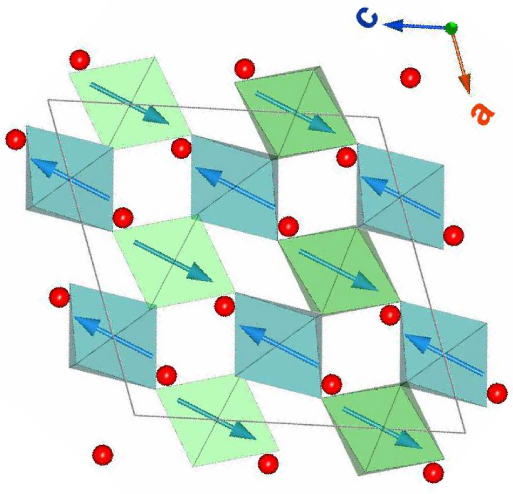
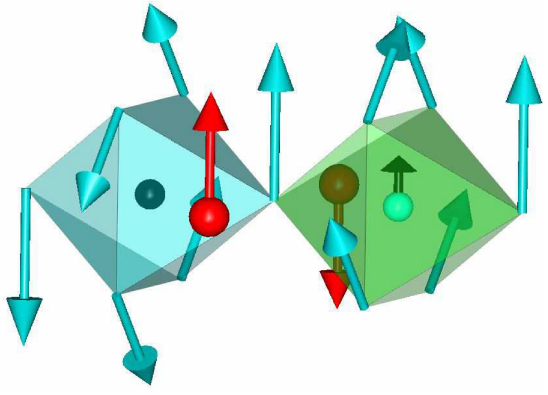
Symmetry adapted analysis of $Bi_{1-x}Y_xCrO_3$ perovskites



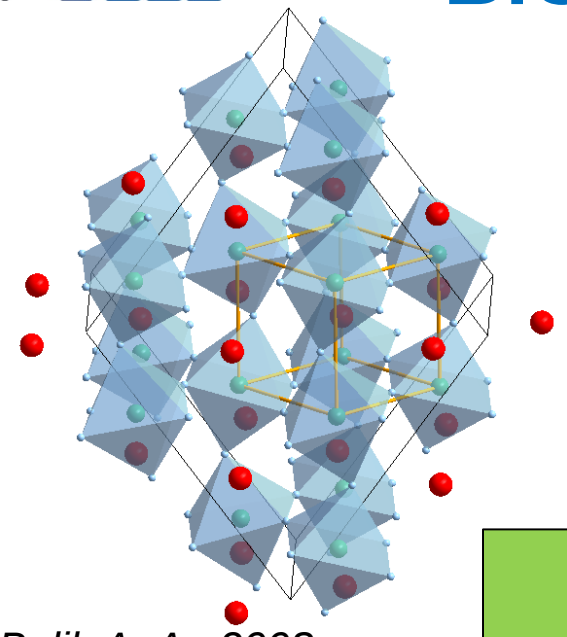


Claire V. Colin, Pierre Bordet, Céline Goujon, Céline Darie

Institut Néel, CNRS and University Joseph Fourier, Grenoble, France

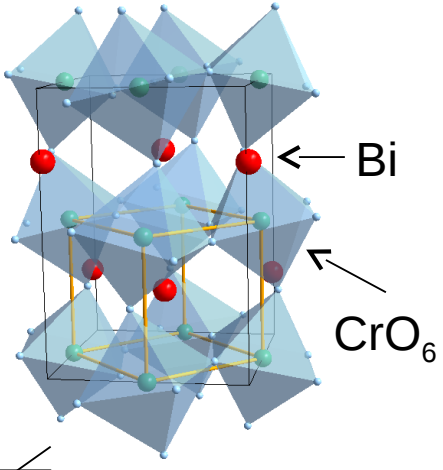
$BiCrO_3$: type I Multiferroic ?

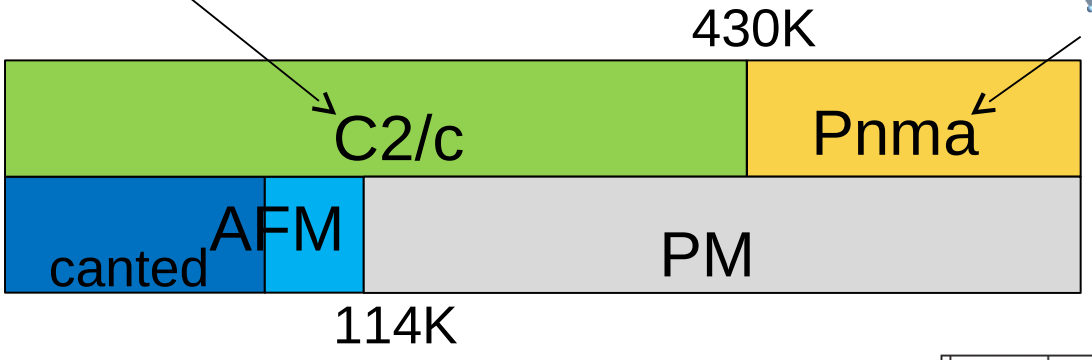
Bi^{3+} Lone pair → ion off-centering
Cr^{3+}, $3d^3$ → Magnetism



Belik A. A., 2008

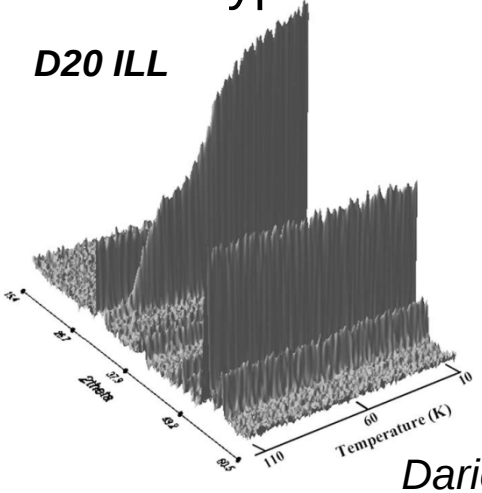
Distorted perovskite
Centrosymmetric SG

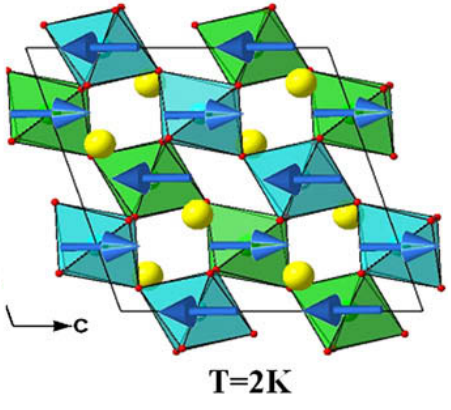




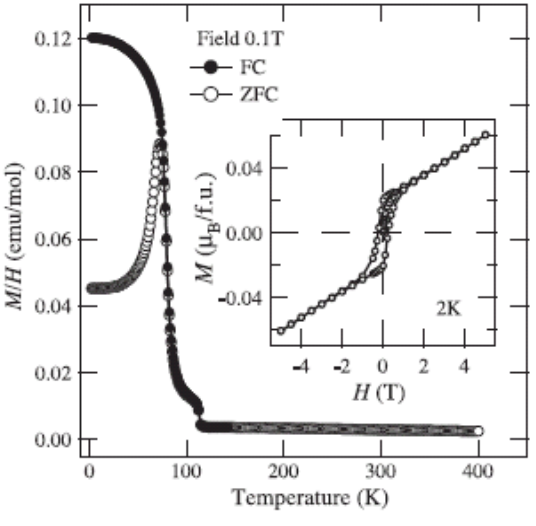
G-Type AFM

D20 ILL



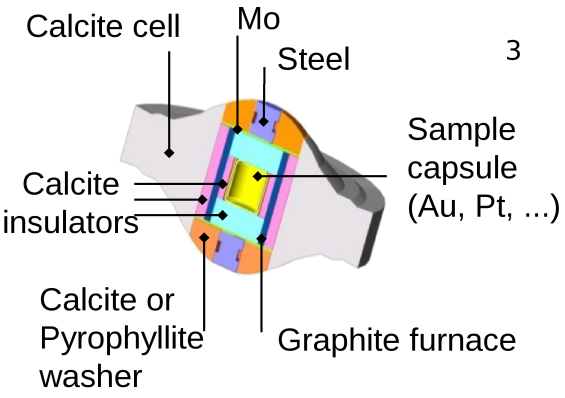


Darie C. et al. 2010



Niitaka et al. 2004

Role of Bi ?
Structure - properties relationship ?



HP synthesis: 4GPa, 1213K

→ $Bi_{1-x}Y_xCrO_3$ lone pair dilution

Y^{3+} Cation isovalent of Bi^{3+}, non magnetic (d^0) and without lone pair

$YCrO_3$: distorted perovskite centrosymmetric SG Pnma,
weak ferromagnet, AFM G-type magnetic structure, T_N=140K

→ Symmetry analysis:

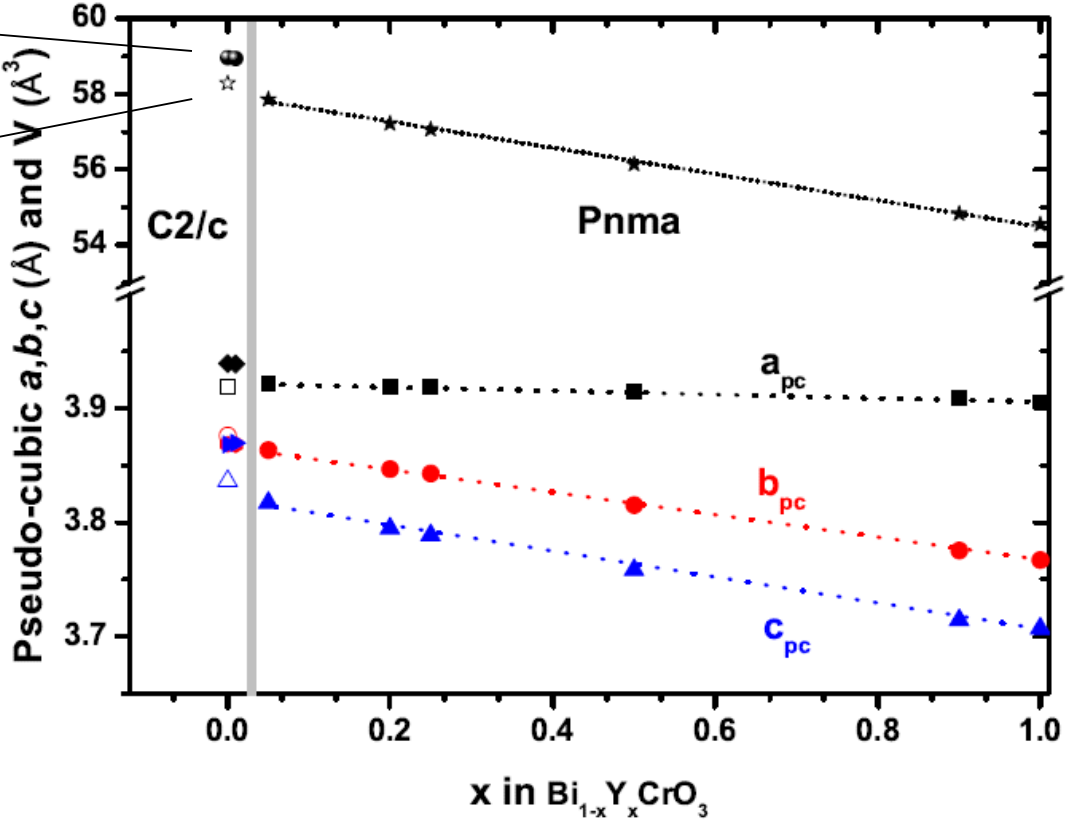
Magnetism: Representation analysis, Bertaut
Calculation: Sarah and BasIreps

