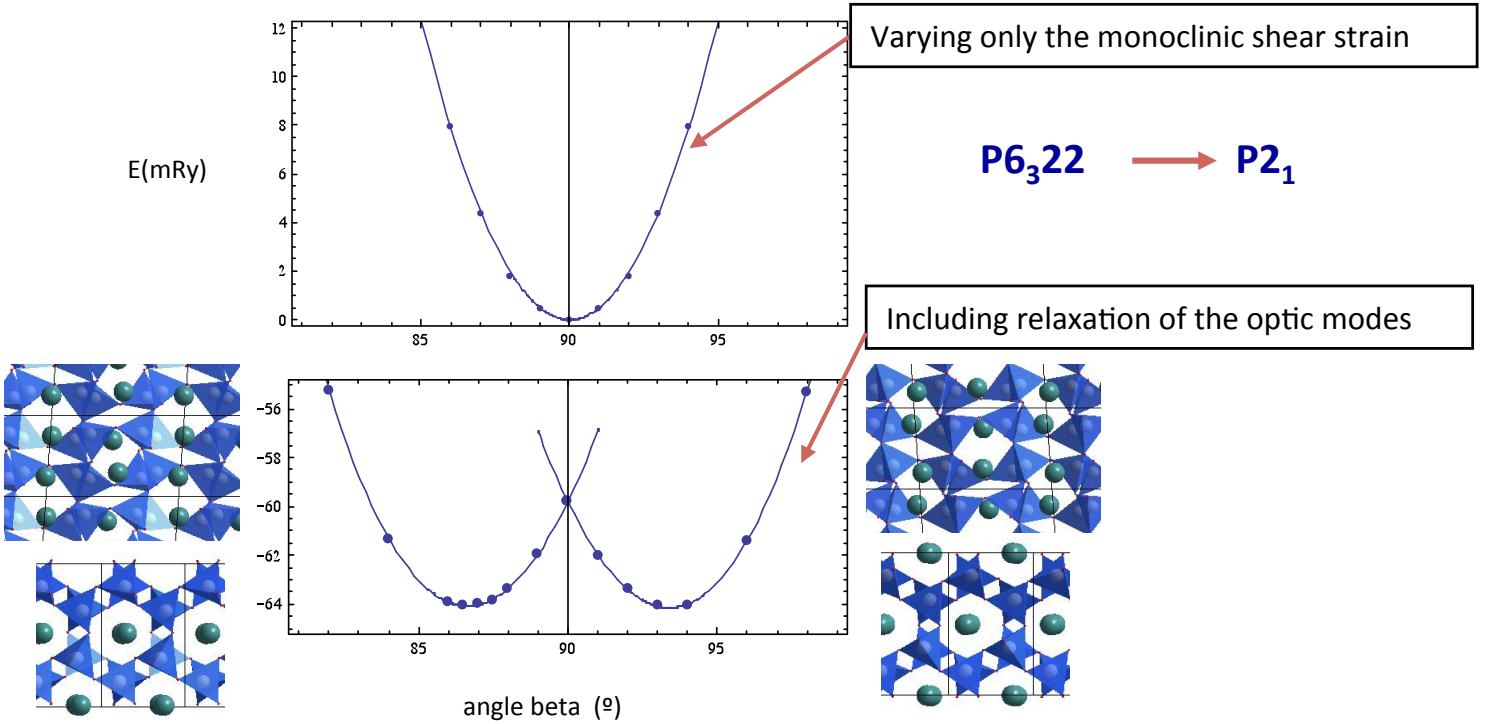


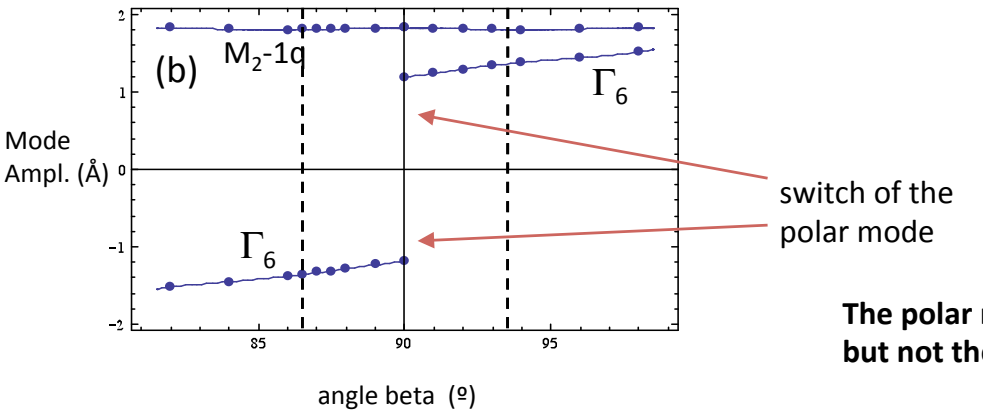
Amplitudes and dot products of polarization vectors :

irrep	M_2-1q		Γ_6		M_3-1q		Γ_5		Γ_4	
dim.	12		7		11		7		3	
	Amp.	prod.	Amp.	prod.	Amp.	prod.	Amp.	prod.	Amp.	prod.
Exp. Struct.	1.70		1.39		0.57		0.32		0.02	
ab-initio	1.81	0.998	1.35	0.9997	0.57	0.997	0.24	0.96	0.03	0.63

$SrAl_2O_4$

Independent various behaviour of modes, seen in ab-initio calculations: ferroelastic-ferroelectric coupling