Structure: Symmetry-mode analysis
Calculation: AMPLIMODES (Bilbao Crystallographic server)
implemented in FullProf

$Bi_{1-x}Y_xCrO_3$: Crystal structure

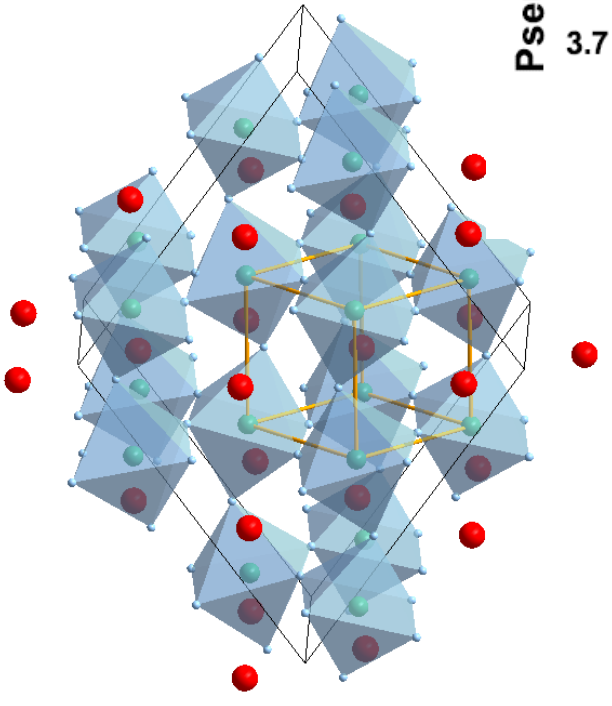
C2/c 300K

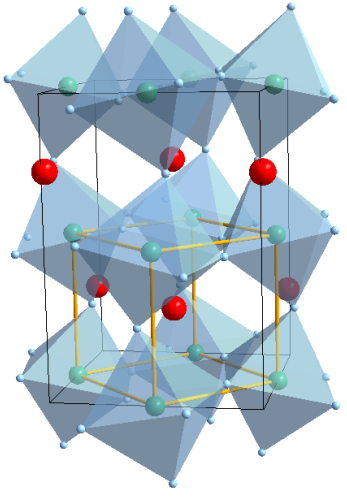
Pnma 430K



C2/c , x<1%

Pnma , x>5%

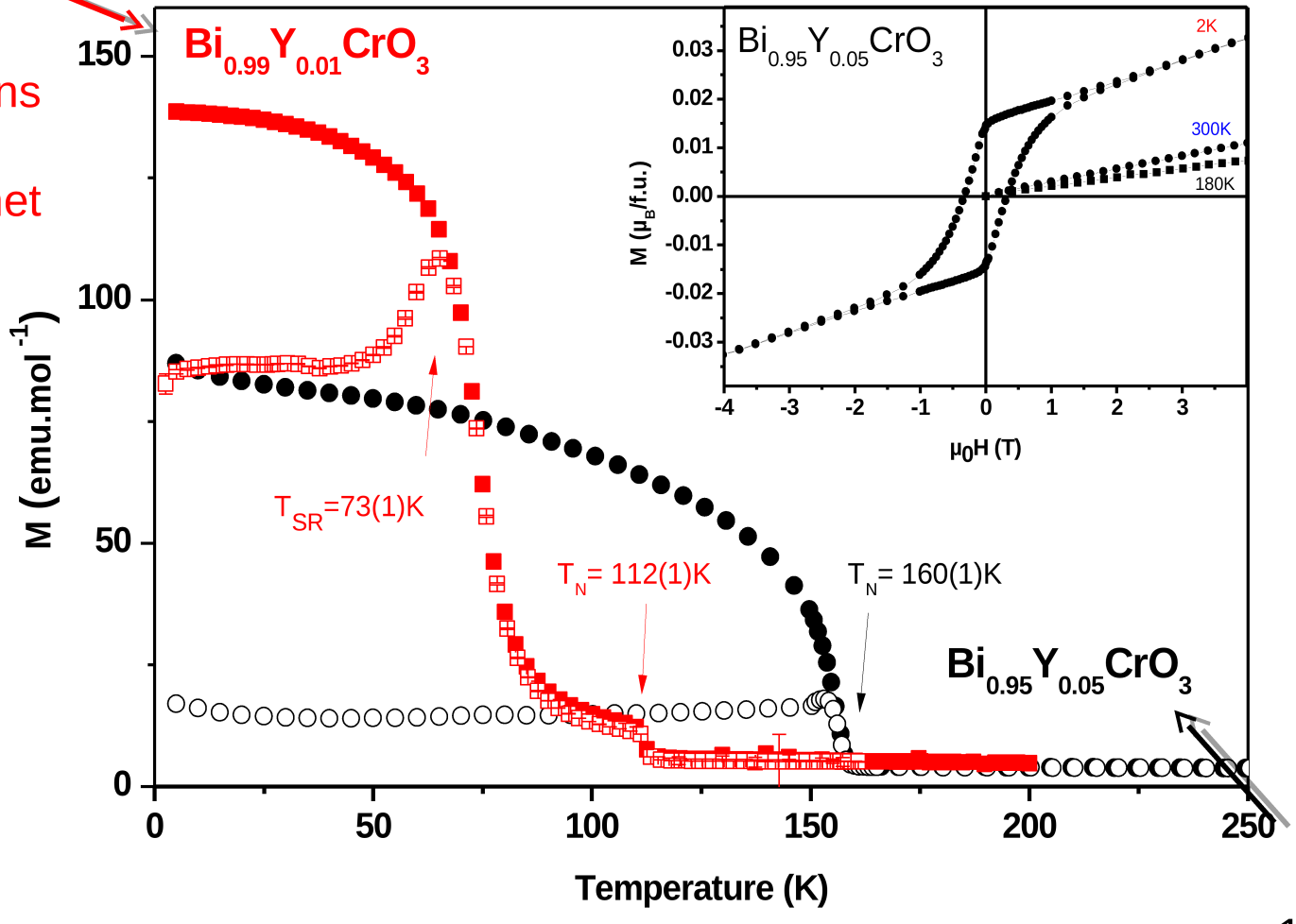




$Bi_{1-x}Y_xCrO_3$: Magnetic properties

C2/c

- 2 transitions
- Weak ferromagnet



Pnma

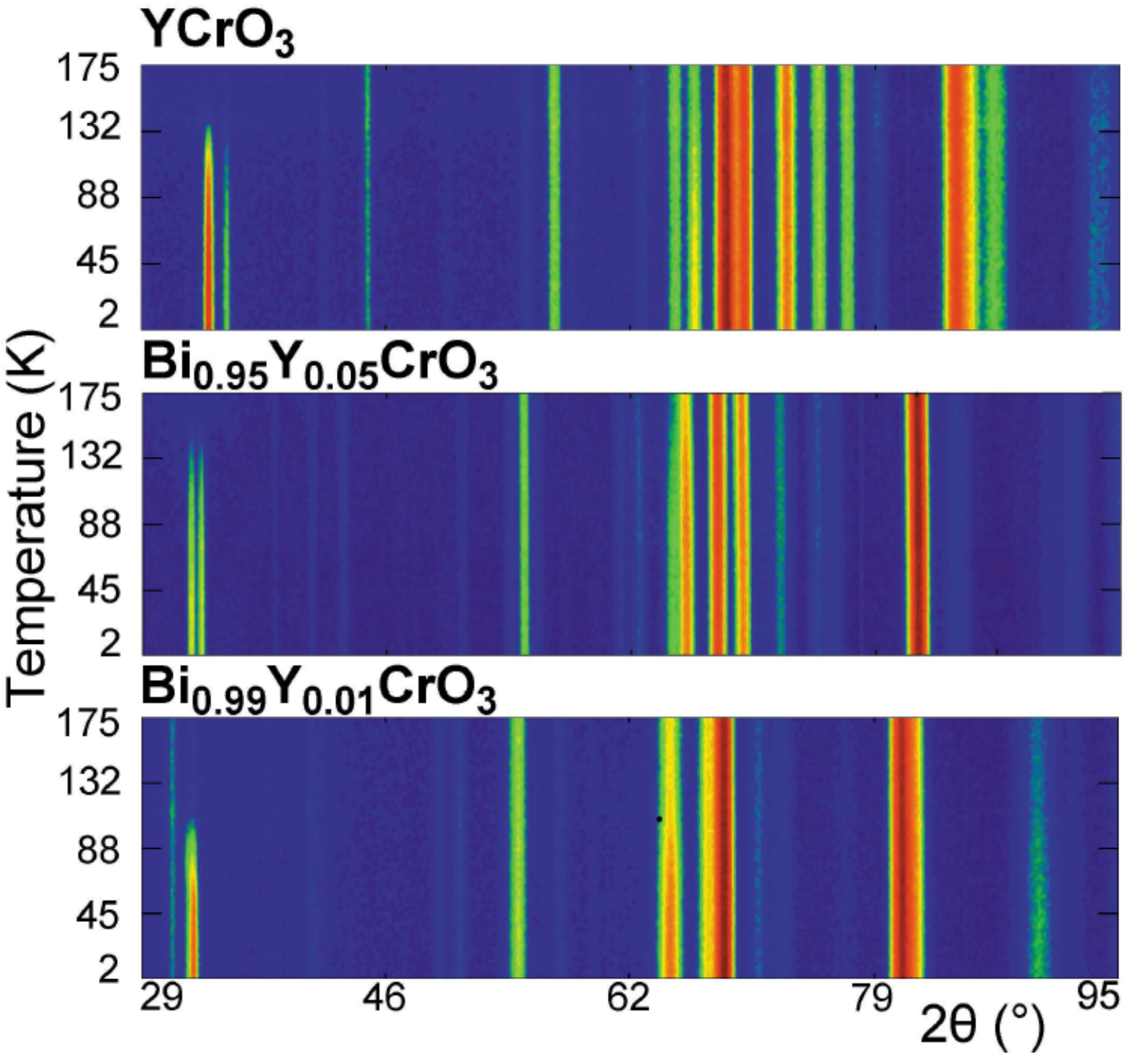
- 1 transition
- Weak ferromagnet

Neutron powder diffraction

λ=2.52Å
D1B, ILL
(x=0.01; 0.05; 1)

λ=2.43Å
G4.1, LLB
(x=0.5; 0.8; 1)

k=(0,0,0)



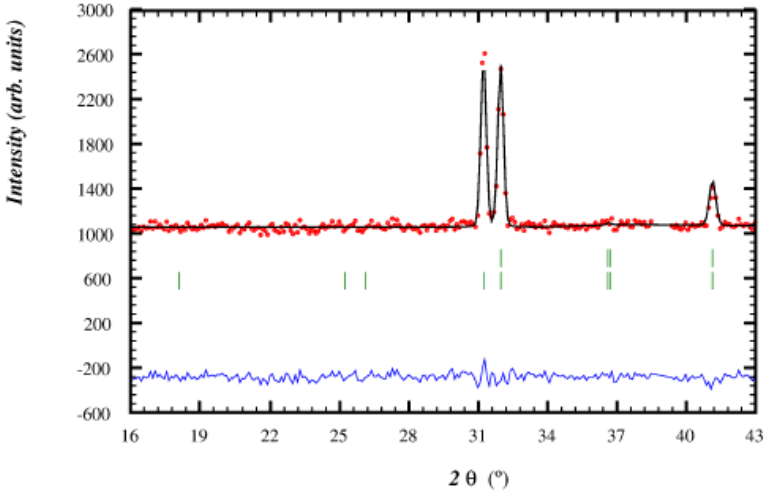
Pnma samples (x>0.05): Magnetic structure

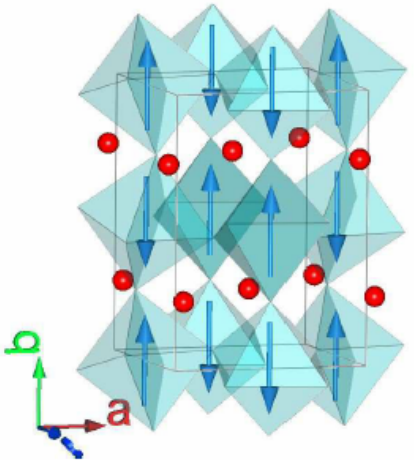
Γ7 IR
Pn'm'a

k=(0,0,0)
1 Cr^{3+} site
G-type AFM

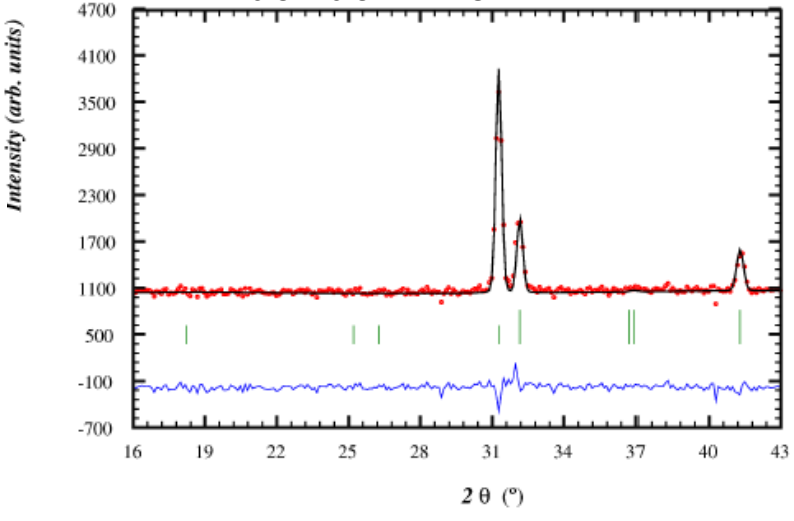
Γ5 IR
Pn'ma'

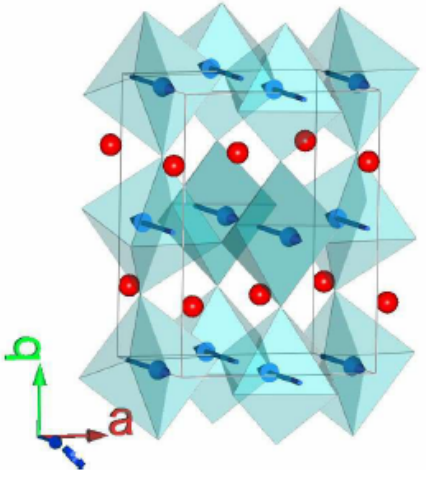
2K, $Bi_{0.8}Y_{0.2}CrO_3$

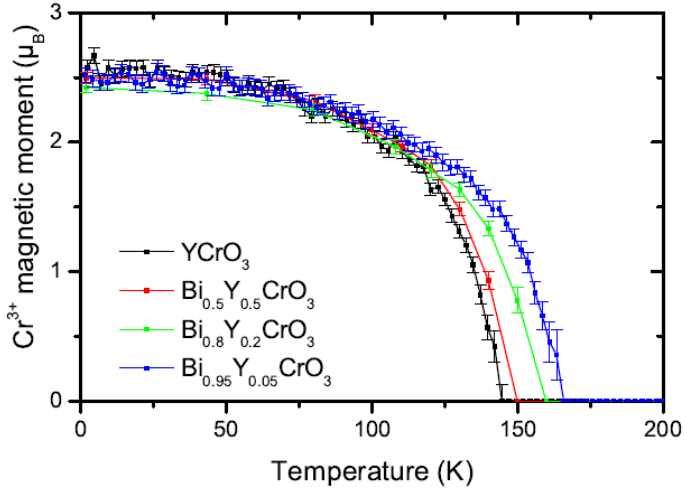




2K, $Bi_{0.5}Y_{0.5}CrO_3$







$M(Cr^{3+})=2.50(5)\mu_B$

Pnma samples (x>0.05)

Symmetry adapted mode analysis

Mode crystallography of distorted structures

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

Departamento de Física de la Materia Condensada, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV-EHU), Apdo 644, 48080 Bilbao, Spain. Correspondence e-mail: jm.perez-mato@ehu.es

Acta Cryst. (2010). A**66**, 558–590

A distorted structure can be described as the parent crystalline structure plus a static symmetry-breaking structural distortion.

Modes are collective correlated atomic displacements fulfilling specific symmetry properties. Structural distortions in distorted structures can be decomposed into contributions from different modes with symmetries given by irreducible representations of the parent space group.

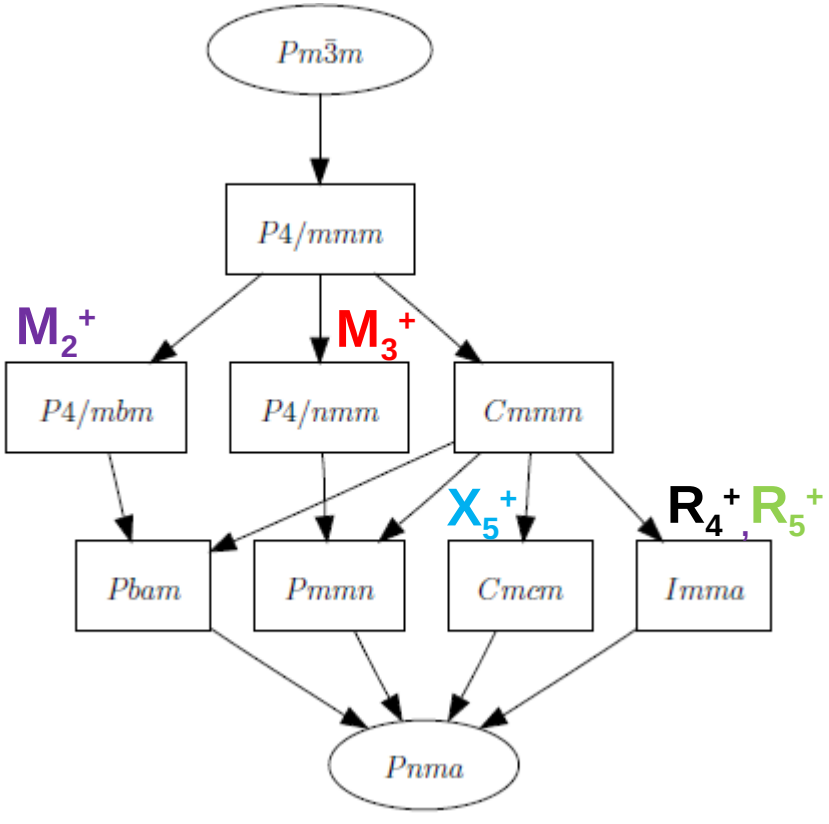
In general, the use of symmetry-adapted modes in the description of distorted structures introduces a natural physical hierarchy among the structural parameters.

Pnma samples (x>0.05)

Symmetry adapted mode analysis

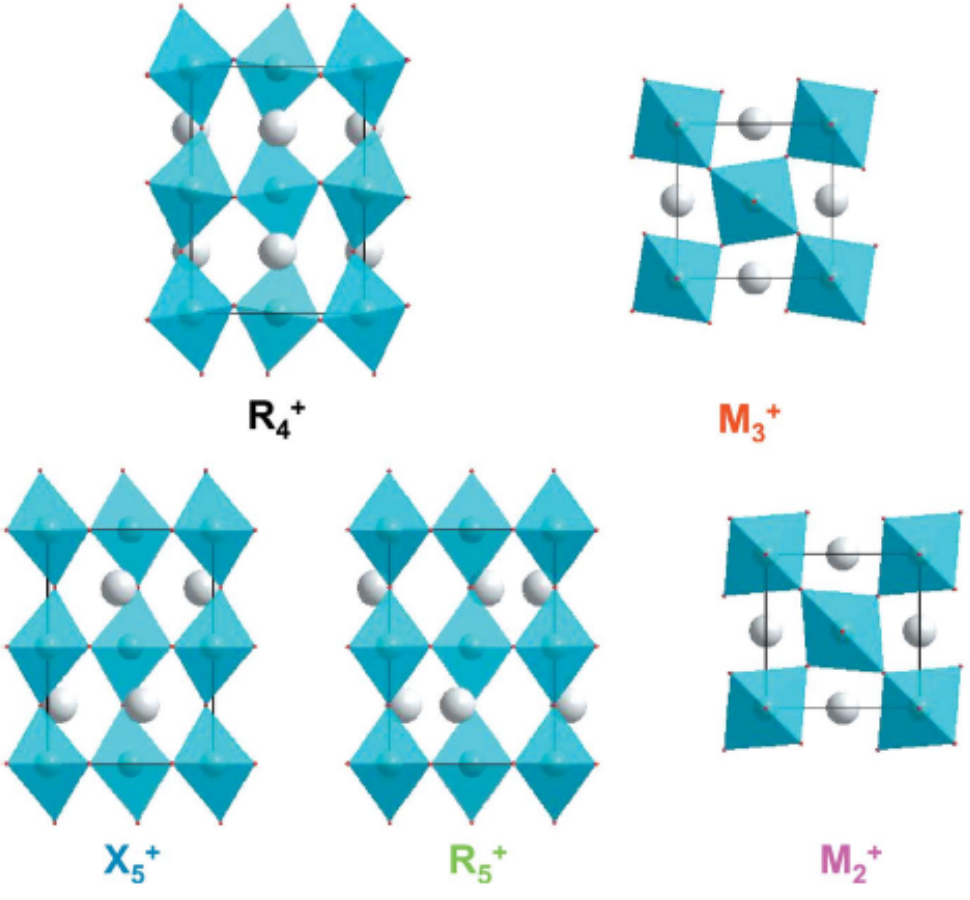
Group-Subgroup relationship:

Ideal cubic perovskite



Distorted orthorombic perovskite

5 distortion modes



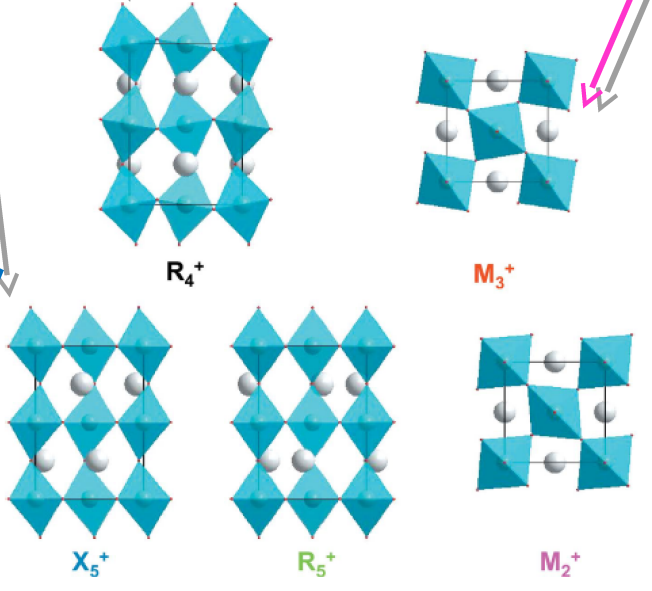
Pnma samples (x>0.05)

Symmetry adapted mode analysis

AMPLIMODES: $YCrO_3$

TABLE IV. Summary of mode decomposition of $YCrO_3$ compound with *Pnma* structure, indicating the amplitude (Å) of all intervening irrep distortion components at room temperature.