shear strain- polar mode bilinear coupling

Behaviour of the structure to external perturbations (i.e. shear stress) is different for different modes….

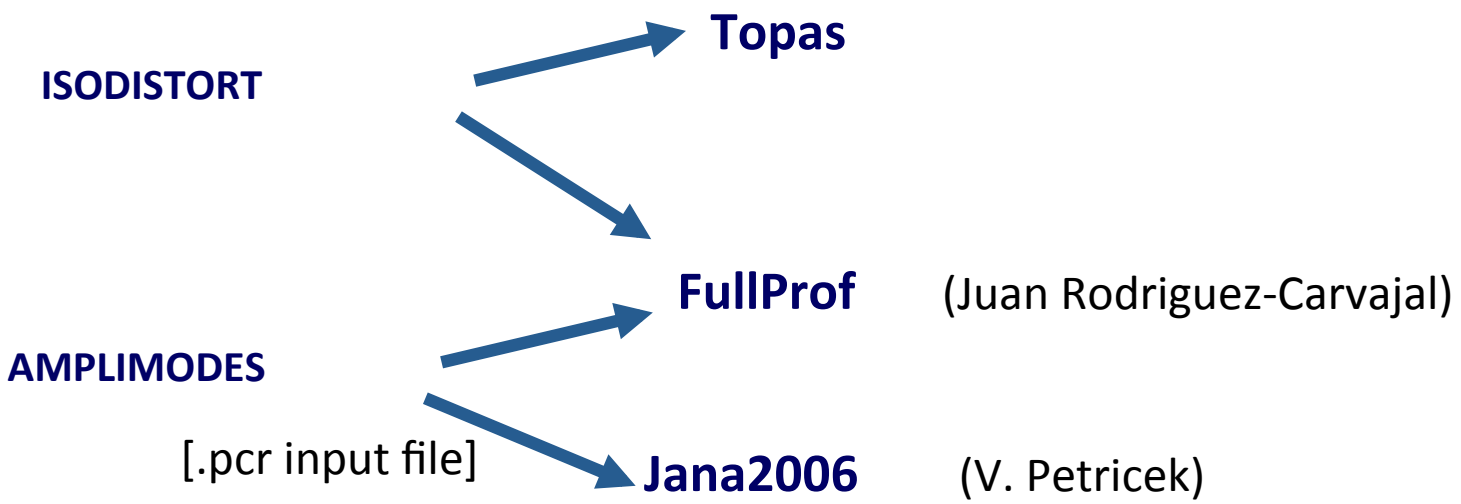
The polar mode Γ_6 is coupled linearly with the shear strain but not the other primary distortion mode M_2-1q

Switch of the polarization through the shear

Use of mode coordinates in the structure refinement, instead of the individual atomic coordinates?