K vector	Irrep	Isotropy subgroup	Dimension	Amplitude (Å)
$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	R4+	Imma(74)	1	1.63
$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	R5+	Imma(74)	2	0.38
$(0, \frac{1}{2}, 0)$	X5+	Cmcm (63)	2	0.82
$(\frac{1}{2}, \frac{1}{2}, 0)$	M2+	P4/mbm (127)	1	0.03
$(\frac{1}{2}, \frac{1}{2}, 0)$	M3+	P4/mbm (127)	1	1.13



Pnma samples (x>0.05)

Symmetry adapted mode analysis

Implemented in fullprof: **AMPLIMODES:**

Non-distorted

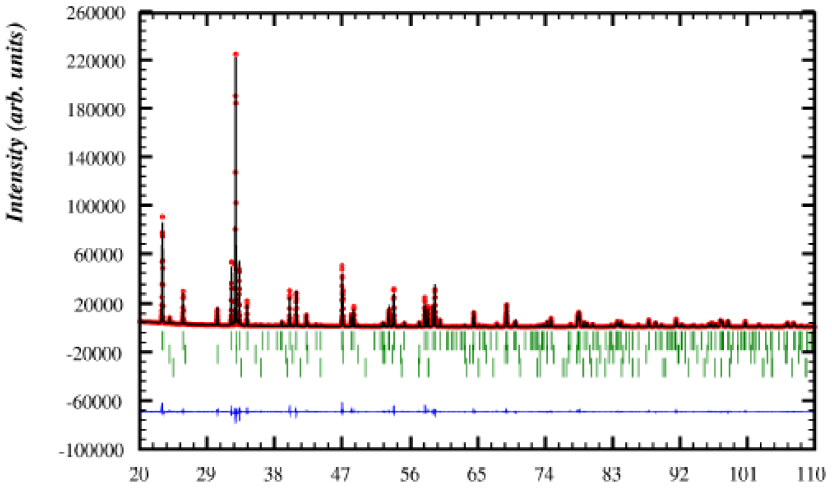
```
062                    <--Space group symbol
!Atom   Typ      X       Y       Z     Biso      Occ     In Fin N_t Spc /Codes
Cr1    CR     0.00000  0.00000  0.00000  0.25005   0.50000   0   0   0    1
Y1     Y      0.50000  0.25000  0.00000  0.25466   0.50000   0   0   0    1
O1     O      0.25000  0.00000  0.75000  0.20000   1.00000   0   0   0    1
O1_2   O      0.50000  0.75000  0.50000  0.20000   0.50000   0   0   0    1
! Polarisation Vectors of Symmetry Modes for each atom
```

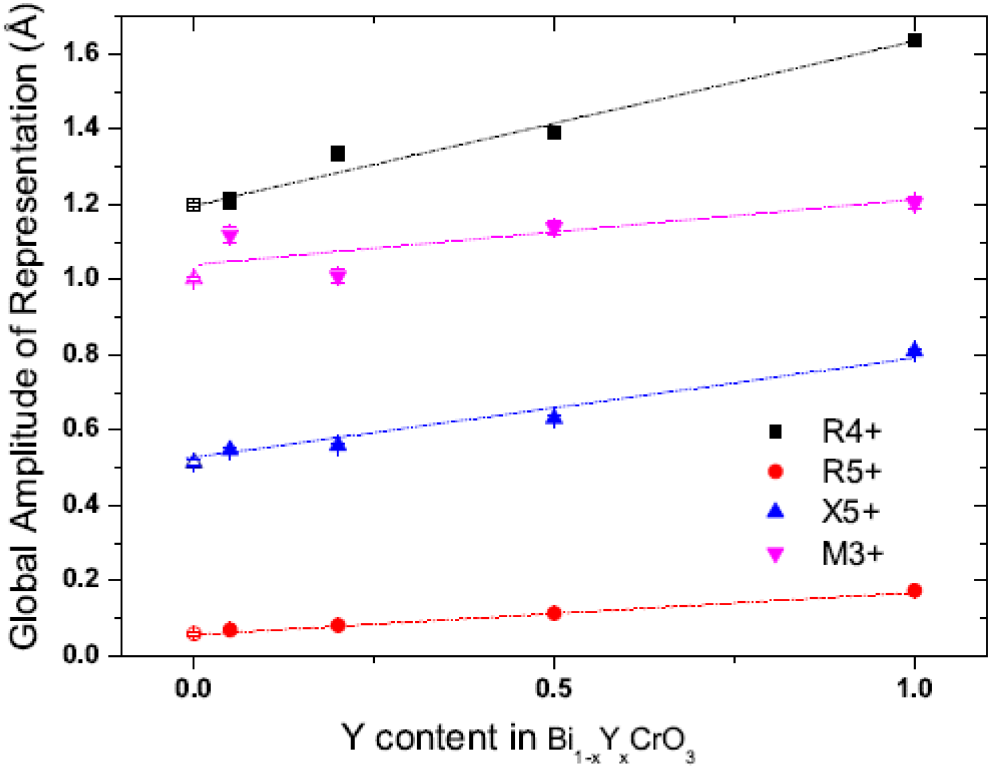
Distortion modes

```
V_MODES   12
! Nm  Atm     Irrep          Vx        Vy        Vz        Coeff
  1  O1      R4+          0.000000  0.033105  0.000000   1.000000
  1  O1_2    R4+          0.000000  0.000000  0.066210   1.000000
  2  Y1      R5+          0.000000  0.000000 -0.093158   1.000000
  3  O1      R5+          0.000000 -0.033105  0.000000   1.000000
  3  O1_2    R5+          0.000000  0.000000  0.066210   1.000000
  4  Y1      X5+         -0.093158  0.000000  0.000000   1.000000
  5  O1      X5+          0.000000  0.000000  0.000000   1.000000
  5  O1_2    X5+         -0.093158  0.000000  0.000000   1.000000
  6  O1      M2+         -0.046579  0.000000  0.046579   1.000000
  6  O1_2    M2+          0.000000  0.000000  0.000000   1.000000
  7  O1      M3+         -0.046579  0.000000 -0.046579   1.000000
  7  O1_2    M3+          0.000000  0.000000  0.000000   1.000000
```

amplitude

```
! Amplitudes of Symmetry Modes
A_MODES    7     2
    A1_R4+          -1.638396   111.000000
    A2_R5+          -0.173880   171.000000
    A3_R5+           0.000000     0.000000
    A4_X5+          -0.707782   131.000000
    A5_X5+          -0.393053   141.000000
    A6_M2+           0.000000     0.000000
    A7_M3+           1.205090   121.000000
```



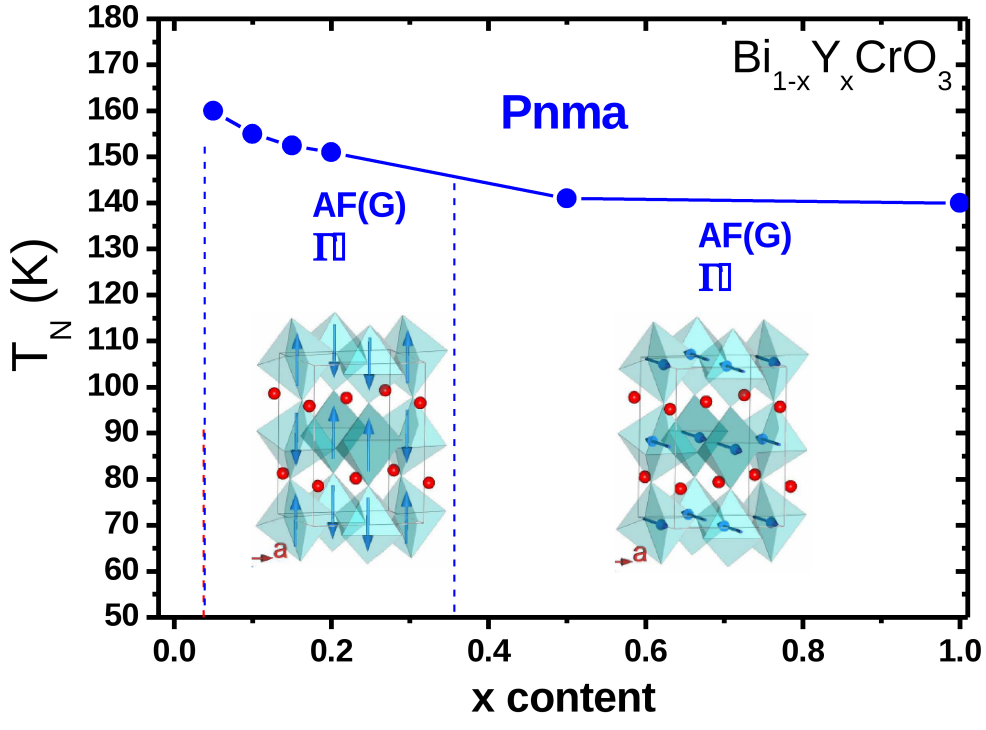


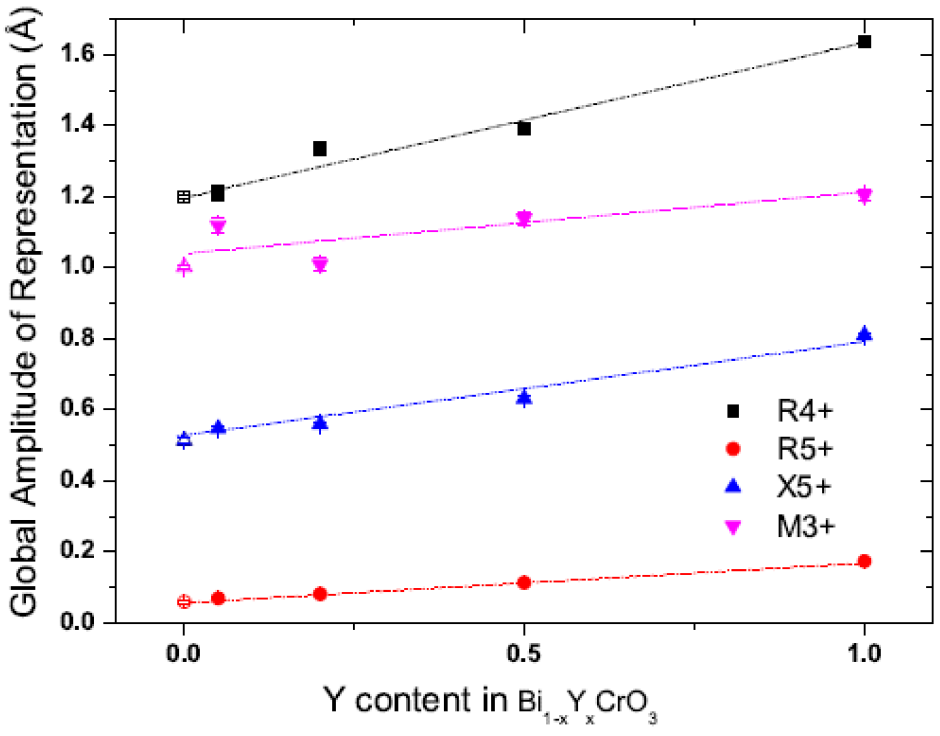
→ Less parameters

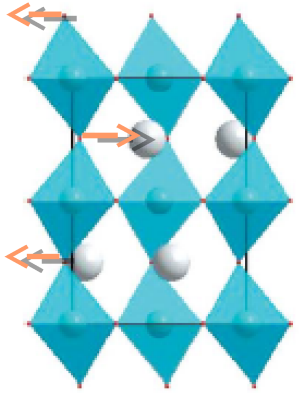
→ Physical meaning:

separation of octahedron tilt and octahedron distortion

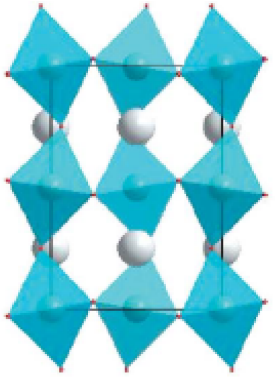
Pnma samples (x>0.05)