One expects:

- a natural hierarchy of parameters
- less correlations with atomic (thermal) displacement parametes
- minimize correlations

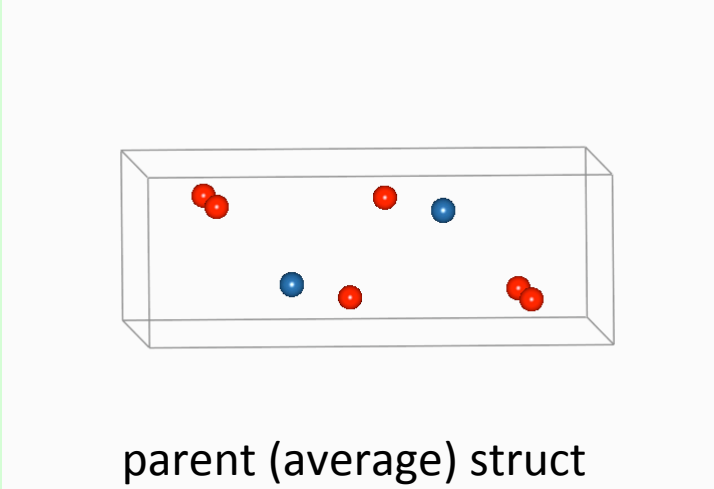


Symmetry-mode decomposition

Exercise A2

A simple example: the triclinic structure of NbS_3

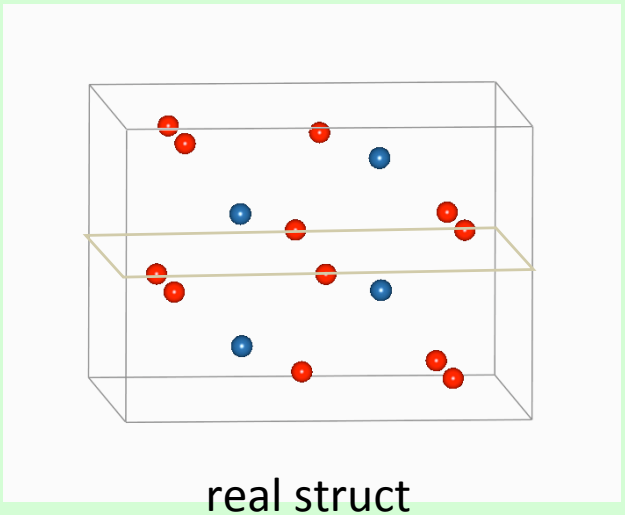
$P2_1/m$ Z=2



parent (average) struct

8 positional parameters

P-1 (a,2b,c;000) Z=4



real struct

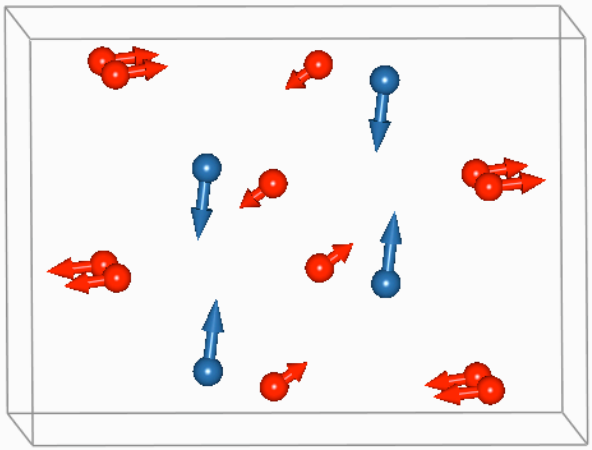
24 positional parameters

parent $P2_1/m$ struct. in the *P-1* setting:

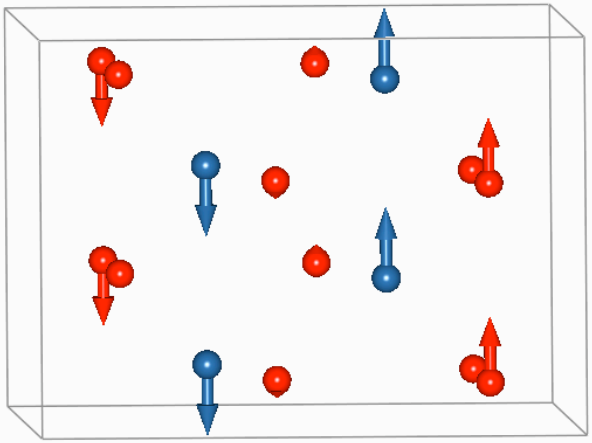
002
4.963 6.730 9.144 90.00 97.17 90.00
8

Nb	1	2i	0.715500	0.375000	0.348650
Nb	1_2	2i	0.715500	0.875000	0.348650
S	1	2i	0.763400	0.125000	0.553550
S	1_2	2i	0.236600	0.375000	0.446450
S	2	2i	0.878850	0.125000	0.169450
S	2_2	2i	0.121150	0.375000	0.830550
S	3	2i	0.466950	0.125000	0.174150
S	3_2	2i	0.533050	0.375000	0.825850

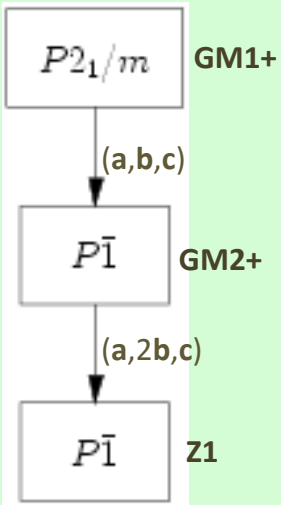
Symmetry-mode decomposition of NbS_3 structure:



Z1 distortion



GM2+ distortion



k-vector	irrep	direction	isotropy subgroup	dim.	amplitude(Å)
(0,0,0)	**GM1+**	(a)	$P2_1/m$ (**a**,**b**,**c**;0,0,0)	8	**0.000(5)**
(0,0,0)	**GM2+**	(a)	*P-1* (**a**,**b**,**c**;0,0,0)	4	**0.036(3)**
(0,1/2,0)	**Z1**	(0,a)	*P-1* (**a**,2**b**,**c**;0,0,0)	12	**0.520(4)**

max atom. displ. : 0.18 Å

Symmetry-mode decomposition of NbS_3 structure. Quantitative description:

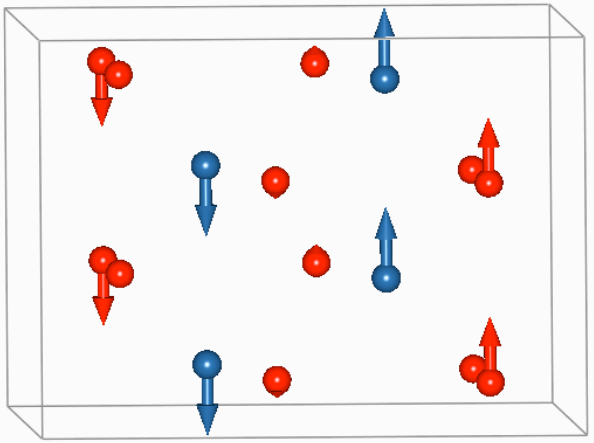
GM2+ distortion (dim 4)

Amplitude: 0.036(3) Å

4 allowed orthogonal symmetry-modes

(normalized) polarization vector:

Atom	δx	δy	δz
Nb1	0.0000	0.0536	0.0000
Nb1_2	0.0000	0.0536	0.0000
S1	0.0000	-0.0137	0.0000
S1_2	0.0000	0.0137	0.0000
S2	0.0000	0.0495	0.0000
S2_2	0.0000	-0.0495	0.0000
S3	0.0000	-0.0027	0.0000
S3_2	0.0000	0.0027	0.0000



GM2+ distortion

4 positional parameters

as a 4 dim vector in terms of normalized symmetry modes (3 indep. parameters):

Nb1 1	S1 1	S2 1	S3 1
-0.7216	-0.1850	0.6661	-0.0370

Symmetry-mode decomposition of NbS_3 structure

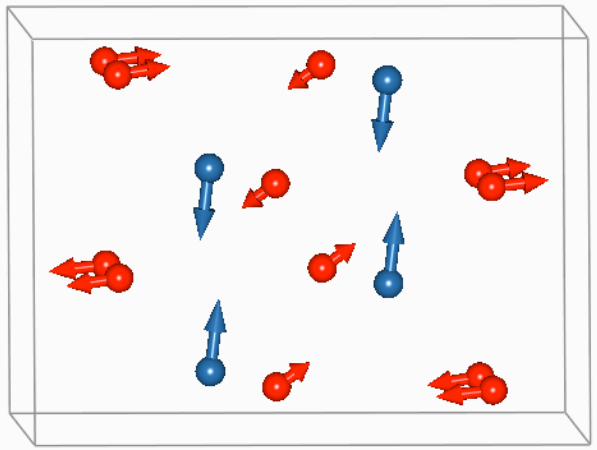
Z1 distortion (dim 12)

Amplitude: 0.520(4) Å

12 allowed orthogonal symmetry-modes

(normalized) polarization vector:

Atom	δx	δy	δz
Nb1	-0.0002	0.0469	-0.0043
Nb1_2	0.0002	-0.0469	0.0043
S1	0.0004	0.0158	-0.0159
S1_2	0.0004	0.0158	-0.0159
S2	0.0080	-0.0039	0.0274
S2_2	0.0080	-0.0039	0.0274
S3	0.0074	-0.0048	0.0253
S3_2	0.0074	-0.0048	0.0253



Z1 distortion

12 positional parameters

or as a 12 dim vector in terms of normalized symmetry modes (11 indep. parameters):

Nb1 1	Nb1 2	Nb1 3	S1 1	S1 2	S1 3	S2 1	S2 2	S2 3	S3 1	S3 2	S3 3
0.6309	0.0790	0.0019	0.2124	0.2909	-0.0038	-0.0518	-0.4917	-0.0787	-0.0648	-0.4537	-0.0730