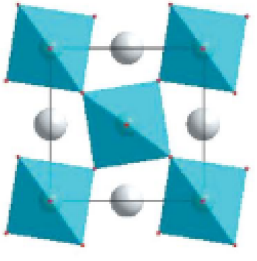




X_5^+



R_4^+



M_3^+

X_5^+ distortion of octahedra→ magnetocristalline anisotropy → spin direction

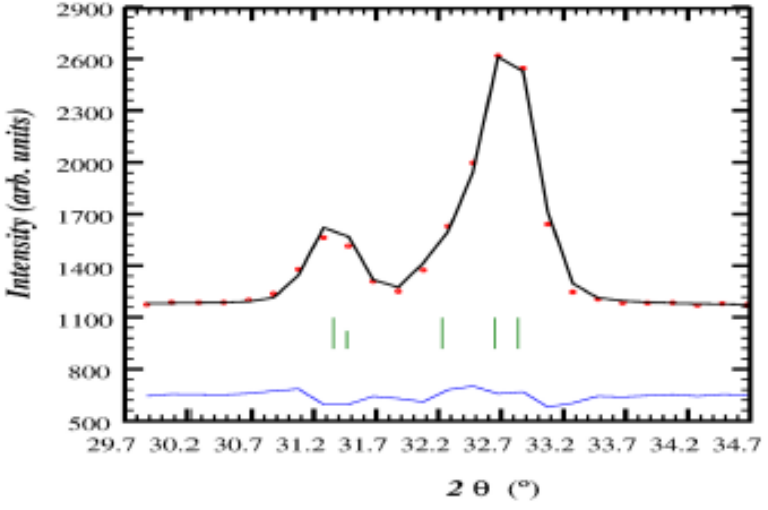
R_4^+,M_3^+: tilt of octahedra → Cr-O-Cr superexchange →T_N

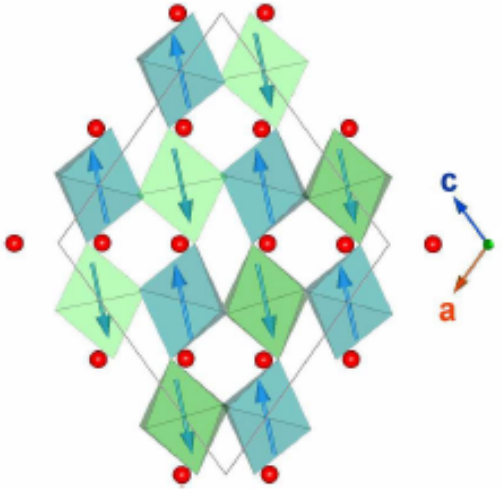
C2/c samples (x<0.01): Magnetic structure

2 Cr^{3+} sites

Γ3 IR
C2'/c'

G-type AFM

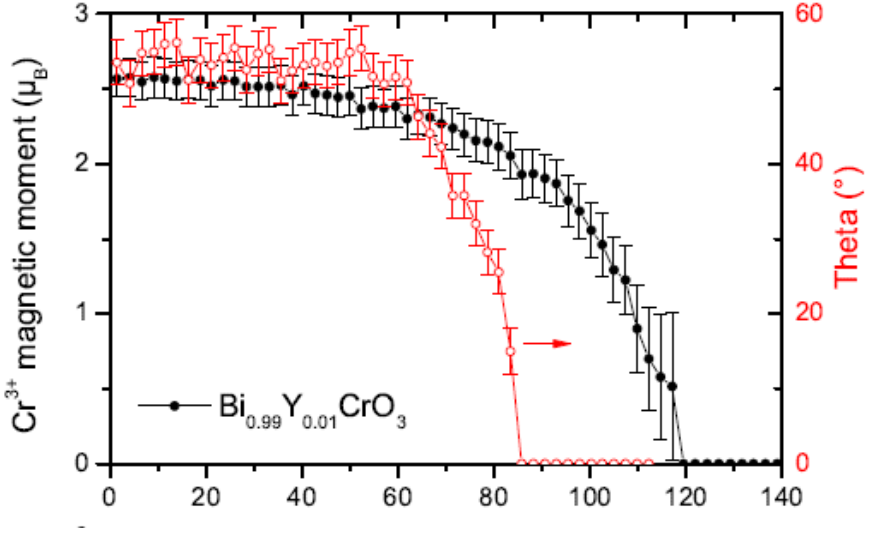




$Bi_{0.99}Y_{0.01}CrO_3$, 2K

$M(Cr^{3+})=2.50(5)\mu_B$

Spin reorientation within the (a,c) plane



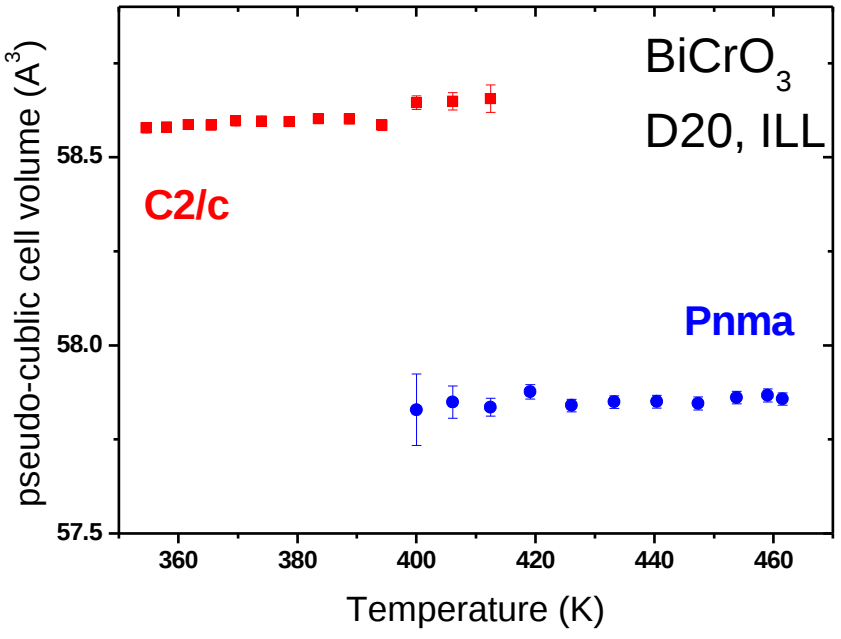
Angle respect to the a axis

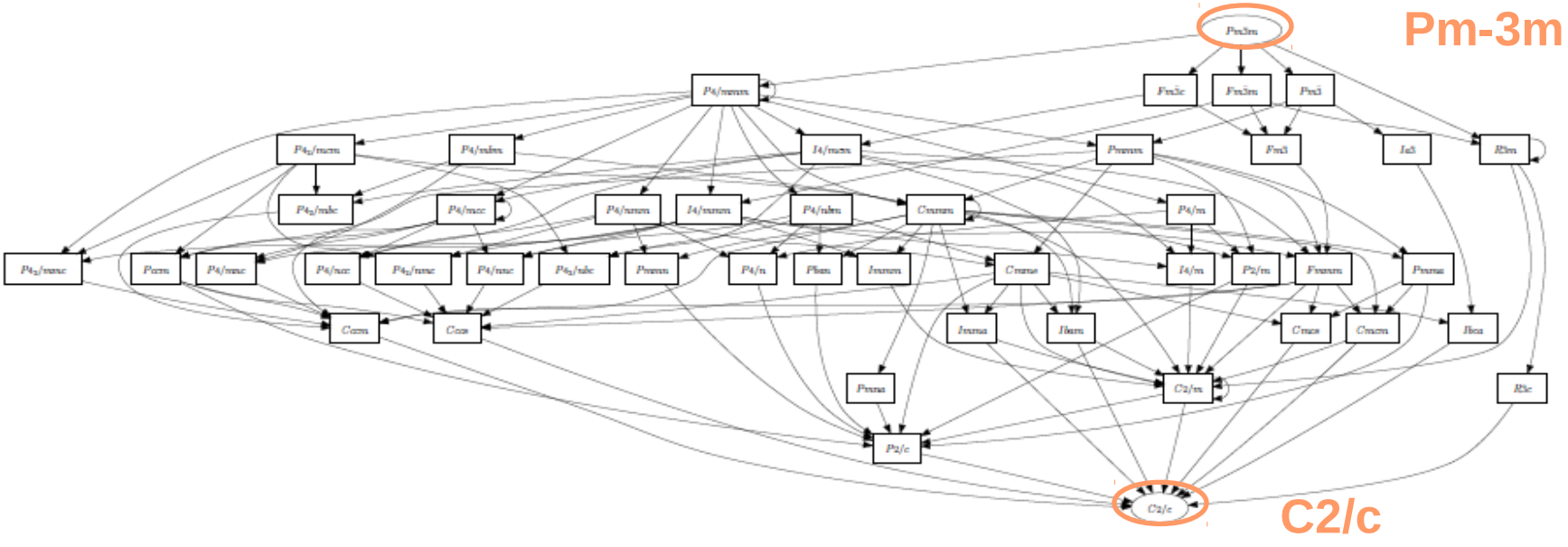
C2/c samples (x<0.01)
Symmetry adapted mode analysis

No group-subgroup relationship between Pnma and C2/c !

→1st order transition

- Large phase coexistence
- Negative thermal expansion





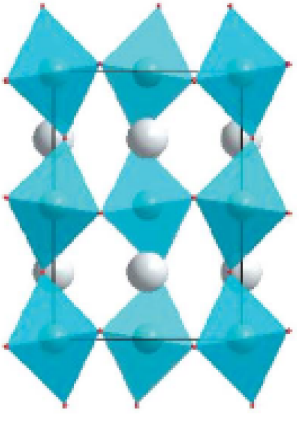
C2/c samples (x<0.01)
Symmetry adapted mode analysis

TABLE VI. Summary of mode decomposition of $BiCrO_3$ compound with $C2/c$ structure, indicating the amplitude (Å) of all intervening irrep distortion components at room temperature.

K vector	Irrep	Isotropy subgroup	Amplitude (Å)	Refined amplitudes (Å)
$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	LD2	R-3c(167)	0.12	0.10(2)
$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	LD3	C2/c(15)	0.82	0.79(1)
$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	R1+	Fm-3m(225)	0.01	0.00
$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	R3+	I4/mmm(139)	0.02	0.00
$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	R4+	Imma(74)	1.28	1.31(1)
$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	R5+	C2/m(74)	0.20	0.19(1)

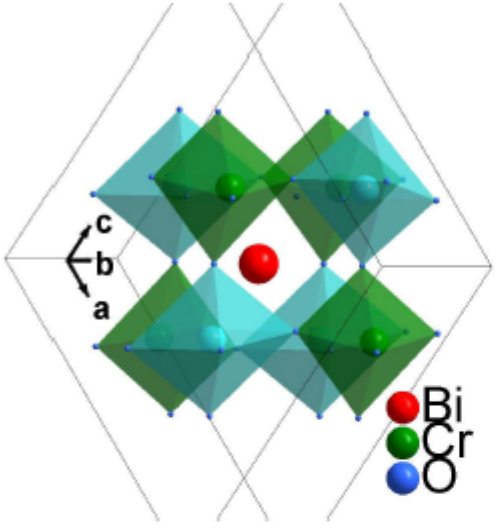
Two primary modes:

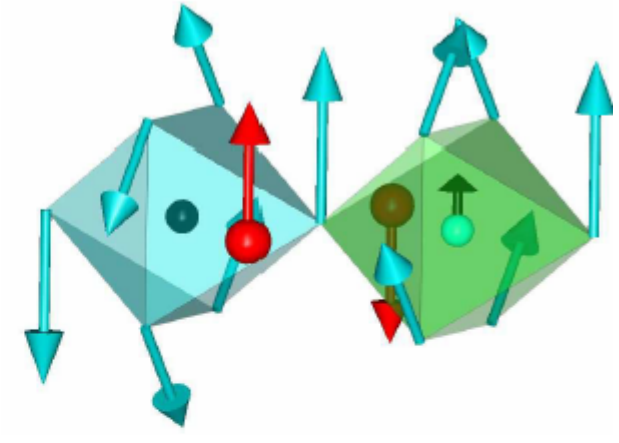
R4+
LD3

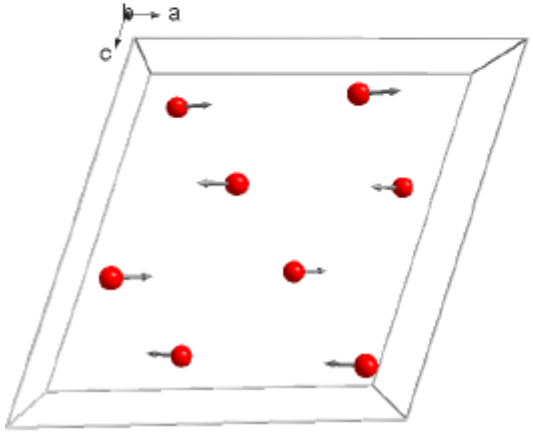


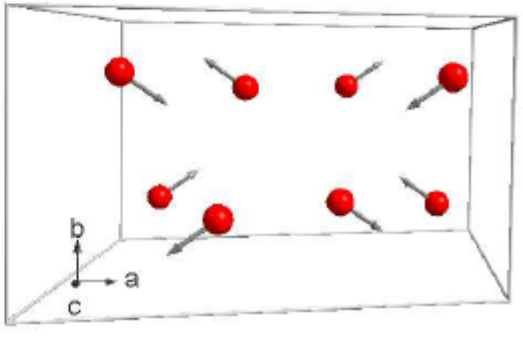
R_4^+

C2/c samples (x<0.01)
Symmetry adapted mode analysis





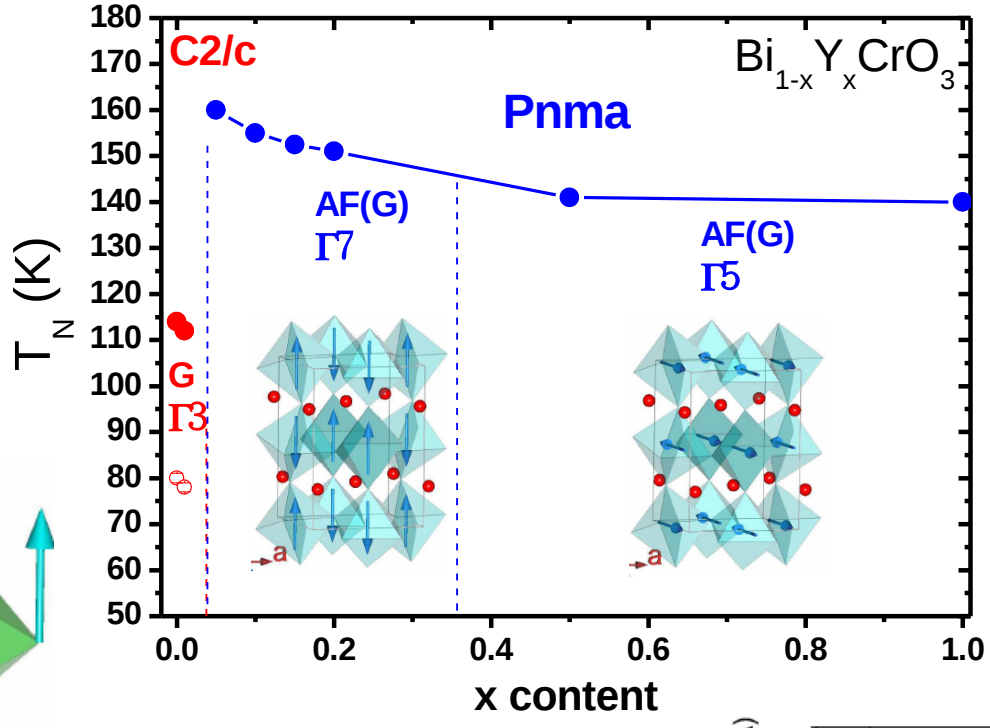




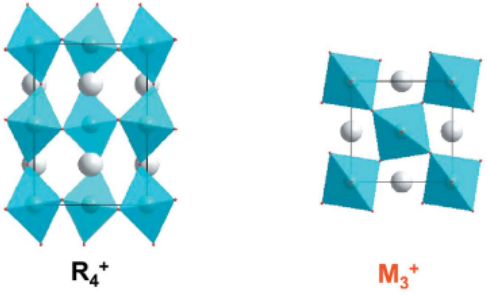
Arrows: local electric dipoles

LD3 mode: Antiferroelectric

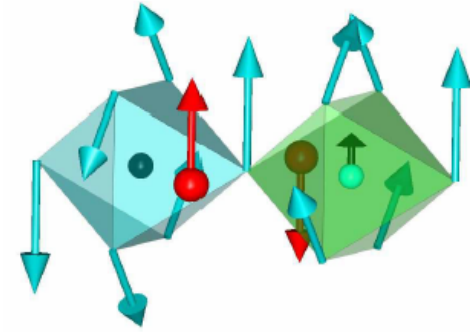
Summary



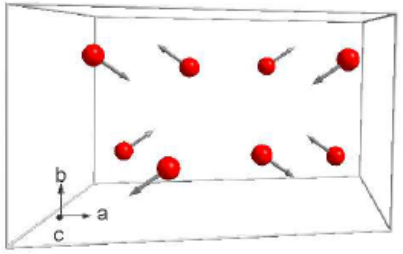
$R_4^+, M_3^+ \rightarrow T_N$

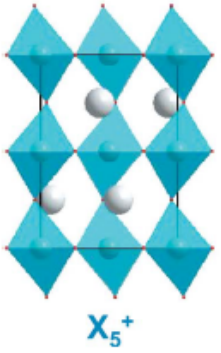


LD3 mode

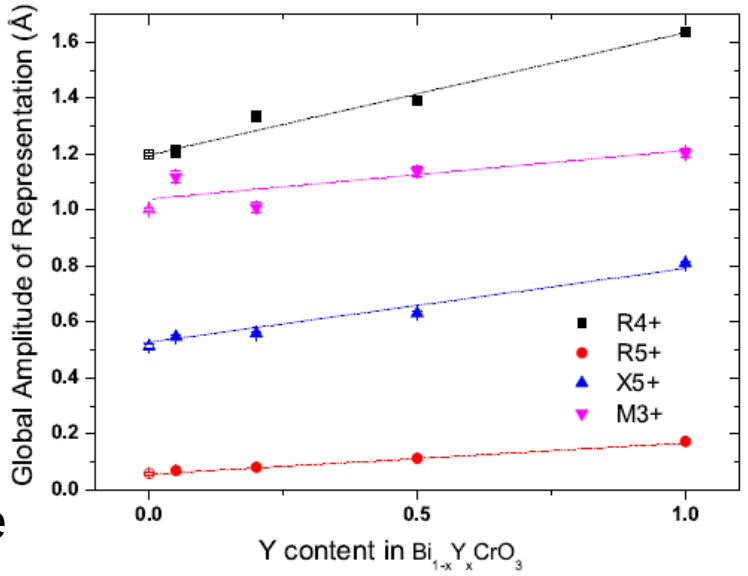


Antiferroelectric





$X_5^+ \rightarrow$ magnetocristalline anisotropy



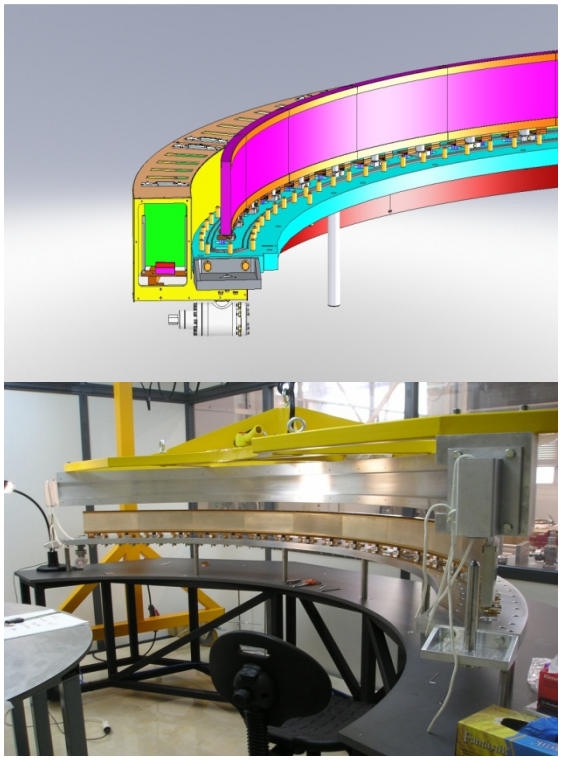
C.V. Colin *et al*, Phys. Rev. B 85, 224103 (2012)

Thanks to

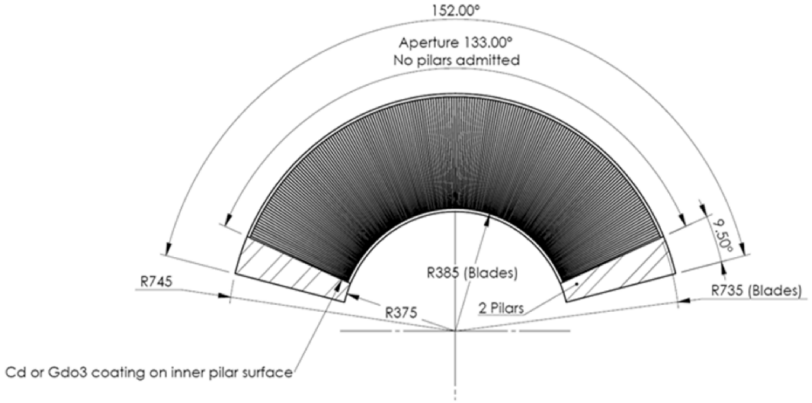
Thank you for your attention !