Exercise A3 **False minimum in the refinement of the structure of $BaMnO_3$**

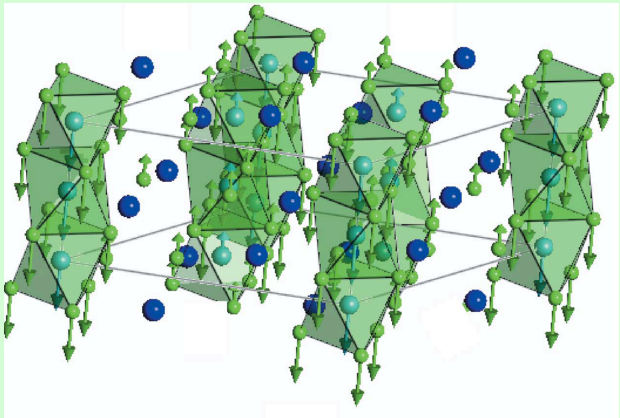
Example 3: $BaMnO_3$ - False minimum

80K

Summary of Amplitudes

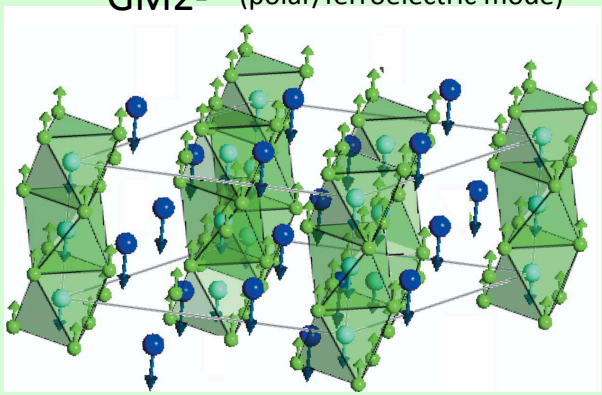
K-vector	Irrep	Direction	Isotropy Subgroup	Dimension	Amplitude (Å)
(0,0,0)	GM1+	(a)	P6_3/mmc (194)	1	0.03(4)
(0,0,0)	GM2-	(a)	P6_3mc (186)	3	0.14(6)
(1/3,1/3,0)	K1	(a,0)	P6_3/mcm (193)	3	0.04(5)
(1/3,1/3,0)	K3	(a,0)	P6_3cm (185)	2	0.42(6)

K_3



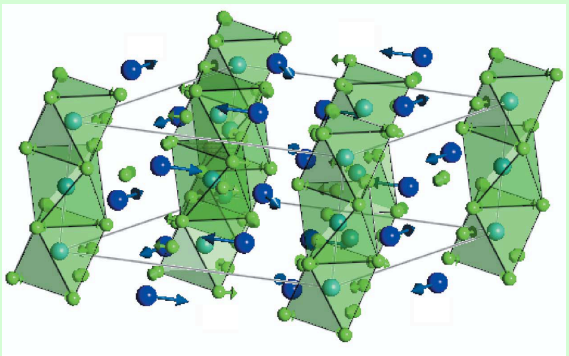
0.42 Å

GM2- (polar/ferroelectric mode)



0.14Å

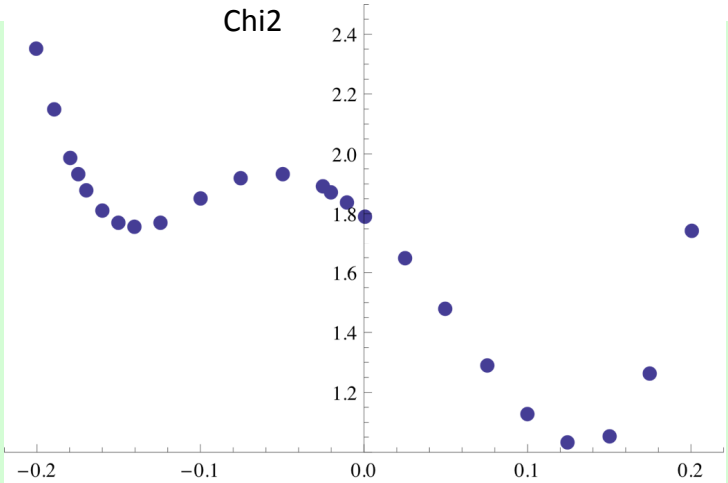
K_1



0.04Å

Example 3: $BaMnO_3$ - False minimum

K-vector	Irrep	Direction	Isotropy Subgroup	Dimension	Amplitude (Å) at 80 K	Amplitude (Å) at 1.7 K	dot product polariz. vectors
(0,0,0)	GM1+	(a)	P6_3/mmc	1	0.00(4)	0.02(2)	
(0,0,0)	GM2-	(a)	P6_3mc	3	0.14(6)	0.14(7)	0.996
(1/3,1/3,0)	K1	(a,0)	P6_3/mcm	3	0.04(5)	0.15(3)	-0.90
(1/3,1/3,0)	K3	(a,0)	P6_3cm	2	0.42(6)	0.53(7)	0.9998



Amplitude of one K1 basis mode