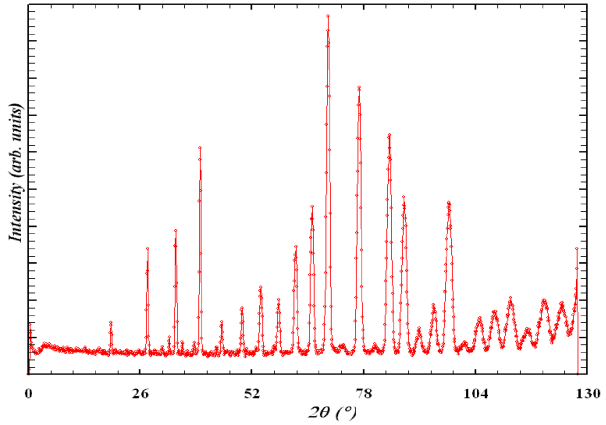
Upgrade of D1B, a high flux neutrons diffractometer at ILL

New Multi-Detecto New Radial Oscillating Collimator (



ROC reduces background and parasitic scattering from the sample environnement





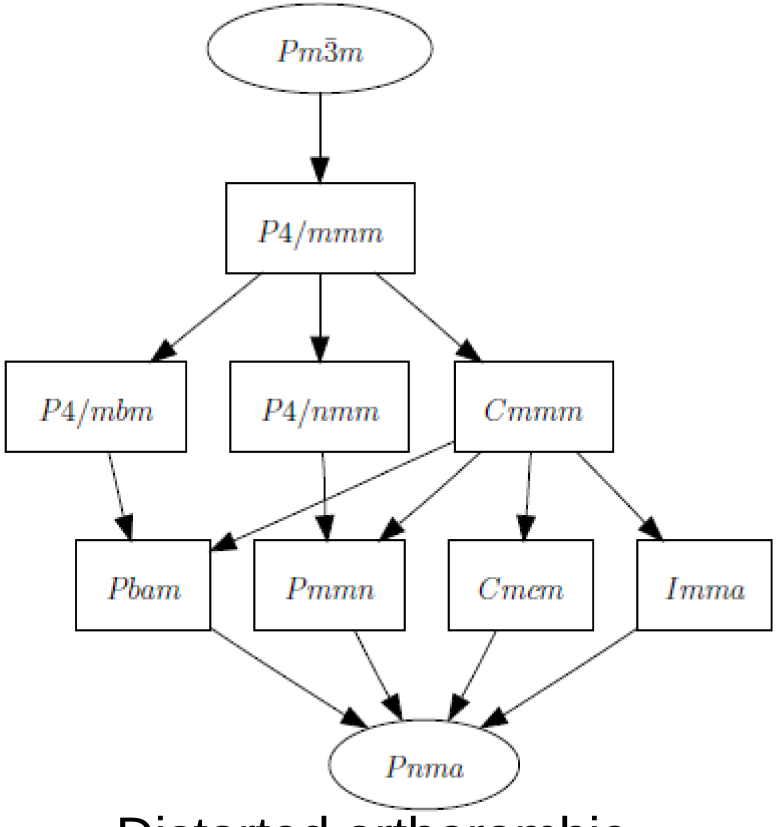
Diffraction pattern of standard NAC sample inside a cryomagnet using the ROC

- Angular coverage & definition: 128°/0.1°
- Detector efficiency @2.5 Å ≥ 80%
- ^{3}He-CF_4 PSD detector (1280 wires)
- Radius : 1.5 m

Pnma samples (x>0.05)

Symmetry adapted mode analysis

Group-Subgroup relationship:
Ideal cubic perovskite

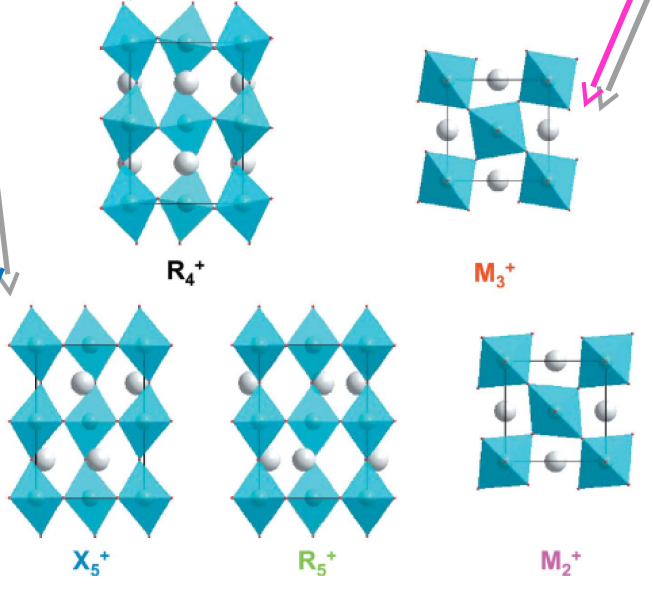


Distorted orthorombic perovskite

AMPLIMODES: $YCrO_3$

TABLE IV. Summary of mode decomposition of $YCrO_3$ compound with $Pnma$ structure, indicating the amplitude (Å) of all intervening irrep distortion components at room temperature.

K vector	Irrep	Isotropy subgroup	Dimension	Amplitude (Å)
$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	R4+	Imma(74)	1	1.63
$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	R5+	Imma(74)	2	0.38
$(0, \frac{1}{2}, 0)$	X5+	Cmcm (63)	2	0.82
$(\frac{1}{2}, \frac{1}{2}, 0)$	M2+	P4/mbm (127)	1	0.03
$(\frac{1}{2}, \frac{1}{2}, 0)$	M3+	P4/mbm (127)	1	1.13



Bi-based perovskite: multiferroics type I

Ferroelectricity from the “stereochemically active lone pair” on Bi^{3+}

+

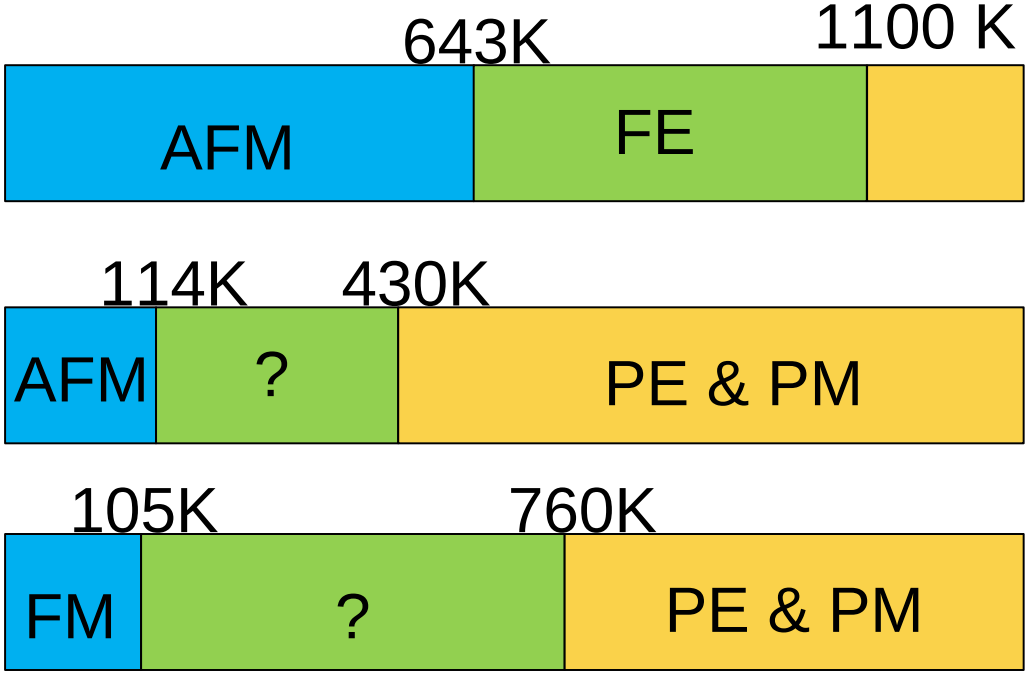
Magnetism from a 3d transition metal (Fe^{3+},Mn^{3+},Cr^{3+})

- $BiFeO_3$: *the* room temperature multiferroic

  R 3c , AF (weak ferro)

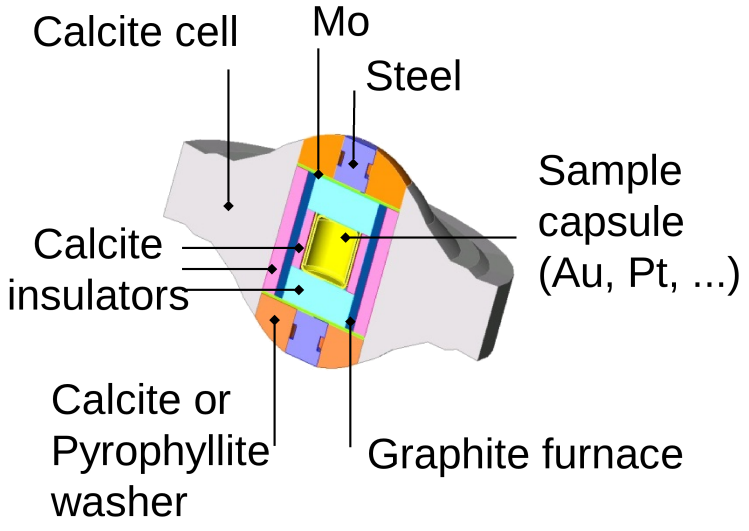
- $BiCrO_3$:

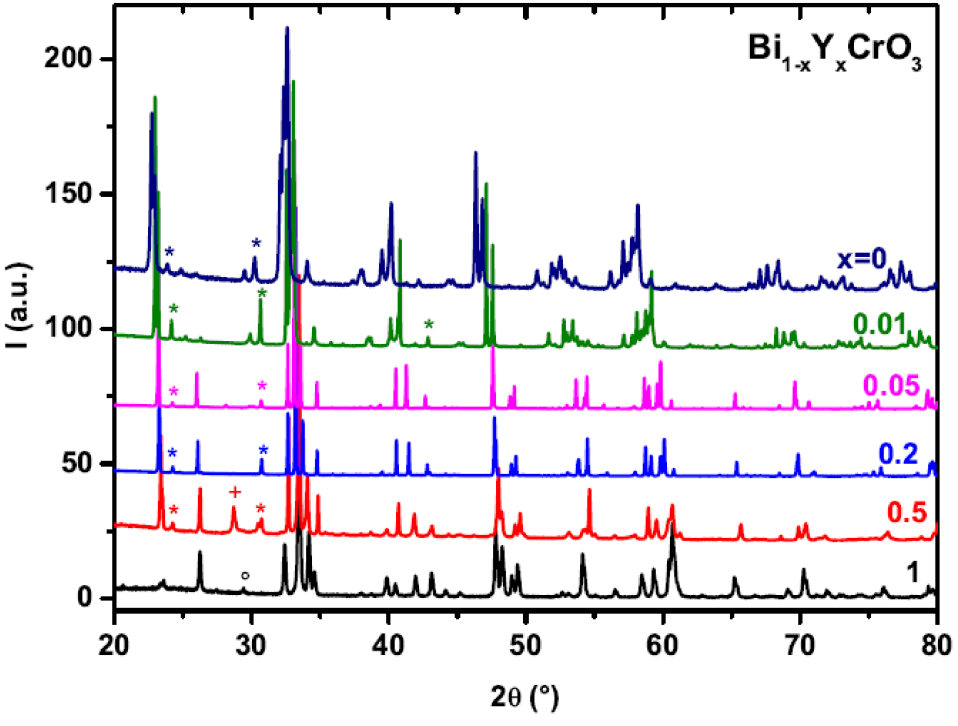
- $BiMnO_3$:



HP synthesis: $Bi_{1-x}Y_xCrO_3$ polycrystalline

Synthesis in Conac Anvil:
4GPa, 1213K



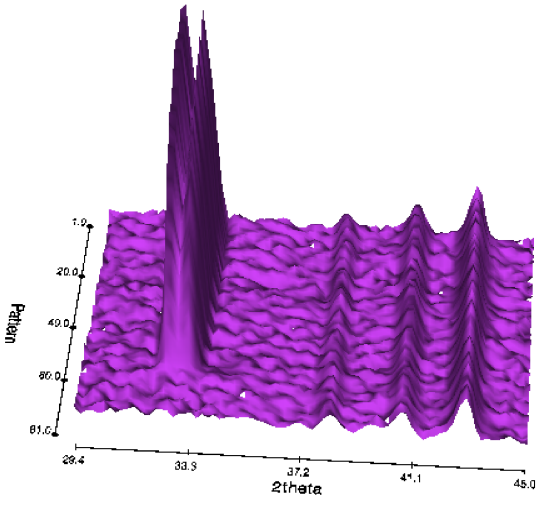


Impurities: $Bi_2O_2CO_3$, γ-Bi_2O_3, Cr_2O_3

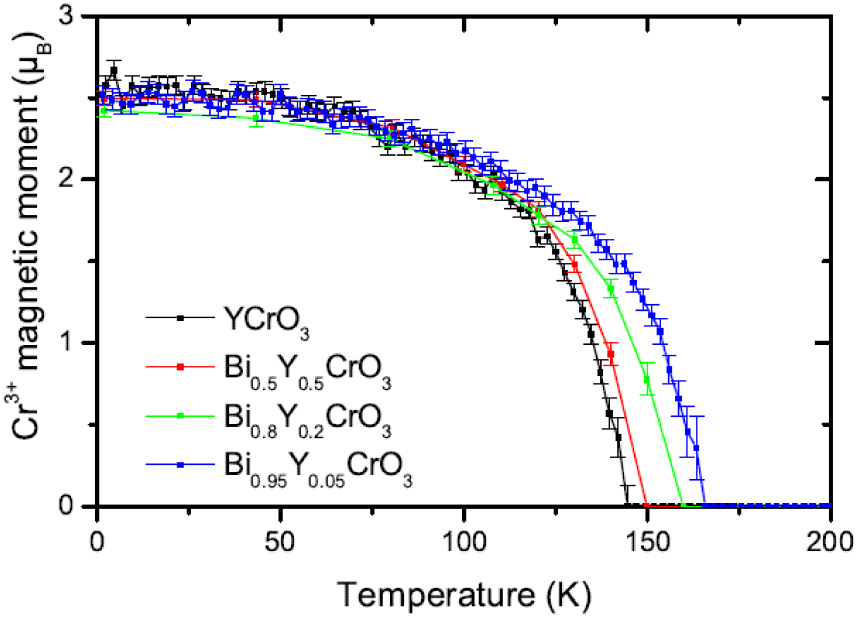
	Conac	
Diamètre utile des cellules	40mm	28mm
Volume des capsules (Au,Pt,acier,CuBe,Ta,BN)	0.8 cm^3	0.2 cm^3
Masse de produit (moy.)	2 g	0.5 g
Gamme de pression	0 - 5.5 GPa	0 - 7 GPa

T_{max} env. 1500°C.

Magnetic structure: Pnma samples (x>0.05)



$M(Cr^{3+})=2.50(5)\mu_B$



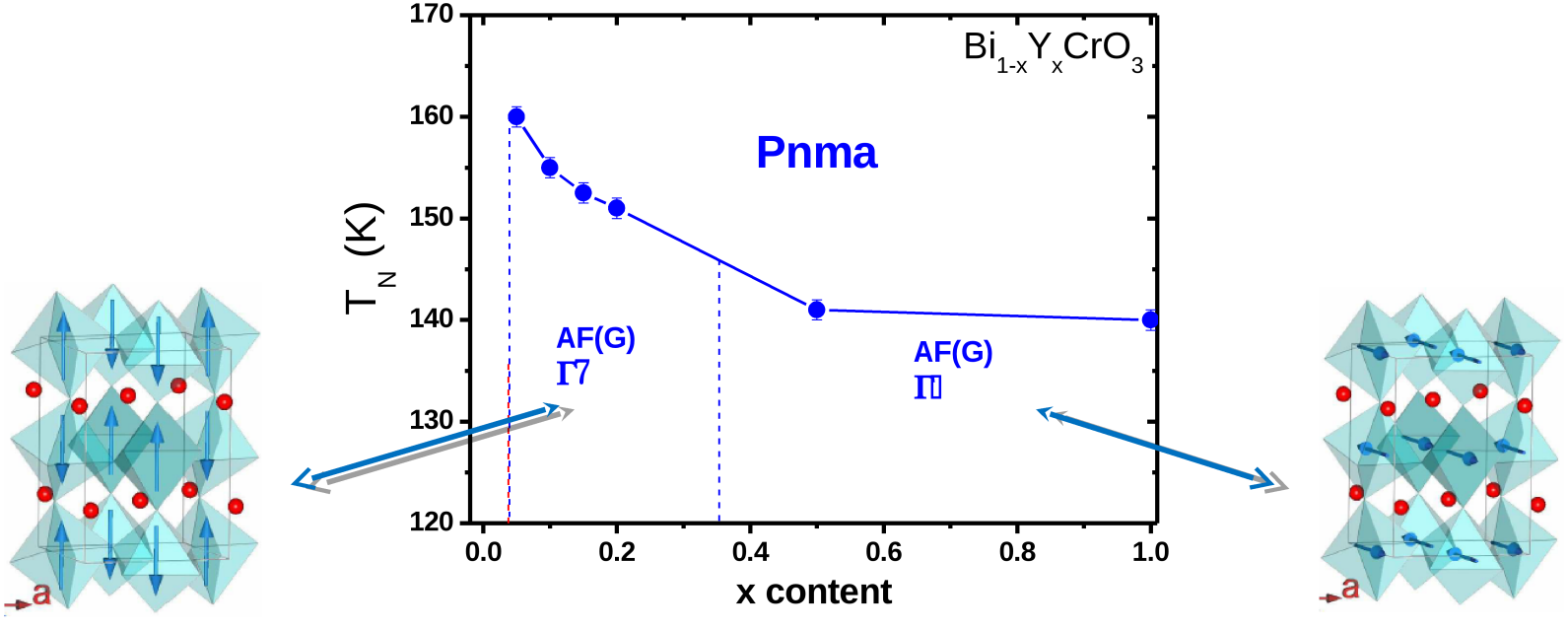
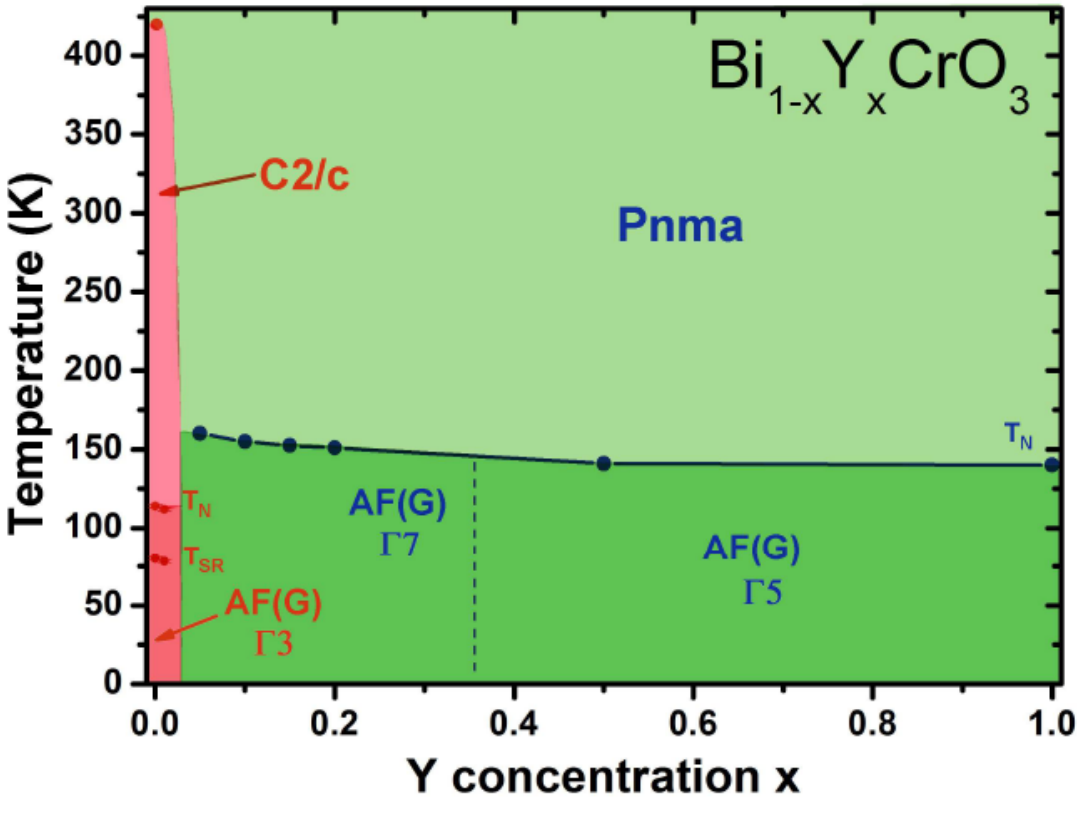


TABLE II. Basis vectors for the space group P nma with $k_{19} = (0,\ 0,\ 0)$. The decomposition of the magnetic representation for the Cr site $(.5,\ .5,\ 0)$ is $\Gamma_{Mag} = 3\Gamma_1^1 + 0\Gamma_2^1 + 3\Gamma_3^1 + 0\Gamma_4^1 + 3\Gamma_5^1 + 0\Gamma_6^1 + 3\Gamma_7^1 + 0\Gamma_8^1$. The atoms of the nonprimitive basis are defined according to 1: $(.5,\ .5,\ 0)$, 2: $(0,\ 0,\ .5)$, 3: $(.5,\ 0,\ 0)$, 4: $(0,\ .5,\ .5)$. For notations see Wollan *et al*[19]

IR	$m_{\parallel a}$	$m_{\parallel b}$	$m_{\parallel c}$	Shubnikov Group
Γ_1	G	C	A	Pnma
Γ_3	B	A	C	Pnm'a'
Γ_5	A	B	G	Pn'ma'
Γ_7	C	G	B	Pn'm'a

TABLE III. Basis vectors for the space group C 1 2/c 1 with $k_6 = (0,\ 0,\ 0)$. Only shared magnetic representations for Cr_1 site $(.25,\ .25,\ .5)$ the Cr_2 site $(0,\ .235,\ .75)$ are shown.

	IR	$m_{\parallel a}$	$m_{\parallel b}$	$m_{\parallel c}$	Shubnikov Group
Cr_1					
	Γ_1	L_x	M_y	L_z	C2/c
	Γ_3	M_x	L_y	M_z	C2'/c'
Cr_2					
	Γ_1		M_y		C2/c
	Γ_3	M_x		M_z	C2'/c'


Bi1-xYxCrO3
C2/c
Pnma
TN
TSR
AF(G)
Γ3
AF(G)
Γ7
AF(G)
Γ5
TN
Temperature (K)
Y concentration x
0
50
100
150
200
250
300
350
400
0.0
0.2
0.4
0.6
0.8
1.0